ABSTRACT

Rate constants for chemical reactions in various aqueous and microheterogeneous systems have been measured and analysed. A large part of the thesis is concerned with interpreting kinetic trends in two water-in-oil microemulsions. Kinetic data for inorganic reactions involving low-spin iron(II) di-imine complexes and for reactions involving the organic substrates, 2,4-dinitrochlorobenzene, crystal violet and malachite green in microemulsions have been collected and used to identify different structural zones in these solvent systems. The kinetic data are interpreted in terms of a model in which reaction occurs at an interphase.

Reactions involving cis-bis(pyridine)tetraacarbonylmolybdenum(0) in oil-in-water, water-in-oil microemulsions and organic solvent mixtures have been studied.

Aquation reactions of iron(II) hexadentate Schiff base have been used to identify microheterogeneous phases in water-rich '2-butoxyethanol + water' mixtures.

Solvent effects on initial and transition states are discussed for reactions of iron(II) glyoxal bis-N methylamine with hydroxide ions in 'methanol + water' mixtures and reactions of iron(II) 1,10-phenanthroline with hydroxide ions in 'isopropanol + water' mixtures.

Transfer chemical potentials for single ions, in 'acetone + water' mixtures, have been estimated, using solubility data for salts in conjunction with the assumption that transfer chemical potentials for tetraphenylboronate and tetraphenylarsonium ions are equal.

Effects of added salt on the neutral hydrolysis of phenyldichloroacetate in aqueous solutions are examined in terms of solvent cosphere interactions between ions.

The temperature dependence of rate constants for reactions of iron(II) 4-methyl, 1,10-phenanthroline have been examined. The results are discussed in terms of isobaric, isothermal and isochoric activation parameters. The meaning of the term 'isochoric' is clarified in this context.
KINETICS IN AQUEOUS & MICROHETEROGENEOUS SYSTEMS

BY

Barbara Briggs

A Thesis submitted for the Degree of

Doctor of Philosophy

in the

Faculty of Science

at the

University of Leicester

OCTOBER 1985
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Barbara Briggs

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"Not that we are competent of ourselves to judge anything we do but our competence comes from God"

— II Corinthians, Chapter 3, Verse 5
Dla Kochanej Babci - dziękuję.
STATEMENT

This thesis is based upon work conducted by the author, in the Department of Chemistry of the University of Leicester, during the period between September 1982 and April 1985.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references. This work is not being presented for any other degree.

OCTOBER 1985

Barbara Briggs
University of Leicester
ACKNOWLEDGEMENTS

I am indebted to my Supervisors, Dr. Mike Blandamer and Dr. John Burgess, for their abundant guidance, assistance, patience and encouragement throughout the period of this research.

Many thanks go to Miss V. Orson-Wright for her excellent production of the typescript and to Mrs. C. A. Crane for drawing most of the diagrams.

The award of a maintenance grant by the Science and Engineering Research Council is acknowledged.
LIST OF PUBLICATIONS - B. BRIGGS (née CLARK)


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CHAPTER
1
Background
1.1 INTRODUCTION

Water provides a suitable solvent in which to study kinetics of many chemical reactions, especially those involving ions. However the rôle of water in chemical reactions is neither straightforward nor fully understood. The effects of added salts, neutral solutes and co-solvents on kinetic parameters can often provide useful insight into understanding the rôle of solvents in chemical reactions. Furthermore, effects of changing the solvent environment on kinetic parameters often provides valuable information about reaction mechanisms.

The work presented in this thesis is concerned with measuring and interpreting kinetic data for several types of reactions in aqueous systems. The aqueous systems range from the relatively simple 'mono-hydric alcohol + water' mixtures to the complicated oil-in-water and water-in-oil microemulsions. Effects of added salts on rate constants for reaction in aqueous solution are also reported. Trends in rate constants and changes in rate expressions are discussed, as the hydrophobic nature of ligands is changed around low-spin iron(II) di-imine complexes in various water-in-oil microemulsions.

Kinetic data for reactions of low-spin iron(II) di-imine complexes with (a) water in acidified solution, (b) hydroxide and (c) cyanide ions, in many of the mixed solvent systems are discussed. The background to the chemistry of these reactions is discussed in section 1.6.

Kinetic trends for various reactions involving organic substrates in mixed solvents are discussed (Chapters 5 and 10) and kinetic data for reactions involving cis-bis-pyridinetetracarbonylmolybdenum(0) in microemulsions and organic solvent mixtures are reported in Appendix 1.

The kinetic and thermodynamic theory underlying the work presented in this thesis is discussed in this Chapter.
1.2 STRUCTURE OF WATER AND EFFECTS ON WATER STRUCTURE BY ADDITION OF APOLAR SOLUTES

The phenomenon of hydrogen bonding is obviously of paramount importance to aqueous solutions. The characteristic properties of water and aqueous solutions appear to originate in fluctuations which differ sharply from those resulting from hydrogen-bond perturbation or breakage in other hydrogen-bonded liquids.

A model for water structure was proposed recently by Lumry and co-workers. The main objective was to determine from thermodynamic arguments to what extent and at what level, the phenomenon of "hydrophobic hydration" depends on the unique properties of water.

The thermodynamic quantities associated with the introduction of hydrophobic compounds in water exhibit a number of novel features. Near room temperature, the transfer of hydrophobic solutes (e.g. rare gases, small hydrocarbons) between solute standard states from a hydrocarbon environment to water occurs typically with: (i) an increase in standard chemical potential, (ii) a decrease in partial molar enthalpy, (iii) a large decrease in partial molar entropy and (iv) a large increase in partial molar isobaric heat capacity.

According to the model proposed by Lumry et al., water consists of a random network of hydrogen-bonded molecules (Fig. 1.1).

![Figure 1.1](image)

**FIGURE 1.1**
Water dimer; \( H_1 \) and \( H_2 \) are in the \( xy \)-plane and \( H_3 \) and \( H_4 \) are in the \( xz \)-plane.

The distributed energies, angles and donor-acceptor distances are
almost constant throughout the network. Embedded in this connected system are clusters having appropriate geometry to allow cooperative hydrogen bonding into short-lived but structured tetrahedral hydrogen bonded units. The minimum cluster size is the symmetrical pentamer or tetrameric fragment, which allows simultaneous bond contraction with increased bond strength in the bonds to the "central" water molecule. Such cluster fluctuation between the long-bond and short-bond forms is called "geometric relaxation" (Fig. 1.2).

![Geometric Relaxation Diagram](https://example.com/geometric-relaxation.png)

**FIGURE 1.2**
Structural representation of the geometric relaxation of a pentameric cluster neglecting effects of neighbouring molecules.

(i) **Short-bond form**

In a pentameric unit, five water molecules are linked by short, stiff, linear hydrogen bonds. Bending, torsional and rotational motions are severely hindered. The molar entropy and molar enthalpy are low but the rigid geometry increases the free volume, and therefore, to a smaller extent, the total volume. Much of the free volume associated with this form is available to solutes.

(ii) **Long-bond form**

In some groups of water molecules, the hydrogen-bond length increases and the tetrahedral constraint diminishes. The cluster of cooperatively
hydrogen-bonded water molecules is momentarily replaced by a group of molecules which are held together by simple hydrogen-bonds, having the strength associated with simple water dimers. Bending, librational and rotational freedom increases and a wide variety of hydrogen-bond breaking processes become available. The weakened and broken hydrogen bonds are stabilised by an increase in molar entropy. The local free volume decreases and becomes less available to solutes. Hydrogen-bond bending and better packing produce a reduction in total volume.

In super-cooled water, short-bond structures dominate and the extreme fluctuational behaviour is attributed to equilibria between short- and long-bond forms in larger clusters. At all temperatures the model only requires the identification of almost perfect tetrahedral symmetry about central water molecules in short-bond forms. Flickering between short- and long-bonded states is so fast that large clusters have little structural identity.

Compensation operates between the limiting forms of "short" and "long" hydrogen-bonds in liquid water. The enthalpy required to increase the O-H-O distance is compensated by an entropy gain from hydrogen-bond bending. At 295 K, assumed to be the compensation temperature (i.e. the temperature at which enthalpy-entropy compensation is optimum), only approximately 10% of water molecules are in clusters of the short-bond form. The remaining 90% are part of the network of "long" hydrogen-bonded molecules. The fraction of molecules involved in geometric relaxation depends on the network of "long" hydrogen-bonds. Therefore changes in temperature or addition of hydrophilic co-solvents will affect geometric relaxation because of disruption caused to the "long" hydrogen-bond network.

The occurrence of broken hydrogen bonds was considered as limiting
situations, and even at 373 K there is considerable uncertainty about
the extent of hydrogen-bond breaking.

The increase in partial molar isobaric heat capacity when a hydro-
phobic solute (e.g. Argon) is transferred from a hydrocarbon environment
to water was explained\textsuperscript{1} on the basis that either:-(a) the pentameric
water clusters are shifted into the short-bond form or (b) the argon
increases the probability for formation of pentagonal-dodecahedra of
water molecules in which the solute is enclosed. The occupation of
free volume in water by argon increases the average population and
cluster size of the "short" hydrogen bonds responsible for the high
partial molar isobaric heat capacities of solutes.

Water is distinguished\textsuperscript{2} from other associated liquids by effects of
solute or temperature on fluctuations of cold water between forms of
different geometry (long- and short-bond forms). Those properties of
water which reflect its high cohesive energy are also found in other
solvents, e.g. ethylammonium nitrate, hydrazine.
1.3 AQUEOUS SOLUTIONS

The standard properties of solutes in aqueous solution, e.g. partial molar volumes, $V^\circ_2$ and partial molar isobaric heat capacities, $C_p^\circ$, are determined by the intrinsic properties of the solute and by solute-water interactions. The following properties of a solute are considered in analysis of hydration characteristics:

(i) electrical properties, e.g. charge and dipole moment

(ii) number of hydrogen bonding sites

(iii) size of apolar residue, e.g. size of alkyl chain in alcohols

(iv) degree of unsaturation or aromaticity of the hydrocarbon part of the molecule

(v) relative position of polar groups, together with their rotational freedom and their conformation.

One or more of the above properties determine the hydration characteristics of a particular solute. A balance is struck between the demands of water-water interactions in the co-sphere of solvent around the solute, and water-solute interactions.

As noted in section 1.2 apolar solutes increase the short-bond form of water, i.e. they enhance water structure. Apolar solutes are formally regarded as structure-makers.

Solutes which contain both a hydrophilic and a hydrophobic moiety can be envisaged as having the hydrophilic group hydrogen-bonded into the water structure and around the hydrophobic group the organisation of water resembles apolar hydration around hydrocarbons or rare gases.

Introduction of small hydrophilic solutes, e.g. DMSO and hydrogen peroxide, into aqueous solution results in a disruption of water
structure, and these solutes are classified as structure breakers. The thermodynamic properties of these solutes show clearly that their solution properties are dominated by strong intercomponent hydrogen-bonding interactions (e.g. $\Delta (\ell \rightarrow \text{aq})C_p^\circ$ for hydrogen peroxide is negative), which disrupt the solvent-solvent hydrogen-bonded system.

Similarly the introduction of a hydrophilic group into a solute dramatically changes its hydration properties because it destroys apolar hydration. In practice there is no clear distinction between apolar and hydrophilic solutes but rather a gradual change as the hydrophilic nature of the solute increases. Ionic solutions are discussed as a separate topic in section 1.3.5.

1.3.1 Standard states for aqueous solutions

Various standard states are used in descriptions of properties of solutions and mixtures. Consider a liquid comprising $n_1$ moles of substance, 1, and $n_2$ moles of substance, 2, at fixed temperature, $T$, and pressure, $p$. If $n_1 > n_2$, the system is described as a solution of solute 2 in solvent 1 (e.g. a dilute aqueous solution of urea). The chemical potential, $\mu_2$, of solute 2 in the system can be related to the composition of the solution in three ways:-

(i) The molal scale (m)

The molality of solute, 2, $m_2 = n_2/n_1 M_1$ where $M_1$ is the molar mass of solvent, 1. $\mu_2$ is related by definition to $m_2$ by equation

$$\mu_2 (\text{system}; T; p) = \mu_2^\circ (\text{soln}; T) + R T \ln \left( m_2 \gamma_2 / m_2^\circ \right)$$

$$+ \int_{p^\circ}^{p} v_2 (\text{soln}; T; p) dp$$

where limit ($m_2 \rightarrow 0$), the activity coefficient, $\gamma_2 = 1.0$ at all $T$ and $p$. 
\( m^\Phi \) is the standard molality (1 mol kg\(^{-1}\)) and \( V_2^\infty \) is the partial molar volume of 2 at infinite dilution \((m_2 \to 0)\). \( \mu_2^\Phi \) is the chemical potential of solute 2 in its standard state, i.e. a solution of 2 in solvent 1 where \( m_2 = 1 \) and \( y_2 = 1 \) at temperature, \( T \) and standard pressure, \( p^\Phi \). The partial molar volume, \( V_2 \), of 2 is related to \( \mu_2 \) by:

\[
V_2 = \left( \frac{\partial \mu_2}{\partial p} \right)_T \quad \ldots (1.2)
\]

Combining equations 1.1 and 1.2 yields:

\[
V_2(\text{system}, T, p) = V_2^\infty(\text{sln}, T, p) + R.T.(\frac{\partial (\ln y_2)}{\partial p})_T \quad \ldots (1.3)
\]

Then Limit \((m_2 \to 0)\):

\[
V_2(\text{system}, T, p) = V_2^\infty(\text{sln}, T, p) \quad \ldots (1.4)
\]

From the Gibbs-Helmholtz equation:

\[
\left( \frac{\partial \mu_2}{\partial T} \right)_p = \frac{H_2}{T^2} \quad \ldots (1.5)
\]

where \( H_2 \) is the partial molar enthalpy of 2. Combining equations 1.1 and 1.5 yields:

\[
H_2(\text{system}, T, p) = H_2^\Phi(\text{sln}, T) + R.T.(\frac{\partial (\ln y_2)}{\partial p})_T + \int_p^P \frac{V_2^\infty(\text{sln}, T, p)}{T} \frac{\partial p^\Phi}{\partial T} \quad \ldots (1.6)
\]

From the Maxwell relation:

\[
\left( \frac{\partial H_2}{\partial p} \right)_T = V_2 - T.\left( \frac{\partial V_2}{\partial T} \right)_p \quad \ldots (1.7)
\]

Integrating equation 1.7 with respect to pressure yields:

\[
H_2^\infty(\text{sln}, T, p) - H_2^\Phi(\text{sln}, T) = \int_p^P \left( V_2^\infty - T.\left( \frac{\partial V_2^\infty}{\partial T} \right)_p \right) dp \quad \ldots (1.8)
\]

Equation 1.6 can be rewritten:

\[
\frac{-H_2(\text{system}; T; p)}{T^2} = \frac{-H_2^\Phi(\text{sln}; T)}{T^2} + R.(\frac{\partial (\ln y_2)}{\partial T})_p + \int_p^P \left[ \frac{-V_2^\infty}{T^2} + \frac{1}{T}.\left( \frac{\partial V_2^\infty}{\partial T} \right)_p \right] dp \quad \ldots (1.9)
\]
Combining equations 1.8 and 1.9 yields:

\[ \frac{-H_2}{T^2} = \frac{-H_2}{T^2} (sln;T) + R. \left( \frac{\beta}{\beta T} (\ln \gamma_2) \right) + \frac{H_2}{T^2} - \frac{H_2}{T^2} \]

or

\[ H_2 (system;T;p) = H_2^\infty (sln;T;p) - R. T. \left( \frac{\beta}{\beta T} (\ln \gamma_2) \right)_p \]

\[ or \]

\[ Hz (system;T;p) = Hz^\infty (sln;T;p) - R.T. \left( \frac{\beta}{\beta T} (\ln \gamma_2) \right)_p \]

Where Limit \((m_2 \to 0)\), \( H_2 (system;T;p) = H_2^\infty (sln;T;p) \) .... (1.10)

Similarly Limit \((m_2 \to 0)\), \( Cp_2 (system;T;p) = Cp_2^\infty (sln;T;p) \) .... (1.12)

where \( Cp_2 \) is the partial molar isobaric heat capacity of solute, 2.

Therefore equation 1.1 satisfies the criteria\(^6\) that at infinite dilution where \( X_2 = V_2, H_2 \) or \( Cp_2 \):

Limit \((m_2 \to 0)\), \( X_2 (system;T;p) = X_2^\infty (sln;T;p) \)

or at ambient pressure, \( p \) \(\approx p^\phi (101325 \approx 10^5 \text{ N m}^{-2})\)

Limit \((m_2 \to 0)\), \( X_2 (system;T;p^\phi) = X_2^\infty (sln;T;p^\phi) = X_2^\phi (sln;T) \) (1.13)

Equation 1.13 does not hold for partial molar entropies, \( S_2 \) (since \( S_2 = - (\beta u_2/\beta T)_p \)) or partial molar Gibbs function, \( G_2 \) (i.e. \( u_2 \)) because in the limit \((m_2 \to 0)\), \( \ln m_2 = -\infty \).

(ii) The concentration scale \((c)\)

If the volume of the system at temperature \( T \) and ambient pressure, \( p \) \(\approx p^\phi \), is \( V \), the concentration of solute 2, \( c_2 = n_2/V \). A common alternative\(^7\) to equation 1.1 expresses \( u_2 (system;T;p^\phi) \) as a function of the concentration, \( c_2 \)

\[ u_2 (system;T) = u_2^m (c;sln;T) + R.T.\ln(c_2 \cdot y_2/c_T) \]

where \( c_T \) is a reference molarity (1 mol dm\(^{-3}\)).

In the Limit \((c_2 \to 0)\), the activity coefficient, \( y_2 = 1.0 \) at all \( T \) and \( p \).

\( u_2^m (c;sln;T) \) is the reference chemical potential of solute, 2, in a solution where \( c_2 = 1 \) and \( y_2 = 1 \) at the same \( T \) and \( p \).

Equation 1.14 does not satisfy the criteria that in the limit \((c_2 \to 0)\), \( X_2 = X_2^\infty = X_2^\phi \), because the differentials \((dc_2/dp)_T\) and \((dc_2/dT)_p\) are not
zero and depend on the system.

(iii) The mole fraction scale (x)

In this formulation $\mu_2$ is related to the mole fraction, $x_2$ of solute, 2, where $x_2 = n_2/(n_1 + n_2)$. At constant $T$ and ambient pressure, $p(= p^\circ)$:

$$
\mu_2(\text{system}; T) = \mu_2^\circ(x; \text{sln}; T) + R.T.(\ln x_2.f_2^\ast) \quad \text{.... (1.15)}
$$

where Limit ($x_2 \to 0$), the activity coefficient, $f_2^\ast = 1.0$ at all $T$ and $p$. $\mu_2^\circ(x; \text{sln}; T)$ is the reference chemical potential of solute 2 in a solution where $x_2 = 1$ and $f_2^\ast = 1$ at the same $T$ and $p$.

The chemical potential, $\mu_1$, of solvent 1 in the system at constant $T$ and ambient pressure, $p(= p^\circ)$ is related to the mole fraction, $x_1$, of solvent 1 by equation 1.16 (considering only the mole-fraction scale definition):

$$
\mu_1(x; \text{system}; T) = \mu_1^\circ(\ell; T) + R.T.\ln(x_1.f_1) \quad \text{.... (1.16)}
$$

where Limit ($x_1 \to 1.0$), the activity coefficient, $f_1 = 1.0$ at all $T$ and $p$. $\mu_1^\circ(\ell; T)$ is the chemical potential of pure liquid 1 at the same $T$ and ambient pressure $p(= p^\circ)$.

1.3.2 Conversions between molar, molal and mole-fraction standard chemical potentials in aqueous solutions

Three alternative formulations of the same quantity $\mu_2(\text{system}; T; p)$ for solute 2 were presented in section 1.3.1. Assuming ambient pressure, $p(= p^\circ)$

$$
\mu_2(\text{system}; T) = \mu_2^\circ(\text{m; sln}; T) + R.T.\ln(m_2.Y_2/m^\circ) \quad \text{.... (1.1)}
$$

$$
= \mu_2^\circ(c; \text{sln}; T) + R.T.\ln(c_2.Y_2/cr) \quad \text{.... (1.14)}
$$

$$
= \mu_2^\circ(x; \text{sln}; T) + R.T.\ln(x_2.f_2^\ast) \quad \text{.... (1.15)}
$$

Therefore combining equations 1.1 and 1.14 yields:--

$$
\mu_2^\circ(\text{m; sln}; T) = \mu_2^\circ(c; \text{sln}; T) + R.T.\ln \left( \frac{c_2.Y_2}{cr} \cdot \frac{m^\circ}{m_2.Y_2} \right) \quad \text{.... (1.17)}
$$

-10-
In the limit of dilute solutions, \( \frac{y_2}{\gamma_2} = 1.0 \) and \( c_2/m_2 = \rho_1^* \), the density of solvent 1, which to preserve the arithmetic of the units is expressed in \( \text{kg dm}^{-3} \) \( \approx \text{g cm}^{-3} \). Thus equation 1.17 becomes:

\[
\mu_2^\theta(m;\text{sln};T) = \mu_2^\#(c;\text{sln};T) + R.T. \ln \left( \frac{\rho_1^*}{\rho_r} \right) \quad \ldots \quad (1.18)
\]

where \( \rho_r \) is a reference density (\( \text{1 kg dm}^{-3} \)). The term \( \text{RT ln} \left( \frac{\rho_1^*}{\rho_r} \right) \) in equation 1.18 is sometimes called the "cratic" contribution, because it arises from two formulations of the composition of the same mixture.

Combining equations 1.1 and 1.15 yields:

\[
\mu_2^\theta(m;\text{sln};T) = \mu_2^\#(x;\text{sln};T) + R.T. \ln \left( \frac{x_2.\rho_1^*}{m_2.\gamma_2} \right) \quad (1.19)
\]

In the limit of dilute solutions \( f_2^*/\gamma_2 = 1.0 \). Also \( m_2 = n_2/(n_1.M_1) \) and \( x_2 = n_2/(n_1 + n_2) \). Hence:

\[
\frac{x_2}{m_2} = \frac{n_2}{(n_1 + n_2)} \cdot \frac{n_1.\gamma_1}{n_2} \quad \ldots \quad (1.20)
\]

but in dilute solutions \( n_1 \gg n_2 \). Therefore from equation 1.20

\[
\frac{x_2}{m_2} = M_1 \quad \ldots \quad (1.21)
\]

Therefore in the limit of dilute solutions equation 1.19 becomes:

\[
\mu_2^\theta(m;\text{sln};T) = \mu_2^\#(x;\text{sln};T) + R.T. \ln \left( M_1.m_1^\theta \right) \quad \ldots \quad (1.22)
\]

Combining equations 1.14 and 1.15 yields:

\[
\mu_2^\#(c;\text{sln};T) = \mu_2^\#(x;\text{sln};T) + R.T. \ln \left( \frac{x_2.\gamma_1^-}{c_2.\gamma_2} \right) \quad (1.23)
\]

In the limit of dilute solutions \( f_2^*/\gamma_2 = 1.0 \) and \( c_2/m_2 = \rho_1^* \); \( \gamma_2^\theta = \gamma_1^- \).

Then:

\[
\mu_2^\#(c;\text{sln};T) = \mu_2^\#(x;\text{sln};T) + R.T. \ln \left( \frac{x_2.\gamma_1^-}{m_2.\rho_1^*} \right) \quad (1.24)
\]

Combining equations 1.21 and 1.24 in the limit of dilute solutions yields:

\[
\mu_2^\#(c;\text{sln};T) = \mu_2^\#(x;\text{sln};T) + R.T. \ln \left( M_1.m_1^\theta.\frac{\gamma_1^-}{\rho_1^*} \right) \quad (1.25)
\]
1.3.3 Apparent Partial Molar Properties

For a solute, 2, in solvent, 1, the partial molar property of the solute in the mixture is related to the corresponding property of the solution by:-

\[ X = n_1X_1 + n_2X_2 \quad \ldots (1.26) \]

For a solution in 1 kg of solvent:-

\[ X = \frac{m_1}{M_1}X_1 + m_2 X_2 \]

where \( X = G, H, S, V, Cp \).

\( X_1 \) and \( X_2 \) in equation 1.26 are two unknowns and therefore in practice equation 1.26 cannot be readily solved. Therefore new quantities, \( f_2 \), are defined as apparent partial molar properties of the solute, i.e. at constant temperature, \( T \), and pressure, \( p \), for a solution in 1 kg of solvent, by definition for \( X = V, H \) and \( Cp \):-

\[ X = m_2 f_2 + \left( \frac{1}{M_1} \right) X_1^* \quad \ldots (1.27) \]

where \( X_1^* \) is the molar property of pure solvent 1.

1.3.4 Binary Aqueous Mixtures

In section 1.3.1 the aqueous systems contained solute, 2, in solvent, 1, where \( n_1 \gg n_2 \) (e.g. aqueous solution of urea). In this section, attention is turned to a system where \( n_1 \) and \( n_2 \) are of comparable magnitude, e.g. a binary liquid mixture of alcohol and water.

For two liquids, 1 and 2, at constant temperature \( T \), and at ambient pressure, \( p(\approx p^\circ) \), the chemical potentials for each liquid (using definitions on the mole fraction scale), are related to their mole fraction, \( x \), by:-

\[ \mu_1(\text{system},T) = \mu_1^\circ(\ell,T) + R.T \ln (x_1.f_1) \quad \ldots (1.28) \]

\[ \mu_2(\text{system},T) = \mu_2^\circ(\ell,T) + R.T \ln (x_2.f_2) \quad \ldots (1.29) \]

where \( \mu^\circ \) is the chemical potential of the pure liquid at temperature, \( T \).
For each liquid \((i = 1 \text{ and } 2)\) in the limit \((x_i + 1.0), f_i + 1.0\). In an ideal mixture \(f_1 = f_2 = 1.0\).

The molar Gibbs function for the mixture formed by \(n_1\) moles of liquid 1 and \(n_2\) moles of liquid 2 at fixed \(T\) and \(p\), is given by:

\[
G_m = \frac{(n_1 \mu_{1} + n_2 \mu_{2})}{(n_1 + n_2)}
\] .... (1.30)

Combining equations 1.28, 1.29 and 1.30 yields:

\[
G_m = x_1 [\mu_1(\ell;T) + R.T. \ln (x_1.f_1)] + x_2 [\mu_2(\ell;T) + R.T. \ln (x_2.f_2)]
\] .... (1.31)

\(\Delta_{\text{mix}} G_m\) describes the change in \(G\) on mixing \(n_1\) moles of 1 and \(n_2\) moles of 2:

\[
\Delta_{\text{mix}} G_m = G_m - [x_1 \mu_1(\ell;T) + x_2 \mu_2(\ell;T)]
\]

or

\[
\Delta_{\text{mix}} G_m = x_1 [\mu_1(\text{system};T) - \mu_1(\ell;T)] + x_2 [\mu_2(\text{system};T) - \mu_2(\ell;T)]
\] .... (1.32)

Combining equations 1.28, 1.29 and 1.32 yields:

\[
\Delta_{\text{mix}} G_m = x_1 R.T. \ln (x_1.f_1) + x_2 R.T. \ln (x_2.f_2)
\] .... (1.33)

But

\[
\Delta_{\text{mix}} G_m \text{ (ideal)} = x_1 R.T. \ln x_1 + x_2 R.T. \ln x_2
\]

\[.\] \[.\] \[.\] \[.\] \[.\] \[.\]

\[
G_m^E = x_1 R.T. \ln f_1 + x_2 R.T. \ln f_2
\] .... (1.34)

the deviations of the properties of a mixture from ideal is called the Excess Molar Gibbs Function of mixing, \(G_m^E\).

\(G_m^E\) can be calculated from the dependence of the vapour pressure of the mixture on composition \(^9\) (i.e. \(x_i f_i = \text{[equilibrium partial vapour pressure of } 1 \text{ in the mixture]} / \text{[vapour pressure of pure } 1]\)).

For an ideal mixture the excess molar enthalpies, \(H_m^E\); volumes, \(V_m^E\); and heat capacities \(C_p^E\) of mixing are zero. Therefore these quantities directly measure deviations from ideal.

Excess molar entropies of mixing, \(S_m^E\) are calculated using the relationship:

\[
G_m^E = H_m^E - T S_m^E
\] .... (1.35)

Aqueous mixtures can be divided into two main groups \(^3\):-

\[.\] \[.\] \[.\] \[.\] \[.\] \[.\]
(i) Typically Aqueous, T.A.

(ii) Typically Non-Aqueous, T.N.A.

For typically aqueous mixtures $G_m^E$ is positive, $H_m^E$ is negative and $T_{Sm}^E$ is negative with $|TS_{m}^E| > |H_m^E|$. Mixing of typically aqueous mixtures is therefore said to be entropy controlled. Solvents forming such mixtures include 'monohydric alcohols + water' mixtures and 'acetone + water' mixtures. The dependences of $S_m^E$ and $H_m^E$ on mole fraction, $x_2$, are complex, although the overall dependence of $G_m^E$ is not. Fig. 1.3 shows the dependences of $G_m^E$, $H_m^E$ and $T_{Sm}^E$ on mole fraction in 'acetone + water' mixtures. The striking feature is the S-shaped $H_m^E$ curve, indicating how the interactions between components in the mixture change as the mole fraction is varied. Further consequences of the importance of $S_m^E$ in the systems are discussed in Chapter 8, Section 8.1.1.

Typically non-aqueous mixtures are divided into two further groups:

(i) T.N.A.P., where $G_m^E$ is positive, e.g. 'acetonitrile + water' mixtures.

(ii) T.N.A.N., where $G_m^E$ is negative, e.g. 'hydrogen peroxide + water' mixtures.

The sign and magnitude of $G_m^E$ in this class of mixtures is determined by the enthalpy term, $H_m^E$, i.e. $|H_m^E| > |T_{Sm}^E|$.

More complicated systems containing three substances, e.g. a 'water + methanol' mixture containing a solute where $n($solute$) \ll n$(H$_2$O), n(MeOH), are discussed in Chapter 3.

1.3.5 Ionic Solutions

(i) Ionic Hydration

Around an ion in aqueous solution, the water molecules are subject to intense ion-solvent dipole interactions, which are reflected by
FIGURE 1.3

$X^E$ functions (in J mol$^{-1}$) for 'acetone + water' mixtures at 323 K vs $x_1$ for water.

[Reprinted from Ref. 10]
negative enthalpies of hydration, \( \Delta(g \rightarrow aq)H^\ominus(\text{ion}) \). Entropies of hydration, \( \Delta(g \rightarrow aq)S^\ominus(\text{ion}) \), are also negative but, surprisingly, not as negative as would be expected from considerations of the strong ion-solvent dipole interactions alone. The model,\(^{11}\) Fig. 1.4, described below accounts for the observations cited above.

![Figure 1.4 Model for ionic hydration in aqueous solution.](image)

The model identifies three zones:

(i) **Zone A**: water molecules hydrate the ion in an electrostricted layer of solvent molecules.

(ii) **Zone C**: water molecules are essentially unperturbed from bulk water at the same \( T \) and \( p \) but they are subject to the electric field from the ion.

(iii) **Zone B**: water molecules are disordered, i.e. water structure is broken in this zone. Zone B increases as the size of ions increases. Therefore the larger the ion the more water structure is broken. Large ions such as chloride, bromide and iodide are called "electrostrictive structure breakers". For small ions (e.g. lithium and fluoride ions), Zone B is absent. These latter ions are called "electrostrictive structure formers".
With tetra-alkyl ammonium ions larger than ethyl the apolar alkyl chains dominate the hydration properties, and these ions are hydrophobic structure formers; the extent of structure forming increasing with increase in the size of the alkyl chain. The Me₄N⁺ ion is usually classed as an electrostrictive structure breaker, and Et₃N⁺ ion appears to have no marked effect on water structure.

The ionic hydration model only applies to ions in their solution standard states where ion-ion interactions are absent.

(1) "Real" Salt Solutions

The average separations of ions in a 1:1 electrolyte solution of 10, 1 or 0.1 mol dm⁻³ are 4.4, 9.4 and 20 Å respectively. Therefore for a 1:1 electrolyte, dilute solutions contain [electrolyte] < 0.1 mol dm⁻³.

In dilute salt solutions ion-ion interactions can be described fairly accurately in terms of charge-charge interactions. These long-range interactions produce a stabilizing influence, the chemical potential of the salt in solution being less than in the corresponding ideal solution.

Consider an electrolyte that dissociates completely in solution as:

\[
M\nu^+ X\nu^- \rightarrow \nu^+ M^\nu^+ + \nu^- X^- 
\]

With complete dissociation one mole of electrolyte produces \( \nu^+ \) moles of cations and \( \nu^- \) moles of anions in aqueous solution (e.g. \( \nu^+ = \nu^- = 1 \) for NaCl or CuSO₄, but \( \nu^+ = 1 \) and \( \nu^- = 2 \) for MgCl₂). By definition, \( \nu = \nu^+ + \nu^- \), which denotes the total number of moles of ions produced by one mole of electrolyte. In the system let there be \( n_j \) moles of the electrolyte, \( j \), at temperature, \( T \) and ambient pressure, \( p(=p^o) \). If \( \gamma_\pm \) is the mean ionic activity coefficient of the electrolyte and \( \gamma_\pm \) and \( \gamma_\pm \) are the single ion activity coefficients of cations and anions respectively,
then these are related by definition using equation 1.36;

\[ \gamma_\pm \mu = \gamma_+ \mu^+ - \gamma_- \mu^- \]

or \( \mu \ln \gamma_\pm = \mu_+ \ln \gamma_+ + \mu_- \ln \gamma_- \) .... (1.36)

Similarly the mean ionic molality, \( m_\pm \), of the electrolyte is given by equation 1.37;

\[ m_\pm \mu = m_+ \mu^+ - m_- \mu^- \] .... (1.37)

or \( m_\pm \mu = (\nu_+ m_j) \mu^+ - (\nu_- m_j) \mu^- \)

\( = \nu_+ \mu^+ - \nu_- \mu^- m_j \mu \)

Let \( Q^\mu = \nu_+ \mu^+ - \nu_- \mu^- \)

Then \( m_\pm \mu = (Q m_j)^\mu \) .... (1.38)

Considering definitions on the molal scale only, the chemical potential, \( \mu_j \), of the electrolyte is given by equation 1.39;

\[ \mu_j (\text{system};T) = \mu_j^\phi (\text{soln};T) + \nu_+ R T \ln \left( \frac{Q m_j \gamma_+}{m^\phi} \right) \] .... (1.39)

where Limit \((m_j \to 0), \gamma_\pm = 1.0\) at all \( T \) and \( p \).

For a 1:1 salt \( \nu_+ = 1 \) and \( \nu_- = 1 \), therefore \( Q = 1.0 \)

and \[ \mu_j (\text{system};T) = \mu_j^\phi (\text{soln};T) + 2 R T \ln \left( \frac{m_j \gamma_+}{m^\phi} \right) \] .... (1.40)

For a 1:2 salt, \( \nu = 3 \) and \( Q = 4 \) \( [\text{i.e. } Q = (1^1 2^2) = 4] \). \( \mu_j^\phi \) is the standard chemical potential of the electrolyte in a solution where \( m_j = 1 \) and \( \gamma_\pm = 1 \) at the same \( T \) and \( p \). For a 1:1 salt, \( \mu_j^\phi = \mu_+^\phi + \mu_-^\phi \)

where \( \mu_+^\phi \) and \( \mu_-^\phi \) are the standard chemical potentials of the cation and anion respectively.

For a 1:1 salt at ambient pressure, \( p(z p^\phi) \), equation 1.40 can be rewritten as:

\[ \mu_j (\text{system};T) = \mu_j^\phi (\text{soln};T) + 2 R T \ln \frac{m_j}{m^\phi} + 2 R T \ln \gamma_+ \]

\[ \text{IDEAL} \quad \text{NON-IDEAL} \]

.... (1.41)
The Debye-Hückel Limiting Law (D.H.L.L.) treats $\gamma_{\pm}$ in terms of charge-charge interactions. The limiting law is:

$$\ln(\gamma_{\pm}) = -S_{\gamma}(I)^{1/2}$$

(1.42)

where $I$ = ionic strength ($I = \frac{1}{2} \sum_{j=1}^{n} m_j Z_j^2$ and for a 1:1 salt $I = m_j$) and $S_{\gamma}$ is a function of the solvent properties at the given temperature and pressure and charges on the ions.

The presence of some underlying pattern to ionic activity coefficients, $\gamma_{\pm}$, not readily accounted for by the D.H.L.L. have been known for many years. Such patterns are apparent when $\gamma_{\pm}$ for salt solutions at fixed molality and temperature are examined as a function of the anion. For example, $\gamma_{\pm}(\text{Pr}_4\text{N}^+\text{F}^-) > \gamma_{\pm}(\text{Cs}^+\text{F}^-)$ but $\gamma_{\pm}(\text{Cs}^+\text{I}^-) > \gamma_{\pm}(\text{Pr}_4\text{N}^+\text{I}^-)$. These and related trends can be understood in terms of the effect on $\gamma_{\pm}$ of overlapping solvent co-spheres (Chapter 5). As a general rule, two solute ions will attract each other if their tendencies to orient water molecules are compatible, but they will repel each other if their influences are incompatible. Attraction will lower and repulsion raise the activity coefficients.

The success of the D.H.L.L. is often limited to analysis of chemical potentials and related quantities, e.g. effect of ionic strength on solubility products. The failure of the D.H.L.L. to account for dependences of enthalpy, entropy and volume properties on salt concentrations is often striking; compensation between enthalpy and entropy quantities minimizing the changes in Gibbs function. The dependence of these derived parameters on salt concentration highlights the importance of co-sphere interactions.
1.4 SOLVENT EFFECTS ON RATES OF REACTION

The standard enthalpy of solvation of an ion in a polar solvent can be very large, often of the order of the strength of a covalent bond. Therefore a change from a less polar to a more polar solvent will increase or decrease the change in enthalpy of reaction, $\Delta_r^\Theta H^\Theta$, depending on the polarity of the products.\textsuperscript{13} There may be countering changes of entropy. However, it is a generally valid assumption that the enthalpy change will dominate the change in Gibbs function for reaction, $\Delta_r^\Theta G^\Theta$, and that equilibria will shift towards more polar products in more polar solvents.

According to this theory\textsuperscript{13} of solvent effects on reaction kinetics, a change to a more polar solvent will decrease or increase the enthalpy of activation, $\Delta_r^\Theta H^\Theta$, depending on whether the transition state is more or less polar than the initial state of the reactants. The theory assumes that changes in $\Delta_r^\Theta H^\Theta$ dominate the rate change. Concerning reactants and transition states, the following three assumptions were made as to the amount of solvation to be expected in the presence of electric charges.

(i) Solvation will increase with the size of the charge.
(ii) Solvation will decrease with increasing dispersal of a charge.
(iii) Decrease in solvation due to dispersal of a charge will be less than that due to its destruction.

Concerning solvents the theory\textsuperscript{13} assumed that polarity (i.e. power to solvate charges in solutes) will:-

(i) increase with increase in the molecular dipole moment of the solvent,
(ii) decrease with increased thickness of shielding of dipole charges.

The analysis outlined in Table 1.1 is noteworthy because it sets down
### TABLE 1.1

Predicted and observed solvent effects on rates of nucleophilic substitutions

<table>
<thead>
<tr>
<th>Charge disposition (is → ts)</th>
<th>Effect of increased solvent polarity on rate</th>
<th>Predicted</th>
<th>Obs. rate const.(^b) in EtOH + H(_2)O (vol. % H(_2)O) / (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(^{-}) + RX → Y---R---X (\delta^{-}) (\delta^{-})</td>
<td>Small decrease</td>
<td>Pr(^{1})Br + OH(^{-}) (10^{5}k_{55})</td>
<td>6.0</td>
</tr>
<tr>
<td>Y + RX → Y---R---X (\delta^{+}) (\delta^{-})</td>
<td>Large increase</td>
<td>Pr(^{1})Br + H(<em>2)O (10^{7}k</em>{55})</td>
<td>1.73</td>
</tr>
<tr>
<td>Y(^{-}) + RX(^{+}) → Y---R---X (\delta^{-}) (\delta^{+})</td>
<td>Large decrease</td>
<td>Me(<em>3)S(^{+}) + OH(^{-}) (10^{4}k</em>{100})</td>
<td>7240</td>
</tr>
<tr>
<td>Y + RX(^{+}) → Y---R---X (\delta^{+}) (\delta^{+})</td>
<td>Small decrease</td>
<td>Me(_3)S(^{+}) + NMe(<em>3) (10^{5}k</em>{45})</td>
<td>6.67</td>
</tr>
<tr>
<td>RX → R---X (\delta^{+}) (\delta^{-})</td>
<td>Large increase</td>
<td>Bu(^{\text{t}})Cl (10^{6}k_{25})</td>
<td>9.14</td>
</tr>
<tr>
<td>RX(^{+}) → R---X (\delta^{+}) (\delta^{+})</td>
<td>Small decrease</td>
<td>Bu(^{\text{t}})Me(<em>2)S(^{+}) (10^{5}k</em>{50})</td>
<td>1.90</td>
</tr>
</tbody>
</table>


\(^b\) Subscripts indicate temperature in °C.
the basic principles for the analysis of solvent effects on rate
constants for different types of nucleophilic substitution reactions.

Analysis of solvent effects on rates of reaction is discussed in
Chapters 3 and 4.

1.5 SUBSTITUTION REACTIONS

In the main, chemical reactions for which kinetic data are reported
here involve substitution reactions. Therefore a short resumé of the
background of substitution reactions is presented.

During the course of a substitution reaction a bond is made and a
bond is broken. Molecularity can be defined in terms of the timing of
the bond-making and bond-breaking aspects of substitution. Bond-making
and bond-breaking can be either (a) synchronous or (b) non-synchronous.

(a) Synchronous bond-making/breaking

The substitution process takes place in one step. No intermediates
are formed, only one transition state (T-S). For a reaction;

\[ Y + AX \rightarrow YA + X \]

the reaction profile is represented by Fig. 1.5.

(b) Non-Synchronous bond-making/breaking

During a non-synchronous bond-making/breaking substitution reaction
an intermediate is formed. Such substitutions can be of two different
types:-

(i) bond-breaking before bond-making

The intermediate has a lower coordination number than the reactant
and the process is dissociative; Fig. 1.6 represents the reaction
profile.

(ii) bond-making before bond-breaking

The intermediate has a higher coordination number than the reactant
FIGURE 1.5
Reaction Free Energy profile illustrating a synchronous substitution reaction. $\Delta r G^\circ$ is the Gibbs function for reaction. $\Delta^+ G^\circ$ is the Gibbs function for activation.

FIGURE 1.6
Reaction Free Energy profile for a non-synchronous dissociative substitution reaction.
and the process is associative (Fig. 1.7).

For both non-synchronous substitution reactions the intermediate is NOT the transition state. If an intermediate is formed during the course of a substitution reaction then two transition states will also be formed, one for each stage of the substitution. There are no restrictions on the lifetime of an intermediate but usually the lifetime is very short.

1.5.1 Nomenclature of the different types of nucleophilic substitution reactions

If, during a substitution reaction, an intermediate is formed of lower coordination number than the reactant (i.e. bond-breaking first), the reaction is called an 'SN1.lim.' reaction (where lim. = limiting).

If an intermediate of higher coordination number than the reactant, is formed during the course of a reaction (i.e. bond-making first), the
reaction is called an 'SN2.1lim.' reaction. All other types of substitution reactions fall between 'SN1.1lim.' and 'SN2.1lim.'.

Langford and Gray\textsuperscript{14} nomenclature is slightly more detailed. A 'D' mechanism refers to a dissociative process analogous to 'SN1.1lim.' An 'A' mechanism refers to an associative process analogous to 'SN2.1lim.' and 'I' is the interchange process where substitution occurs with synchronous bond-making/breaking. Other types of substitution reaction between the limits of an 'A' or 'D' mechanism are called the "intimate mechanism". This latter mechanism is sub-divided into 'd' and 'a' processes. For the 'd' process the entering group does not interact directly with the reaction centre in the transition state; in the 'a' process the entering group does interact directly with the reaction centre. Therefore for a 'd' intimate mechanism the rate of reaction is insensitive to the nature of the entering group except for solvation interactions and the opposite is true for an 'a' mechanism.

An 'I' mechanism is assigned to reactions where there is no evidence for an intermediate and these can be of two types:-(i) I\textsubscript{a} or (ii) I\textsubscript{d}. 'I\textsubscript{a}' is the synchronous bimolecular process. 'D' and 'I\textsubscript{d}' are distinguished in terms of the lifetime of the intermediate. A 'D' mechanism is assigned to reactions in which the life-time of the intermediate is long enough to equilibrate its solvation environment, otherwise an 'I\textsubscript{d}' mechanism is assigned to the reaction.

1.5.2 Substitution at six-coordinate reaction centres (d-block elements)

Apart from Cr(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{3+} and Rh(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{3+}, the M(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{m+} (where M = d-block elements) complexes exchange their ligands with water very rapidly, e.g. for high spin Fe(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{2+} the first order rate constant for the exchange of a single water molecule at 298 K is 3 \times 10^{6} \text{ s}^{-1}. N.m.r. techniques are used to determine the number of solvent molecules around M\textsuperscript{m+} and the
average time spent by a solvent molecule in the coordination shell of $M^{n+}$.

Usually the higher the charge on $M^{n+}$, the more inert the aquo complex and the rate of solvent exchange increases as the ionic radius increases.

Complex formation is characterised by two relaxation processes:

(i) A diffusion controlled process which has a half life between $10^{-8}$ and $10^{-10}$ seconds. The diffusion process is dependent on the charges on the species and the nature of the solvent.

(ii) A slower step which is almost independent of the nature and concentration of the ligand but very sensitive to the nature of $M^{n+}$ and the solvent.

For example, consider the reaction:

$$Fe(H_2O)_6^{3+} + Cl^- \rightleftharpoons Fe(H_2O)_5^{2+}Cl + H_2O$$

(i) **Step 1**

$$Fe(H_2O)_6^{3+} + Cl^- \rightleftharpoons Fe(H_2O)_6^{3+} \rightleftharpoons Cl^-$$

Step 1 is rapid diffusion controlled formation of an outer sphere complex, in this case an ion pair.

(ii) **Step 2**

$$Fe(H_2O)_6^{3+} \rightleftharpoons Cl^- \rightleftharpoons Fe(H_2O)_5^{2+}Cl \rightleftharpoons H_2O$$

Step 2 is a slow interchange process. The chloride ion has to 'wait' for a water molecule to vacate a coordination site before it can occupy the site.

Generally the actual rate of the interchange process is approximately the same as the rate of solvent exchange in the absence of the ligand. However, if the rate of formation of a stable chelate complex is controlled by another factor, e.g. ring closure, the reaction will be much slower than the rate of solvent exchange because of the relative "slow-
ness" of, for example, ring closure.

Complex formation reaction is therefore typically 'I_d' mechanism for a typical octahedral substitution reaction.

1.5.3 General kinetic features of octahedral substitution

Kinetic evidence shows that the rate of substitution is rarely very strongly dependent on the nature or concentration of the incoming group, which suggests a 'D' or an 'I_d' mechanism. However, there is little evidence for five-coordinate intermediates.

The concentration of the solvent is usually in vast excess over the concentration of incoming ligand. When the solvent is a potential ligand, it can dominate the substitution reaction. Even if the solvent is a poor ligand it often dominates the substitution reaction because of the much greater concentration of the solvent with respect to the ligand. However, weak bonds between the solvent and \( \text{M}^{n+} \) causes this latter species to dissociate repeatedly thus allowing other ligands to bond to \( \text{M}^{n+} \). In all cases, competition between the solvent and other potential ligands for a place in the inner solvation shell is of great kinetic significance.

1.6 LOW SPIN IRON(II) COMPLEXES

The majority of iron(II) complexes are high spin (\( t_{2g}^4 e_g^2 \)), but complexes containing ligands which have a large crystal field effect are low spin (\( t_{2g}^5 \)) and kinetically inert. Ligands which have a large crystal field effect include cyanide ion and a series of aromatic nitrogen bases containing the chelating unit (I).

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{C} \\
\text{N}
\end{array}
\]

(I)
Many of the reactions for which kinetic data are reported in this thesis involve iron(II), 1,10-phenanthroline complex ion \([\text{Fe(phen)}]^{2+}\). The cation (II) resembles a three-bladed propeller\(^{15}\) the blades being the planar phenanthroline ligands. There are three large V-shaped pockets between the phenanthroline ligands, each large enough to allow small molecules such as water or anions to approach quite closely to the central metal atom.\(^{16}\)

A model\(^{16}\) for the solvation of \(\text{Fe(phen)}]^{2+}\) was proposed by Meter and Neumann. The solvation energy was considered to be the sum of two separate contributions: (i) that due to ion-dipole interaction with the solvent and (ii) that due to Van-der-Waals' interaction between the solvent and the aromatic ligands. The contribution to the solvation energy arising from ligand-solvent interaction was obtained from the solubility data for naphthalene.

Low spin iron(II) di-imine complexes have intense colours, which are a result of electron transfer (\(\pi\)-back bonding) from the filled \(t_{2g}\) orbitals of \(\text{Fe}^{2+}\) to the \(\pi^*\) orbitals of the di-imine ligands (synergic effect) (III).

\(\pi\)-back bonding between the metal ion and the ligand stabilises the complex and is the reason why such complexes are unreactive in aqueous solution. The change in energy due to \(\pi\)-back bonding for \(\text{Fe(phen)}]^{2+}\) is such that the wavelength of maximum absorbance is at 510 nm, resulting in a very intense red coloured compound.
1.6.1 Reactions of low spin iron(II) di-imine complexes

Kinetic data have been reported for a variety of reactions including aqutation of Fe(phen)$_3^{2+}$ and reactions with hydroxide and cyanide ions in aqueous solution.$^{17}$

The formation and dissociation of Fe(phen)$_3^{2+}$ cation were first investigated by Lee, Kolthoff and Leussing.$^{18}$ They showed that the dissociation was first order in [complex] in an excess of acid and independent of the acid concentration. The results were accounted for by suggesting stepwise dissociation of the complex involving three equilibria (coordinated water is not included):

\[
\begin{align*}
\text{Fe(phen)$_3^{2+}$} & \rightleftharpoons \text{Fe(phen)$_2^{2+}$} + \text{phen} \\
\text{Fe(phen)$_2^{2+}$} & \rightleftharpoons \text{Fe(phen)$_1^{2+}$} + \text{phen} \\
\text{Fe(phen)$_1^{2+}$} & \rightleftharpoons \text{Fe$^{3+}$} + \text{phen}
\end{align*}
\]

In acid solution the equilibria are displaced to the right by protonation of the ligand molecules. The rate-determining step was shown to be loss of the first phen ligand (i.e. the first step in the equilibria shown above).

Later$^{17}$ it was found that aqutation of Fe(phen)$_3^{2+}$ was strongly dependent both on solvent composition and on the nature of added acid.
Whether kinetic effects of the latter are a consequence of ion-pairing or of effects of the added ions on solvent structure is still not clear.

Reactions of Fe(phen)$_3^{2+}$ and many of its derivatives with nucleophiles, $Y$, where $Y =$ hydroxide or cyanide ions follow the rate expression:

$$-\frac{d[\text{Fe(phen)}_3^{2+}]}{dt} = \{k_1 + k_2[Y]\} \cdot [\text{Fe(phen)}_3^{2+}] \quad \ldots \quad (1.43)$$

The simplest interpretation of this rate expression implies a reaction mechanism involving two simultaneous reactions; one involving direct participation of, $Y$, in the rate determining step or a pre-equilibrium, and the other not. The latter, $Y$-independent part is analogous to the mechanism for acid dissociation, followed by fast reaction of dissociation products with $Y$.

The presence of dissolved oxygen$^{19}$ is essential for reactions of Fe(phen)$_3^{2+}$ with hydroxide ions, i.e. iron(II) is oxidised to iron(III) during the process (eqn. 1.44):

$$\text{Fe(phen)}_3^{2+} + \text{OH}^-, \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3(\text{aq}) + 3(\text{phen}) \quad \ldots \quad (1.44)$$

Plots of first order rate constants against cyanide ion concentration are linear and pass through the origin. Therefore the $k_1$-term (eqn. 1.43) is negligible under these conditions. Reaction of Fe(phen)$_3^{2+}$ and many of its substituents with cyanide ions produces the mixed ligand complex, bis-(1,10-phenanthroline)biscyano iron(II) (eqn. 1.45);

$$\text{Fe(phen)}_3^{2+} + 2\text{CN}^- \rightarrow \text{Fe(phen)}_2(\text{CN})_2^{2-} + \text{phen} \quad \ldots \quad (1.45)$$

The ultimate reaction product of Fe(phen)$_3^{2+}$ with cyanide ions would be Fe(CN)$_6^{4-}$. Kinetic data have been reported$^{20}$ for reactions of Fe(phen)$_2(\text{CN})_2$ with cyanide ions in aqueous solution to form the tetra-cyano complex, [Fe(phen)(CN)$_4$]$^{2-}$. Two consecutive steps during the formation of this latter complex were detected. The variation of rate constants with cyanide ion concentration were consistent with the rate
laws shown in equation (1.46) for the first step and equation (1.47) for the second step;

\[-d[\text{Fe(phen)}_2(CN)_2]/dt = k_2[\text{Fe(phen)}_2(CN)_2][CN^-] \quad \ldots \quad (1.46)\]

\[-d[\text{intermediate}]/dt = k_1[\text{intermediate}] \quad \ldots \quad (1.47)\]

The rate laws in equations (1.46) and (1.47) were explained by suggesting the reaction sequence shown below;

\[
\text{Fe(phen)}_2(CN)_2 \xrightarrow{k_2} \text{intermediate} \xrightarrow{k_1} \left[\begin{array}{c}
\text{(CN)}_2\text{(phen)}\text{Fe}
\end{array}\right] \xrightarrow{\text{FAST}} \text{CN}^- \rightarrow \text{[Fe(phen)(CN)]}^{2-}
\]

\text{phen}^1 = \text{unidentate phenanthroline.}

The suggested intermediate was of type (IV)

\[
\left[\begin{array}{c}
\text{(CN)}_2\text{(phen)}\text{Fe}
\end{array}\right]
\]

\text{(IV)}

For reactions involving nucleophilic attack at low spin iron(II) di-imine complexes, various mechanisms have been proposed to explain the bimolecular term of the experimental rate laws. The nucleophile can either attack directly at the metal ion or at the ligand. The latter reaction would result in formation of transient intermediates. Evidence for such intermediates is discussed in Chapter 7.

1.7 EFFECTS OF HYDROPHOBIC LIGANDS ON KINETIC PARAMETERS IN AQUEOUS SOLVENT AND AQUEOUS MIXTURES

With reference to the reaction of Fe(phen)$_3^{2+}$ with hydroxide ions in aqueous solution, when a co-solvent (e.g. acetone) is added the second
order rate constant increases. Using kinetic data and the extrathermo-
dynamic analysis for the solvation energy for Fe(phen)$_3^{2+}$ as suggested
by Van Meter and Neumann$^{16}$ a fairly complete picture of the effect of
added co-solvent on the kinetic parameters was obtained.$^{21}$ It was
shown that both the initial state of the complex and the transition
state are stabilised, but to slightly different extents, on addition of
(i) methanol and (ii) acetone to the aqueous solution. The overall
trend in rate constant was controlled by the gradual destabilisation of
hydroxide ions as the mole fraction of the added co-solvent increases.
The transition state was assumed to be of type (IV), i.e. attack of
hydroxide ion at the ligand producing a species in which the aromatic
character of one pyridine ring is partially lost.

The model for the solution characteristics of Fe(phen)$_3^{2+}$ (Section
1.6) is very similar to the model for ionic solvation (Section 1.3.5).
Thus interactions between Fe(phen)$_3^{2+}$ and neighbouring water molecules
are dominated by the hydrophobic phenanthroline rings. Beyond the co­
sphere, ion-solvent interactions can be treated using a Born-type
expression,$^{22}$ in which $\Delta (g \cdot sln)^{\circ}$ (ion) is related to the radius of
the ion and the relative permittivity of the solvent.

The initial and transition states stabilisation as the mole fraction,
x$_2$, of co-solvent increases is dominated by the hydrophobic groups.
Incorporation of a hydroxyl group into one phenanthroline ring in the
transition state would drastically alter the interaction of this ligand
with the solvent. If the hydroxyl group was extensively hydrogen-bonded
to the solvent then the effect of co-solvent on the change in ligand-
solvent interactions on going from the initial to the transition states
of the complex would be equivalent to the effect of co-solvent on the
difference in solubility of naphthalene and naphthol. However, results
indicated that the hydroxyl group is not completely exposed to the solvent and that in the transition state there has already developed considerable HO---Fe interaction from the hydroxyl group attached to the phenanthroline ligand, (V).

![Diagram](V)

Effects of medium and of pressure on kinetics of reactions of inorganic complexes in water and in water-rich binary mixtures were investigated. Pressure effects are indicative of changes in solvation on going from the initial to the transition state, while solvent effects give indications of changes in solvation of (i) the initial state and (ii) the transition state on transfer between media. Activation volumes, $\Delta^\pm V^\infty$, are derived from dependences of rate constants on pressure at constant temperature, i.e. $(\partial \ln k / \partial p)_T$. $\Delta^\pm V^\infty$ can be divided into intrinsic and solvation contributions:

$$\Delta^\pm V^\infty = \Delta V_{\text{intr.}} + \Delta V_{\text{solvn.}}.$$

In weakly solvating solvents or in the gas phase positive $\Delta^+ V^\infty$ is assigned to a dissociative process and negative $\Delta^- V^\infty$ to an associative process. Even in aqueous solution $\Delta^+ V^\infty$ can be used in establishing mechanisms as solvation effects will be small for an uncharged leaving and entering group. In reactions involving ions in aqueous solution, solvation effects may dominate over intrinsic effects in determining the size and even the sign of $\Delta^\pm V^\infty$.

For reactions involving nucleophilic attack at di-imine complexes,
solvent effects are important both in terms of $\Delta^\circ V^\infty$ and of initial state - transition state analysis with a marked change in emphasis on going from water-rich media to non-aqueous solvents.

The most striking feature concerns $\Delta^\circ V^\infty$. Results reported$^{23}$ for reactions of Fe(bipy)$_3^{2+}$ and Fe(phen)$_3^{2+}$ with hydroxide and cyanide ions in aqueous solvent and for Mo(CO)$_4$ bipy with cyanide ions in methanol and in DMSO respectively suggest that desolvation of cyanide or hydroxide ions necessary for transition state formation may dominate the observed $\Delta^\circ V^\infty$ in water but may be negligible in DMSO.

An analysis for reaction of Fe(bipy)$_3^{2+}$ with cyanide ions in zero to 30% (ideal volume) methanol shows that the modest increase in rate can be attributed to slightly greater stabilisation of the transition state than of the initial state as the proportion of methanol increases. Both are, however, markedly stabilised by adding methanol, the situation being dominated by the hydrophobic groups. The chemical potential of the cyanide ion changes by less than 1 kJ mol$^{-1}$ over this solvent range. This anion is sufficiently hydrophilic to retain its hydration shell essentially intact.

In non-aqueous media for reactions of Mo(CO)$_4$ bipy with cyanide ions, changes in rate constant with solvent are relatively small. In this case, it is the chemical potential of the cyanide ion which changes markedly with solvent, dominating the transfer chemical potentials of the initial and transition state.

The two regions of water-rich and non-aqueous behaviour can be linked by analysis of reactions of Mo(CO)$_4$ bipy with cyanide ion in 'DMSO + water' mixtures. The changeover from cyanide solvation control to hydrophobic complex control can be seen in this latter system.
REFERENCES TO CHAPTER 1

CHAPTER 2

Experimental Details of Collection and Analysis of Kinetic Data
2.1 INTRODUCTION

Details of how kinetic data were measured are presented in this Chapter together with a description of the computer-driven spectrophotometers used to collect absorbance data. Methods of data analysis are reported. Details of programs for minicomputers will not be covered but the underlying principles involved in data analysis are discussed. Analysis of reactions following first order kinetics are presented in this Chapter. Analysis of reactions following more complicated kinetic schemes are dealt with in the appropriate sections.

2.2 FIRST ORDER RATE CONSTANTS

Consider a first order reaction in which reactant A changes to products, C (equation 2.1);

\[ A \xrightarrow{k_1} C \]  

Let the course of reaction 2.1 be monitored by measuring the changes in concentration of A with respect to time. At constant temperature, T, and pressure, P, the concentration of A, \( A_t \), at time, t, is given by equation (2.2);

\[ A_t = A_0 \exp(-k_1 t) \]  

where \( A_0 \) is the initial concentration of A and \( k_1 \) is the first order rate constant for reaction 2.1. Equation 2.2 can be rewritten as;

\[ \ln \left( \frac{A_0}{A_t} \right) = k_1 t \]  

The half life, \( t_{1/2} \), of reaction 2.1 is the time when \( A_t = A_0/2 \). Therefore, at \( t_{1/2} \), equation 2.3 becomes:-

\[ \frac{\ln(2)}{k} = t_{1/2} \]  

For all systems studied here kinetics of reaction were monitored for at least two-and-a-half half lives (i.e. \( t_{1/2} \times 2.5 \)). In many of the
systems following first order kinetics with respect to [A], the reaction was bimolecular but the concentration of all reactants other than A was much higher than A and hence remained virtually constant throughout the reaction, i.e. the reaction medium was engineered to produce first order conditions.

The observed first order rate constant (k_{obs}) in many of the systems varied as the concentration of reactants other than A was varied. Consider a reaction:

\[ \text{A} + \text{B} \rightarrow \text{C} \] .... (2.5)

where [B] \gg [A]. A common pattern which emerged was a dependence where:

\[ k_{obs} = k_1 + k_2 [B] \] .... (2.6)

where \(k_1\) is a first order rate constant and \(k_2\) is a second order rate constant for reaction 2.5 (Chapter 1, Section 1.6.1). This type of kinetic pattern is illustrated, for example, in Chapters 3, 4 and 11.

In all systems studied here, kinetics of reaction were monitored by observing changes in concentration of either the reactants or the products with respect to time. Concentration changes of any species were measured spectrophotometrically by measuring changes in absorbance, \(P\).

Absorbance, \(P\), arising from a single chemical species, \(A\), in solution is related to its concentration by the Beer-Lambert Law:

\[ P = \log_{10} \frac{I_o}{I_t} = \varepsilon_{\lambda \lambda} \cdot \ell \cdot [A] \] .... (2.7)

where \(I_o\) and \(I_t\) are the intensities of incident and transmitted light at wavelength, \(\lambda\); \(\varepsilon_{\lambda \lambda}\) is the molar extinction coefficient of \(A\) at wavelength, \(\lambda\) and \(\ell\) is the path-length. This law is obeyed only for monochromatic light and in dilute solutions of \(A\). Mixtures of species usually give additive absorbances;
\[
\frac{P}{\ell} = \epsilon_A[A] + \epsilon_B[B] + \ldots. \tag{2.8}
\]

Therefore from the absorbance changes in the mixture changes in concentration are analysed.

For a first order reaction (equation 2.1), in which the rate of reaction is measured at \(\lambda_{\text{max}}(A)\) by monitoring the absorbance change for only the one species, A, combining equations 2.3 and 2.7 yields;

\[
\ln \left( \frac{A_0}{A_t} \right) = \ln \left( \frac{P_o - P_\infty}{P_t - P_\infty} \right) = k_1 t \tag{2.9}
\]

where \(\lambda_{\text{max}}(A)\) is the wavelength of maximum absorbance for species A; \(P_o\) is the initial absorbance of A (i.e. at time, \(t=0\)); \(P_t\) is the absorbance of A at time \(t\) and \(P_\infty\) is the absorbance of A at \(t=\infty\) (i.e. when the reaction is completed). In the majority of reactions the absorbances at \(\lambda_{\text{max}}(A)\) of any other species present in the reaction mixture are negligible. From equation 2.9 the rate constant \(k_1\) is calculated using a Non-Linear Least Squares Analysis (Section 2.3).

Visible and ultraviolet monitoring is particularly useful because reactions of transition metal complexes are accompanied by absorption changes in these regions.

2.3 ANALYSIS OF ABSORBANCE DATA

Absorbance data for first order reactions were analysed using the Non-Linear Least Squares procedure suggested by Moore.\(^1\)

Rearranging equation 2.9 yields;

\[
P_t = P_\infty + (P_o - P_\infty) \exp(-k_1 t) \tag{2.10}
\]

Hence at time, \(t\), the absorbance, \(P_t\), is defined by the variables, \(P_o\), \(P_\infty\) and \(k_1\);

\[
P_t = P_t [P_o, P_\infty, k_1] \tag{2.11}
\]

The general differential of equation 2.11 is given by;
\[
dP_t = \left( \frac{\partial P_t}{\partial P_o} \right)_{P_o, k_1} dP_o + \left( \frac{\partial P_t}{\partial P_{oo}} \right)_{P_o, k_1} dP_{oo} + \left( \frac{\partial P_t}{\partial k_1} \right)_{P_o, P_{oo}} d k_1 \quad \cdots \quad (2.12)
\]

From equation 2.10, the partial differentials in equation 2.12 are given by:

\[
\frac{\partial P_t}{\partial P_o} = \exp (-k_1 t) = \alpha_1 \quad \cdots \quad (2.13)
\]

\[
\frac{\partial P_t}{\partial P_{oo}} = 1 - \exp (-k_1 t) = \alpha_2 \quad \cdots \quad (2.14)
\]

\[
\frac{\partial P_t}{\partial k_1} = -t \cdot (P_o - P_{oo}) \exp (-k_1 t) = \alpha_3 \quad \cdots \quad (2.15)
\]

Equation 2.12 can be rewritten to give:

\[
dP_t = \alpha_1 dP_o + \alpha_2 dP_{oo} + \alpha_3 d k_1 \quad \cdots \quad (2.16)
\]

The procedure for calculating P_o, P_{oo} and k_1 starts from guessed estimates for P_o, P_{oo} and k_1. Therefore at each time, t, (i.e. for every data point), P_t(calc) is obtained using equation 2.10. The difference, dP_t, between the observed and calculated absorbance is then calculated [i.e. dP_t = P_t(obs) - P_t(calc)] for each data point. From equations 2.13, 2.14 and 2.15, \alpha_1, \alpha_2 and \alpha_3 are calculated at each time, t. A linear least squares technique, based on equation 2.16, is used to estimate the correctors dP_o, dP_{oo} and d k_1. The analysis seeks to minimise over n data points, the quantity Q defined by equation 2.17;

\[
Q = \sum_{n=1}^{n} (dP_t - \alpha_1 dP_o - \alpha_2 dP_{oo} - \alpha_3 d k_1)^2 \quad \cdots \quad (2.17)
\]

When Q is a minimum:

\[
\frac{\partial Q}{\partial (3P_o)} = 0 = 2(\Sigma \alpha_1 dP_t + \Sigma \alpha_1^2 dP_o + \Sigma \alpha_1 \alpha_2 dP_{oo} + \Sigma \alpha_1 \alpha_3 d k_1) \quad \cdots \quad (2.18)
\]

\[
\frac{\partial Q}{\partial (3P_{oo})} = 0 = 2(\Sigma \alpha_2 dP_t + \Sigma \alpha_2 \alpha_1 dP_o + \Sigma \alpha_2^2 dP_{oo} + \Sigma \alpha_2 \alpha_3 d k_1) \quad \cdots \quad (2.19)
\]

\[
\frac{\partial Q}{\partial (3k_1)} = 0 = 2(\Sigma \alpha_3 dP_t + \Sigma \alpha_3 \alpha_1 dP_o + \Sigma \alpha_3 \alpha_2 dP_{oo} + \Sigma \alpha_3^2 d k_1) \quad \cdots \quad (2.20)
\]
Equations 2.18, 2.19 and 2.20 can be rewritten in matrix form:

\[
\begin{bmatrix}
\Sigma a_1^2 & \Sigma a_1a_2 & \Sigma a_1a_3 \\
\Sigma a_2a_1 & \Sigma a_2^2 & \Sigma a_2a_3 \\
\Sigma a_3a_1 & \Sigma a_3a_2 & \Sigma a_3^2
\end{bmatrix}
\begin{bmatrix}
dP_0 \\
dP_{\infty} \\
dk_i
\end{bmatrix}
= 
\begin{bmatrix}
\Sigma a_1 \\
\Sigma a_2 \\
\Sigma a_3
\end{bmatrix}
\begin{bmatrix}
dP_t \\
dP_t \\
dP_t
\end{bmatrix}

\ldots (2.21)

\]

or \( Y = X\beta \)

Following matrix inversion (Chapter 11, Section 11.3),
\( dP_0, dP_{\infty} \) and \( dk_i \) are calculated. The correctors yield improved values for \( P_0, P_{\infty} \) and \( k \), e.g. \( k_i(\text{improved}) = k_i(\text{previous}) + dk_i \). From the improved values and equation 2.10, \( P_t(\text{calc}) \) is re-calculated. This latter value is compared with \( P_t(\text{obs}) \). If \( \Sigma [P_t(\text{obs}) - P_t(\text{calc})]^2 \) is either a minimum or the agreement of comparable magnitude to the estimated experimental precision, the analysis is complete and \( P_0, P_{\infty} \) and \( k_i \) are fitted satisfactorily to equation 2.10. If agreement between \( P_t(\text{obs}) \) and \( P_t(\text{calc}) \) is poor the cycle is repeated.

2.4 SPECTROPHOTOMETRIC APPARATUS

2.4.1 Pye Unicam SP800 and SP1800

Both the SP800 and the SP1800 spectrophotometers measured the absorbance of solutions using a double beam system. A chart recorder on the SP800 produced scans of spectra in the range 14,500-50,000 cm\(^{-1}\) (approximately 690-200 nm). The scan could be repeated at intervals of between 0.5 and 15 minutes. Preliminary investigations into a particular system were performed using the SP800. From the repeat scans kinetic complexities could be identified; for first order reactions, \( P_0, P_{\infty} \) and \( k_1 \) (equation 2.4) were estimated; the wavelength identified at which the kinetics of reaction could be monitored and isosbestic points identified.

The SP1800 spectrophotometer was used to monitor the dependence of absorbance, \( P \), on time at a single wavelength. The SP1800 was linked
through a digital voltmeter and an analogue-to-digital converter to an
HP9825A minicomputer (Fig. 2.1). The SP1800 was also connected directly
to the 'MIKE' interface (MIKE - Microprocessor Instrumentation of
Kinetic Experiments).

The computer was linked to an HP7245A plotter. The cell compartment
of the SP1800 could hold four sample (and four reference) cells in a
thermostatted cell block, which could be moved automatically to place
a given cell in the light beam.

The MIKE interface was the key communication device between computer
and spectrophotometer. The computer supplied a 'cell select' binary
number to call one of the four possible cells. The MIKE interface
compared the cell selected by the computer with the cell currently
located in the light beam of the spectrophotometer. If the cell selected
by the computer and the cell in the light beam of the SP1800 were the
same a reading was taken; if they were not the same, the MIKE interface
activated the spectrophotometer to move the cell block until the correct
cell was positioned.

At this stage, the interface activated the digital voltmeter to
record the absorbance. A one-and-a-half second delay between the
positioning of the cell in the light beam and activation of the digital
voltmeter allowed the pointer of the analogue meter in the SP1800 to
come to rest after a cell change. For measurements of rates of reactions
in a single cell run a delay was not necessary. The MIKE interface
allowed manual selection for either single- or multi-cell experiments.

Within the digital voltmeter, an analogue-to-digital converter device,
converted absorbance signals to a form required by the computer. When a
reading was available, the computer accepted it and returned a 'data
transmitted' pulse to clear the last reading in readiness for more data.
FIGURE 2.1
SP 1800 Spectrophotometer and HP 9825 A Apparatus

Analogue to digital converter. Converts absorbance signal to form required by computer.
Programs for analysing absorbance-time data in terms of various kinetic schemes were written by Dr. M. J. Blandamer (only first order kinetics are considered in this section).

The program was stored on a data-tape cartridge and loaded into the computer at the start of a series of kinetic experiments. The program was initiated by typing 'RUN'. The number of cells in the run, the initial and final absorbances and estimated first order rate constants for each cell were fed into the computer. The computer calculated the initial time step for readings using the estimated first order rate constant (i.e. time step, $t = \ln 2/\{k_1 \times N_p\}$, where $N_p$ is the number of readings before the first calculation). A choice was available for the number of readings to be taken on each cell before a calculation of the rate constant was performed, and for the number of readings between successive calculations.

The program awaited the command to begin monitoring and reading the absorbances of the cells. Once this command was given the computer completely controlled the experiment. The thermal printer output from the computer recorded:- (a) absorbance-time data for each cell; (b) results of the iterations at the calculation stages; (c) final rate constants, $P_0$ and $P_\infty$ values when cells had run for at least $2\frac{1}{2}$ half lives and (d) standard deviations on actual absorbances when these were fitted to a first order analysis using the Non-Linear Least Squares Method (Section 2.3). The computer keyboard during a kinetic run was live and could be used to abort any cells giving unsatisfactory data output.

Figure 2.2 shows the flow-diagram for minicomputer control of first order kinetics and Figure 2.3 is an example of a three-cell computer output for a first order reaction.

At the end of a kinetic experiment the computer offered an option for
FIGURE 2.2
Flow Diagram for minicomputer control of first-order kinetic experiments.

1. **RUN**

2. **INPUT PARAMETERS FOR EACH CELL IN TURN**
   - \(k_i\)
   - \(P_{o_i}\)
   - \(P_{o_0}\)
   - \(N_p\) = no. of readings before first calculation
   - \(N_B\) = no. of readings between calculations

3. **Ready to go**
   - NO
   - YES

4. **Read clocks for all cells running. Has 't' elapsed?**
   - NO
   - YES

5. **Select cell, 1; read time, \(P_t\). Store data**

6. **Is no. of points on cell 1 > \(N_p\) for that cell?**
   - NO
   - YES

7. **Enter calc. routine**

8. **Are all cells finished?**
   - NO
   - YES

9. **Parameter summary start with cell 1**

10. **1st. order plot?**
    - NO
    - YES

11. **List \(k, P_o, P_{o_0}\)**

12. **More cells**
    - NO
    - END

13. **Plot**

14. **Solve normal equations**

15. **Return with original parameters**
   - NO
   - YES

16. **Is \(\sum(P_t \text{obs} - P_t \text{calc})^2 < 1\)?**
    - YES
    - NO

17. **6 cycles of calculation**
    - NO
    - YES

18. **\(k \text{ (new)} = k \text{ (prev.)} + dk\)**
    - \(P_o \text{ (new)} = P_o \text{ (prev.)} + dP_o\)
    - \(P_{o_0} \text{ (new)} = P_{o_0} \text{ (prev.)} + dP_{o_0}\)

19. **\(k \text{ (new)}, P_o \text{ (new)}, P_{o_0} \text{ (new)}\)**
    - calculate new \(t_i\) and 't'

20. **Is total time elapsed > 2.5 half lives**
    - NO
    - YES

21. **Cell finished. Store parameters. Set control so that this cell no longer monitored.**
KEY TO FIGURE 2.2

\( t \) = time step between readings.

1* - the test to assess whether \( k, P_0 \) and \( P_\infty \) from the Non-Least Squares Analysis were adequate or whether to go through another iterative cycle was when 
\( \Sigma (P_{\text{obs}} - P_{\text{calc}})^2 \) between successive cycles was \( \leq 10 \).

plotting out the logarithms of the absorbances against time (i.e. a first order plot equation 2.9) on the HP7245A plotter. These latter plots were useful in identifying whether the reaction was following good first order kinetics. Examples of first order plots are given in the appropriate sections, (e.g. Section 2.4.2).

2.4.2 HP8451A Diode Array Spectrophotometer

The HP8451A recorded, displayed and stored absorbances as a function of both time and wavelength. Figure 2.4 illustrates in block diagram form, the essential features of the HP8451A.

Central to the operation of the HP8451A were two microcomputers, the Z.80 and the HP85A. The Z.80 controlled the internal hardware (i.e. lamp, shutter, pre-amp and analogue-to-digital converter [ADC]) and performed measurements. The HP85A handled the data and acted as an interface between user and spectrophotometer.

The HP8451A wavelength range was from 190 to 820 nm at 2 nm resolution. A scan of absorbances over the full range of wavelength required only 0.1 seconds. The spectrophotometer had eight input/output ports (only five I/O ports are shown in Fig. 2.4). The HP1B interface linked the disc drive unit and the external plotter to the system. Another I/O port linked the alphanumeric keyboard to the HP8451A.

The printer/plotter was a thermal printer which used a moving print
FIGURE 2.3
An example of a three-cell computer output, using the SP 1800 spectrophotometer, for a first-order reaction.

<table>
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<th>time</th>
<th>reading</th>
<th>cell</th>
<th>range</th>
<th>cycle</th>
<th>cycle</th>
<th>cycle</th>
<th>cycle</th>
<th>rate constant</th>
</tr>
</thead>
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<td>707</td>
<td>1</td>
<td>650</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>7.74047e-06</td>
</tr>
<tr>
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<td>656</td>
<td>2</td>
<td>690</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>7.10752e-06</td>
</tr>
<tr>
<td>3</td>
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<td>553</td>
<td>3</td>
<td>690</td>
<td>1</td>
<td>1</td>
<td></td>
<td>4</td>
<td>7.43241e-06</td>
</tr>
</tbody>
</table>

run number= 24
comp 3
NAME
andy
solvent
26% meth [g]
temperature
25
full print type
1
1
date
88:88:88:88:88
number of cells
3
for cell
1.00000e 00
est initial reading
.69
est final reading
.1
guessed rate constant
9e-6
if OK, type 1
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FIGURE 2.4
A block diagram of the HP 8451A diode array spectrophotometer.
head on special heat-sensitive paper.

Only one cell could be held in the thermostatted sample compartment in contrast to the SP1800 which could hold four cells.

Within the HP8451A was a VDU display screen which displayed absorbance spectra at selected time intervals.

The external disc-drive unit consisted of two disc compartments. The left-hand (L.H.S.) compartment was used for programmed discs and the right-hand side (R.H.S.) compartment was used for data-storage discs.

At the beginning of a kinetic experiment a program for data-logging was loaded from the L.H.S. disc into the HP8451A. In one data-logging program absorbance data could be stored as a function of time at between one to five different wavelengths. Using another program absorbance data could be stored over the entire wavelength range but at fewer times. This latter program made considerable demands on the data storage capacity of the system.

Usually kinetic data were monitored at one pre-selected wavelength except in cases where absorbances of intermediates were required. Absorbance-time data were collected for a specified number of readings at specified time-intervals, and the spectra were displayed during the course of the experiment. Absorbances of the reference cell and solvent were taken at the start of a kinetic experiment and this latter absorbance was automatically subtracted by the HP8451A from the absorbance of the solution under study. At the end of the experiment the absorbance-time data was transferred to the R.H.S. disc of the external disc-drive unit, and a copy of the spectrum was transferred onto the thermal paper. An option for a printed output of the absorbance-time data was available.
Once data-logging was completed the data-logging program was erased from the HP8451A. A program containing an analysis routine was loaded into the spectrophotometer from the L.H.S. disc of the disc-drive unit. This latter program analysed the data stored in the R.H.S. disc of the disc-drive unit in terms of first-order kinetics (Section 2.2 and 2.3). Options of thermal printer output of absorbance-time plots and first-order plots (equation 2.9) were available. The rate constant, \(k\), for the reaction, \(P_0, P_\infty\) together with standard errors on these latter values and the standard deviations on the actual absorbances when these were fitted to a first-order analysis were recorded on the thermal printer output. Figure 2.5 is a typical example of the output obtained from (a) the data-logging program and (b) a first-order analysis program, in a reaction which was monitored by measuring the rate of appearance of the absorbance band of the products.

2.4.3 Thermostatting and cell composition

Cell blocks for the SP1800 and HP8451A were machined from copper. Copper/platinum heating coils were wound on the outside of the blocks and cooling water was circulated through channels. The whole block was insulated. A temperature probe was embedded in the cell block and connected to an external multi-channel digital display unit. A temperature control unit was connected directly to the cell block. The thermostatted cell blocks allowed the temperature of the solutions in the cells to be maintained and measured accurately to 0.01 K.

1 cm quartz cells of capacity greater than 3 cm³ were used. Cells were made up with reagents to a total volume of 3 cm³. Stock solutions of reagents were prepared such that on mixing the required volumes in the quartz cells, the desired concentrations of solutes and composition of co-solvents were obtained. In an alternative method, one or two drops
FIGURE 2.5(a)
Example of the HP 8451A spectrophotometer computer output obtained from the data-logging program. (time in s.)

FIRST ORDER LOG
SYSTEM= 11.8
WAVELENGTH = 272
TIME STEP= 140
RUN TIME= 7000
NUMBER OF READINGS= 51
RANGE= 200
TO 400

Absorbance vs. Wavelength
DATA ON DISC
FIGURE 2.5(b)
Example of the HP 8451A spectrophotometer computer output obtained from the first-order analysis program.

NO. WAVELENGTHS = 1
RUN = 11.8
NUMBER OF DATA POINTS = 50
EST K = 0.003
ZERG = 0.1
P-INFIN = 0.8
SET = 1
WAVELENGTH = 272
FIGURE 2.5(b) Continued

NO. WAVELENGTHS = 1
RUN = 11.8
NUMBER OF DATA POINTS = 58
EST K = 0.003
P-ZERO = 0.1
P-INF = 0.8
SET = 1
WAVELENGTH = 272
ST DEV ON ABS = 1.6442158925E-3
RATE CONSTANT = 3.80968447502E-4
P-ZERO = 0.150315449869
P-INF = 0.84285035907

ST DEV = 1.6442159232E-3
ST ERROR ON P-ZERO = 0.91592106621E-4
ST ERROR ON P-INF = 1.54046132202E-3
ST ERROR ON K = 2.12318166337E-6
of concentrated reagent (usually metal complex) were added to a cell containing the appropriate concentrations of the reaction medium.

In all systems solutions of reagents in the quartz cells were thermostatted to the required temperature (usually 298 K) before initiating a reaction.
REFERENCE TO CHAPTER 2

CHAPTER 3

Kinetics of Reaction between Iron(II)
glyoxal bis-N-methylamine with hydroxide
ions in methanol-water mixtures:
Derivation of single ion transfer chemical
potentials and their application to analysis
of solvent effects on kinetic parameters
3.1 INTRODUCTION

In this Chapter transfer chemical potentials are reported for single ions in methanol-water mixtures. Kinetic data for reaction of iron(II) glyoxal bis-N-methylamine [Fe(gmi)$_2$]$^{2+}$, (I)] with hydroxide ions in methanol-water mixtures are reported and the solvent effects on initial and transition states for the above reaction are discussed.

In recent years a number of different estimates have been reported of single ion properties in methanol-water mixtures. These single ion parameters have been obtained using different extrathermodynamic assumptions. If these different sets of estimates are used in analysing kinetic data, different conclusions emerge. Therefore the procedures used to obtain single ion parameters, their definition and application are examined in some detail together with a short resumé of the analysis of solvent effects on initial and transition states for reaction.

3.1.1 Standard States, Reference States, Composition and Description of Systems

The relationship between derived parameters and the description of a system is crucially important in distinguishing different descriptions of a given system. A detailed examination of the terminology is presented below because the definitions have a bearing on derived single ion properties.

Descriptions of a system comprising two substances 1 and 2 were
examined in Chapter 1, Section 1.3.1. In this Section attention turns to examining properties of a system comprising three substances 1, 2 and 3. Examination of possible descriptions of this latter system leads to the required formalism for examining the properties of a solute in a binary liquid mixture, e.g. 'water + methanol'.

Consider a system, (B) comprising three substances 1, 2 and 3 at equilibrium at temperature, T, and ambient pressure, p (≈ p°), e.g. a system containing \( n(w) \) (w = water), \( n(\text{MeOH}) \) and \( n(\text{urea}) \) where \( n_j \) is the number of moles of \( j \). The total Gibbs function, \( G \), of system B is given by equation 3.1:

\[
G^\text{eq}(B;T) = n_1 \mu_1^\text{eq}(B;T) + n_2 \mu_2^\text{eq}(B;T) + n_3 \mu_3^\text{eq}(B;T) \quad \text{.... (3.1)}
\]

All descriptions of this system must be consistent with the same \( G^\text{eq}(B;T) \) and yield identical equilibrium chemical potentials of the three substances.\(^1\)\(^2\) In this Section, systems at thermodynamic equilibrium are considered and therefore the superscript, "eq", is omitted.

In system, B, let \( n(\text{urea}) \ll n(w), n(\text{MeOH}) \). In terms of descriptions of system, B, the molality of urea, \( m_u \), can be related to the composition of the solution in three different ways:-

(i) **Description (I):** the solvent is water, then;

\[
m_u(I) = \frac{n(\text{urea})}{n(w) M(w)} \quad \text{.... (3.2)}
\]

where \( M(w) \) is the molar mass of water.

(ii) **Description (II):** the solvent is a mixture of 'water + methanol', then;

\[
m_u(II) = \frac{n(\text{urea})}{[n(w) M(w) + n_{\text{MeOH}} M_{\text{MeOH}}]} \quad \text{.... (3.3)}
\]

where \( M_{\text{MeOH}} \) is the molar mass of methanol.

(iii) **Description (III):** the solvent is methanol, then;
\[ m_u(III) = \frac{n(\text{urea})}{n_{MeOH} M_{MeOH}} \quad \text{(3.4)} \]

For each description there is a corresponding reference or standard state for urea in solution, and an activity coefficient, \( \gamma_u \). For solute urea using description (I) of system B, there are three reference states and three activity coefficients based on molal, molar and mole-fraction definitions. There are three reference states using either description (II) or (III) of system B. In other words, for solute urea there are at least nine reference states and nine activity coefficients. Therefore it is of paramount importance to define clearly the reference states\(^3\) when drawing comparisons of how solvent composition affects a given reactant.

Constant temperature, \( T \), and ambient pressure, \( p(\approx p^\circ) \) are assumed in all descriptions given below.

**Description I of system, B (B;I)**

System B is a solution of solutes 2 (=MeOH), and 3 (=urea) in solvent 1 (=water). The chemical potentials \( \mu_2 \) and \( \mu_3 \) in the system (B;I) are related to the composition of the solution in three different ways:-

(i) the molality, \( m_3(B;I) = n_3/n_1M_1 \). The chemical potential of solute 3, \( \mu_3 \), is related to \( m_3(B;I) \) by;

\[ \mu_3(\text{system};B;I) = \mu_3^\varphi(\text{sln};B;I) + R.T. \ln \left( \frac{m_3(B;I)}{m_3^\varphi(B;I)} \right) \quad (3.5) \]

where Limit \([m_3(B;I) \to 0; m_2(B;I) \to 0]\), \( \gamma_3(B;I) = 1.0 \) at all \( T \) and \( p \).

\( \mu_3^\varphi(\text{sln};B;I) \) is the standard chemical potential of 3 in a solution in liquid 1 where \( \gamma_3(B;I) = 1 \) and \( m_3(B;I) = 1 \) at the same temperature and standard pressure.

A similar equation is written for solute, 2, so that \( \mu_2^\varphi(\text{sln};B;I) \) is the standard chemical potential of 2 in a solution in liquid 1 where \( \gamma_2(B;I) = 1 \) and \( m_2(B;I) = 1 \) at the same temperature and standard pressure.
The standard state for solute 3, using description (I) is identical to the standard state for 3 if it were a single solute in solvent 1 (Chapter 1, Section 1.3.1).

The chemical potentials \( \mu_2 \) and \( \mu_3 \) in the system (B;I) can be related to (ii) the concentration \( c_2 \) and \( c_3 \) respectively [cf. Chapter 1; equation (1.14)] or to (iii) the mole fraction \( x_2 \) and \( x_3 \) respectively [cf. Chapter 1; equation (1.15)]; where limit \( (c_j \rightarrow 0; c_2 \rightarrow 0) \), \( y_j (B;I) = 1.0 \) at all \( T \) and \( p \) where \( j = 2, 3 \) and the limit \( (x_2 \rightarrow 0; x_3 \rightarrow 0) \), \( f_j^*(B;I) = 1.0 \) at all \( T \) and \( p \). The reference chemical potential \( \mu_j^# \) (c-scale;sln;B;I) is the chemical potential of \( j \) in solution in liquid 1 where \( c_j = 1.0 \) and \( y_j(B;I) = 1.0 \) at the same \( T \) and reference pressure; \( \mu_j^# \) (x-scale;sln;B;I) is the chemical potential of \( j \) in solution in liquid 1 where \( x_j = 1.0 \) and \( f_j^*(B;I) = 1.0 \) at the same \( T \) and reference pressure. \( \mu_j^#(c\text{-scale};\text{sln};B;I) \) and \( y_j(B;I) \); and \( \mu_j^#(x\text{-scale};\text{sln};B;I) \) and \( f_j^*(B;I) \) are intimately related.

Description II of system B (B;II)

The solvent is the mixture "1 + 2" having constant composition independent of \( n_3 \) and 3 is the solute in solvent "1 + 2". The chemical potential of \( j \), where \( j = 1 \) or 2 in system (B;II) is given by;

\[
\mu_j (\text{system}; B; II) = \mu_j^*(\ell) + R.T. \ln(x_j.f_j[B;II]) \quad \ldots (3.6)
\]

Where Limit \( (x_j \rightarrow 1.0) \), \( f_j(B;II) = 1.0 \) at all \( T \) and \( p \). \( \mu_j^*(\ell) \) is the chemical potential of pure liquid, \( j \), at the same \( T \) and \( p^\circ \).

The chemical potential of solute 3, \( \nu_3 \), is related to the molality \( m_3(B;II) \) \( [m_3(B;II) = n_3/(n_1M_1 + n_2M_2)] \) by;

\[
\nu_3 (\text{system}; B; II) = \nu_3^\circ(\text{soln}; B; II) + R.T.\ln(m_3(B;II).\gamma_3(B;II)/m^\circ) \quad \ldots (3.7)
\]

Where Limit \( [m_3(B;II) \rightarrow 0; x_2] \), \( \gamma_3(B;II) = 1.0 \) at all \( T \) and \( p \).

The definition of \( \gamma_3(B;II) \) requires that the properties of 3 approach
ideal as the system becomes infinitely dilute in '3' as a solute in the solvent mixture '1+2', where \( x_2 = \frac{n_2}{n_1 + n_2} \). \( \gamma_3(B;II) \neq \gamma_3(B;I) \) and \( \mu_3^\phi(sln;B;II) \neq \mu_3^\phi(sln;B;I) \), but the two equations for \( \mu_3 \) (system) can be linked:

\[
\mu_3^\phi(sln;B;I) + RT \ln \left( \frac{m_3(B;I) \cdot \gamma_3(B;I)}{m^\phi} \right) = \mu_3^\phi(sln;B;II) + RT \ln \left( \frac{m_3(B;II) \cdot \gamma_3(B;II)}{m^\phi} \right)
\]

or \( \mu_3^\phi(sln;B;II) = \mu_3^\phi(sln;B;I) + R.T. \ln \left( \frac{m_3(B;I) \cdot \gamma_3(B;I)}{m_3(B;II) \cdot \gamma_3(B;II)} \right) \)

where Limit \( (x_2 + 0) \mu_3^\phi(sln;B;II) = \mu_3^\phi(sln;B;I) \).

The difference \([\mu_3^\phi(sln;B;II) - \mu_3^\phi(sln;B;I)]\) depends on the two methods for describing the molality and the two activity coefficients. The difference between \( m_3(B;I) \) and \( m_3(B;II) \) are only functions of the description of the system, but the difference between \( \gamma_3(B;II) \) and \( \gamma_3(B;I) \) is more fundamental. In the system urea (\( \equiv 3 \)), methanol (\( \equiv 2 \)) and water (\( \equiv 1 \)), \( \gamma_3(B;I) \) describes deviations from ideal of the properties of the solute, urea, which arise from urea-urea, urea-alcohol and through the Gibbs-Duhem communication, alcohol-alcohol interactions within the aqueous solution. \( \gamma_3(B;II) \) describes deviations from ideal of the properties of the solute, urea, which arise from urea-urea interactions within the solvent "water + methanol".

\( \mu_3 \) (system;B;II) is related to the concentration, \( c_3 \), in a solvent mixture '1+2', mole fraction \( x_2 \) by:

\[
\mu_3(\text{system};B;II;x_2) = \mu_3^\phi(c\text{-scale};sln;B;II;x_2) + R.T. \ln \left( \frac{c_3 \cdot \gamma_3(B;II)}{c_r} \right)
\]

where Limit \( (c_3 + 0; x_2) \), \( \gamma_3(B;II) = 1.0 \) at all T and p.

\( \mu_3 \) (system;B;II) is also related to the mole-fraction \( x_3 \), in a solvent mixture '1+2', mole fraction \( x_2 \) by;
\( \mu_3(\text{system}; B; II; x_2) = \mu_3^*(x\text{-scale}; \text{soln}; B; II; x_2) + R.T. \ln [x_3.f_3^*(B; II)] \)  

(3.10)

where Limit (\( x_3 \to 0; \ x_2 \)), \( f_3^* = 1.0 \) at all \( T \) and \( p \).

Conversions between molal, molar and mole-fraction standard and reference chemical potentials of solute 3 in system (B; II)

Combining equations 3.7 and 3.9 yields;

\( \mu_3^*(m\text{-scale}; \text{soln}; B; II; x_2) = \mu_3^*(c\text{-scale}; \text{soln}; B; II; x_2) + R.T. \ln \left\{ \frac{c_3, \gamma_3(B; II)}{m_3(B; II) \cdot \gamma_3(B; II)} \right\} \)  

(3.11)

\( \gamma_3(B; II) \) and \( \gamma_3(B; II) \) describe solute-solute (3-3) interactions within the solvent '1 + 2'. Therefore in the limit of dilute solutions, \( \gamma_3(B; II)/\gamma_3(B; II) = 1.0 \) and \( c_3/m_3(B; II) = \rho(x_2) \), the density of the solvent '1 + 2' at mole fraction \( x_2 \). Then equation 3.11 can be rewritten;

\( \mu_3^*(m\text{-scale}; \text{soln}; B; II; x_2) = \mu_3^*(c\text{-scale}; \text{soln}; B; II; x_2) + R.T. \ln \left( \frac{\rho(x_2)}{\rho_r} \right) \)  

(3.12)

where \( \rho_r \) is the reference density. If \( \rho(x_2) \) is expressed in g cm\(^{-3}\), then \( \rho_r = 1 \) g cm\(^{-3}\).

Combining equations 3.7 and 3.10 in the limit of dilute solutions where \( f_3^*(B; II)/\gamma_3(B; II) = 1.0 \);

\( \mu_3^*(m\text{-scale}; \text{soln}; B; II; x_2) = \mu_3^*(x\text{-scale}; \text{soln}; B; II; x_2) + R.T. \ln \left\{ \frac{x_3}{m_3(B; II)} \right\} \)  

(3.13)

The total mass, \( M \), of the system in the limit of dilute solutions of solute 3 is given by, \( M = n_1M_1 + n_2M_2 \).

Then \( m_3 = n_3/(n_1M_1 + n_2M_2) \) and \( x_3 = n_3/(n_1 + n_2) \). Therefore;

\[ \frac{x_3}{m_3(B; II)} \cdot m^\phi = \frac{n_1M_1 + n_2M_2}{(n_1 + n_2)} \]

or

\[ \frac{x_3}{m_3(B; II)} \cdot m^\phi = x_1M_1 + x_2M_2 \]  

(3.14)
but $x_1 = (1-x_2)$. Combining equations 3.13 and 3.14 yields:

$$\mu_3^\Phi (m\text{-scale;soln;B;II};x_2) = \mu_3\#(x\text{-scale;soln;B;II};x_2) + R.T. \ln \left(1-x_2 + x_2 \frac{M_2}{M_1} \right) \quad \ldots (3.15)$$

Equation 3.15 is used for conversions between molal and mole-fraction scales where the proportion of added co-solvent is expressed in mole-fraction ($x_2$).

If the composition of the solvent is expressed in mass-per-cent, $w_1\%$ and $w_2\%$, where $w_1\% = (100-w_2)\%$, then in the limit of dilute solutions from $x_3 = n_3/(n_1+n_2)$:

$$x_3 = n_3/\left(\frac{w_1 + w_2}{M_1 + M_2}\right) \quad \ldots (3.16)$$

For 100g of solution:

$$x_3 = n_3/\left(\frac{(100-w_2) + w_2}{M_1 + M_2}\right) \quad \ldots (3.17)$$

Combining equations 3.13, 3.16 and 3.17 yields:

$$\mu_3^\Phi (m\text{-scale;soln;B;II};x_2) = \mu_3\#(x\text{-scale;soln;B;II};x_2) + R.T. \ln \left[ \frac{10^2 m^\Phi}{(100-w_2) + w_2} \right] \quad \ldots (3.18)$$

Combining equations 3.12 and 3.18 yields the conversion between molar- and mole-fraction reference chemical potentials for solute 3 in solvent '1+2' at mole fraction $x_2$ in the limit of dilute solutions:

$$\mu_3 (c\text{-scale;soln;B;II};x_2) = \mu_3 (x\text{-scale;soln;B;II};x_2) + R.T. \ln \left[ \frac{10^2 m^\Phi}{(100-w_2) + w_2} \right] \cdot \frac{\rho}{\rho(x_2)} \quad (3.19)$$

3.1.2 Transfer Chemical Potentials

Considering description II of system B only, where the solvent is
'1 + 2' and the solute is 3, the transfer chemical potential, 
\[ \Delta[(x_2=0) - x_2] \mu_3^\circ \] is defined as the difference between the standard 
chemical potential of solute 3 in a solvent mole-fraction, \( x_2 \) and the 
standard chemical potential of solute 3 in a solvent mole-fraction, 
\( x_2=0 \) (equation 3.20). 
\[ \Delta[(x_2=0) - x_2] \mu_3^\circ (sln;B;II) = \mu_3^\circ (sln;B;II;x_2) - \mu_3^\circ (sln;B;II;x_2=0) \] .... (3.20)

The sign and magnitude of \( \Delta[(x_2=0) - x_2] \mu_3^\circ \) can depend on the particular 
standard or reference states adopted in the comparisons. 4

The reference state, i.e. solvent, \( x_2=0 \) is taken as comprising solute 
3 in solvent 1 (e.g. urea in water) and the changes in standard chemical 
potentials of 3, arise as substance 2 is added (i.e. \( x_2 > 0 \)).

In the following discussion, definitions refer to solutions in 
system (B;II) at constant T and ambient pressure, \( p = p^\circ \) and in the 
limit of dilute solutions. Therefore the terms in brackets [i.e. (sln; 
B;II)] are omitted.

The transfer chemical potentials of solute 3, \( \Delta[(x_2=0) - x_2] \mu_3^\circ (m-scale); \) 
\( \Delta[(x_2=0) - x_2] \mu^\ast (c-scale) \) and \( \Delta[(x_2=0) - x_2] \mu^\ast (x-scale) \) are related using 
equations 3.12, 3.18 and 3.19;

\[ \Delta[(x_2=0) - x_2] \mu_3^\circ (m) = \Delta[(x_2=0) - x_2] \mu_3^\circ (c) + R.T. \ln \left( \frac{\rho(x_2)}{\rho(x_2=0)} \right) \] (3.21)

\[ \Delta[(x_2=0) - x_2] \mu_3^\circ (m) = \Delta[(x_2=0) - x_2] \mu_3^\circ (x) + R.T. \ln \left( \frac{(10^2/M_1)}{(100-w_2) + w_2} \right) \] 
\[ \frac{M_1}{M_2} \] .... (3.22)

[N.B. in pure 1, \( n_2=0 \). Therefore \( x_3/m_3 = n_1 M_1/n_1 = M_1 \)]

\[ \Delta[(x_2=0) - x_2] \mu_3^\circ (c) = \Delta[(x_2=0) - x_2] \mu_3^\circ (x) + R.T. \ln \left( \frac{(10^2/M_1)}{(100-w_2) + w_2} \right) \] 
\[ \frac{M_1}{M_2} \] .... (3.23)
3.1.3 Salt Solutions

Extending description (II) of system, B, at constant T and ambient pressure $p(\equiv p^0)$, let solute 3 be a salt which for one mole with complete dissociation into ions, yields $\nu_+\,$ moles of cations and $\nu_-\,$ moles of anions;

$$M_{\nu_+}X_{\nu_-} \rightarrow \nu_+M^+ + \nu_-X^-$$

For a 1:1 salt the chemical potential of salt, 3, $\mu_3$ is related to the molality, $m_3$ (Chapter 1, Section 1.3.5) by;

$$\mu_3^{(\text{system};m\text{-scale})} = \mu_3^{(\text{soln};m\text{-scale})} + 2R.T. \ln \left( \frac{m_3 \gamma_+}{\overline{m}} \right) \quad \quad \text{.... (3.24)}$$

$\gamma_\pm$ is the mean ionic activity coefficient, where by definition, Limit ($m_3 \rightarrow 0$), $\gamma_\pm = 1.0$ at all $T$ and $p$. Equation 3.24 can be rewritten where the composition of the solution in solvent "1+2" is expressed in terms of either concentration, $c_3$ or mole fraction, $x_3$, leading to definitions of mean ionic activity coefficients $\gamma_\pm$ and $\overline{\gamma_\pm}$ respectively. The chemical potentials of the salt in the corresponding reference standard states for the salt are represented by $\mu_3^{(c)}$ and $\mu_3^{(x)}$.

Although they are a mathematical fiction, $^5 \mu_3^{(m)}$ can be expressed as the sum of single ion chemical potentials for the ions in their standard states in solution;

$$\mu_3^{(\text{soln};m)} = \nu_+ \mu_+^{(\text{soln};m)} + \nu_- \mu_-^{(\text{soln};m)} \quad \text{.... (3.25)}$$

Analogous equations apply on the concentration and mole-fraction scales.

Transfer chemical potentials $\Delta[(x_2=0) \rightarrow x_2] \mu_3^{(m)}$ [or (c) or (x)] have analogous definitions to those used for uncharged solute, 3, (cf. equation 3.20). Conversions between m-, c- and x-scales are obtained from equations 3.21, 3.22 and 3.23. These latter equations are used in conjunction with single ion parameters. For salts the stoichiometric factor '$\nu$' is incorporated into the equations (i.e. "$\nu \cdot R \cdot T "$ replaces
\[ \Delta [(x_2 = 0) \rightarrow x_2] \mu_3^\Phi (m) = \nu_+ \Delta [(x_2 = 0) \rightarrow x_2] \mu_+^\Phi (m) + \nu_- \Delta [(x_2 = 0) \rightarrow x_2] \mu_-^\Phi (m) \]
and similarly for the \(c\) and \(x\)-scales.

Unfortunately there is no thermodynamic method of separating salt parameters into single ion parameters. An extrathermodynamic assumption is required. If the sub-division could be made for just one salt, the remaining ionic parameters would follow and a table constructed for \(\Delta [(x_2 = 0) \rightarrow x_2] \mu_j^\Phi\) for all \(j\)-ions as a function of \(x_2\). A Kohlrausch-type law applies (cf. \(\Lambda^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty\); where \(\lambda_+^\infty\) and \(\lambda_-^\infty\) are molar conductivities at infinite dilution of the cation and anion respectively and \(\Lambda^\infty\) is the molar conductivity of the salt at infinite dilution).

Therefore the transfer parameter for a given salt can be calculated from the appropriate single ion transfer parameters which provides a consistency check for the assignment of single ion reference chemical potentials.

3.1.4 Kinetics of reaction in Binary Solvent Mixtures

The relationship between the description of a system and the definitions of standard states is important in interpretation of kinetic data.

Consider a system at constant temperature, \(T\) and ambient pressure, \(p(\neq p^\Phi)\) comprising \(n_1\) moles of \(1\), \(n_2\) moles of \(2\), \(n_A\) moles of \(A\) and \(n_B\) moles of \(B\). \(A\) and \(B\) react via a transition state \((AB)^+\) to produce products, \(D\);

\[ \text{i.e. } A + B \xrightarrow{\text{reaction}} (AB)^+ \rightarrow D \quad \text{.... (3.27)} \]

In terms of Transition State Theory,\(^6\) the total Gibbs function, \(G\), of the system is given at time, \(t\), by:
\[ G = n_1 \mu_1 + n_2 \mu_2 + n_A \mu_A + n_B \mu_B + n_{AB} \mu_{AB} + n_D \mu_D \]  \hspace{1cm} \text{.... (3.28)}

\[ c_A = n_A / V \] and \[ c_B = n_B / V \], where \( V \) is the total volume of the system.

Using the Law of Mass Action, the second order rate constant, \( k_2 \) (units \( \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \)) for reaction 3.27 is given by:

\[ -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = \frac{dc_P}{dt} = k_2 \cdot c_A c_B \]  \hspace{1cm} \text{.... (3.29)}

The concentration terms, \( c_A \) and \( c_B \) (or \( c_A^* \) and \( c_B^* \)) and \( k_2 \) are independent of the description of the system. The importance of the description of the system emerges from Transition State Theory when reactants and transition state are assumed to be in chemical equilibrium, i.e. at equilibrium.

\[ \mu_A^{eq} + \mu_B^{eq} = \mu_{AB}^{eq} \]  \hspace{1cm} \text{.... (3.30)}

or

\[ \mu_A^\phi(m) + R.T. \ln \left( \frac{m_A \cdot y_A}{m^\phi} \right) + \mu_B^\phi(m) + R.T. \ln \left( \frac{m_B \cdot y_B}{m^\phi} \right) = \] \[ \mu_{AB}^\phi(m) + R.T. \ln \left( \frac{m_{AB} \cdot y_{AB}}{m^\phi} \right) \]  \hspace{1cm} \text{.... (3.31)}

Similar equations can be written on the \( c^- \) and \( x^- \) scales. How the system above is described is entirely a matter of choice:

(i) **Description 1:** the system is a solution of solutes \( A, B, AB^*, D \) and 2 in solvent 1 (cf. system \( [B;I] \)). At constant \( T \) and ambient pressure, \( p(\equiv p^\phi) \), assuming the transmission coefficient is 1.0, the standard equilibrium constant for activation \( ^*K^\phi \) is given by:

\[ ^*K^\phi = \left[ \frac{m_{AB} \cdot y_{AB}}{m^\phi} \right] \cdot \left[ \frac{m^\phi}{m_A \cdot y_A} \right] \cdot \left[ \frac{m^\phi}{m_B \cdot y_B} \right] \]  \hspace{1cm} \text{.... (3.32)}

Alternatively the equilibrium constant for activation can be expressed in terms of concentrations of \( A, B \) and \( (AB)^* \), [i.e. \( ^*Q^\#(c) \) - the reference equilibrium constant for activation on the \( c^- \) scale];

\[ ^*Q^\#(c) = \frac{C^* \cdot y^*}{c_A \cdot c_B \cdot y_A \cdot y_B} \]  \hspace{1cm} \text{.... (3.33)}

\[ C_{AB} = ^*Q^\#(c) \cdot c_A \cdot c_B \cdot y_A \cdot y_B \]  \hspace{1cm} \text{.... (3.33)}
From Transition State Theory;\(^6\)

\[-\frac{dc_A}{dt} = -\frac{dc_B}{dt} = \frac{dc_p}{dt} = \left(\frac{k_B T}{h}\right) \cdot c_\ast \quad \ldots \quad (3.34)\]

and

\[\Delta^\ast G^\#(c) = -RT \ln \ast Q^\#(c) \quad \ldots \quad (3.35)\]

where \(k_B\) is the Boltzmann constant, \(h\) is Planck's constant and \(\Delta^\ast G^\#(c)\) is the reference Gibbs function for activation on \(c\)-scale. Combining equations 3.33 and 3.34 yields;

\[-\frac{dc_A}{dt} = \left(\frac{k_B T}{h}\right) \cdot \left[c_A \cdot c_B \cdot y_A \cdot y_B / y^\ast\right] \cdot Q_{(c)}^\# \quad \ldots \quad (3.36)\]

and combining equations 3.36 and 3.29 yields;

\[k_2 = \left(\frac{k_B T}{h}\right) \cdot y_A \cdot y_B \cdot \frac{y_A \cdot y_B}{y^\ast} \quad \ldots \quad (3.37)\]

Therefore combination of equations 3.35 and 3.37 provides a direct relationship between \(\Delta^\ast G^\#(c)\) and the rate constant, \(k_2\);

\[\Delta^\ast G^\#(c) = -R.T. \left[\ln k_2 - \ln \left(\frac{k_B T}{h}\right) - \ln \left(\frac{y_A \cdot y_B}{y^\ast}\right)\right] \]

or

\[k_2 = \left(\frac{k_B T}{h}\right) \exp \left(-\Delta^\ast G^\#(c) / R.T.\right) \cdot \left(\frac{y_A \cdot y_B}{y^\ast}\right) \quad \ldots \quad (3.38)\]

Similarly expressions can be written on the \(x\)- and \(m\)-scales, leading to definitions of \(\Delta^\ast G^\#(m)\); \(\Delta^\ast G^\#(x)\); \(\ast K^\#(m)\) and \(\ast Q^\#(x)\). However, the rate constant, \(k_2\), will be the same whichever option (i.e. \(c\)-, \(x\)- or \(m\)-scales) is chosen.

If the composition of the solution is changed by increasing the number of moles of the chemically inert solute, \(2\), the dependence of \(k_2\) on \(m_2\) (\(c_2\) or \(x_2\)) is accounted for in terms of the corresponding activity coefficients defined in equation 3.37 [i.e. \((y_A \cdot y_B) / y^\ast\)]. \(\ast Q^\#\) and \(\Delta^\ast G^\#\) are independent of the quantity of solute \(2\) which is added to solvent \(1\), when the system is described in terms of description (I).

This approach is used in the Brønsted-Bjerrum treatment\(^6\) of salt effects, where \(A\) and \(B\) are ions and solute \(2\) is an inert salt. Any
changes in k when inert salts are added are accounted for in terms of changes in the activity coefficients of A, B and (AB)* (i.e. \(y_A \cdot y_B / y_*\)).

(ii) **Description (II):** the system is a solution of solutes A, B, (AB)* and D in a solvent mixture of substances "1 + 2", having mole fraction composition, \(x_2\). Equations 3.37 and 3.38 linking the rate constant, \(k_2\) for reaction 3.27, with \(\Delta^{*} Q^{(c)}\) and \(\Delta^{*} G^{(c)}\) have the same form in system (II), but their meaning is different.

The activity coefficients \(y_A \cdot y_B / y_*\) describe the deviations from ideal of the properties of solutes A, B and (AB)* resulting from solute-solute interactions. In the limit of dilute solutions (i.e. \(c_j \rightarrow 0\), where \(j = A, B, (AB)*\) or D) \(y_A \cdot y_B / y_* = 1.0\) and this latter limit is assumed at mole fractions \(x_2\). The reference solvent is chosen when \(x_2 = 0\), and the dependence of the rate constant \(k_2\) on \(x_2\) is accounted for in terms of changes in \(\Delta^{*} Q^{(c)}\) and \(\Delta^{*} G^{(c)}\).

\[
\Delta[(x_2=0) \rightarrow x_2] \Delta^{*} G^{(c)}(c) = \Delta^{*} G^{(c)}(c; x_2) - \Delta^{*} G^{(c)}(c; x_2=0) \quad .... \ (3.39)
\]

Combining equations 3.38 and 3.39 and assuming the limit of dilute solutions (i.e. \(y_A \cdot y_B / y_* = 1.0\));

\[
\Delta[(x_2=0) \rightarrow x_2] \Delta^{*} G^{(c)}(c) = -R.T. \ln \left[ \frac{k_2(x_2)}{k_2(x_2=0)} \right] \quad .... \ (3.40)
\]

If the rate constant, \(k_2(x_2=0) > k_2(x_2)\), \(\Delta[(x_2=0) \rightarrow x_2] \Delta^{*} G^{(c)}(c) > 0\); but if \(k_2(x_2=0) < k_2(x_2)\), \(\Delta[(x_2=0) \rightarrow x_2] \Delta^{*} G^{(c)}(c) < 0\).

### 3.1.5 Solvent effects on initial and transition states for reaction

Complexities can emerge in the analysis of solvent effects on \(\Delta^{*} G^{(c)}\). Figure 3.1 summarises what might happen to \(\Delta^{*} G^{(c)}\) for a reaction of type 3.27. Figure 3.1(a) shows how on going to a second solvent an increase in rate constant (i.e. a decrease in \(\Delta^{*} G^{(c)}\)) at fixed temperature and pressure can stem from either:-
FIGURE 3.1
Formalised representation of the effect of changing the solvent on $\Delta^*G^\#$, the initial state (I.S.), and the transition state (T.S.).

[Taken from Ref. 7]
(i) a destabilisation of both states with the initial state being destabilised more than the transition state, or

(ii) a stabilisation of both states with the transition state being stabilised to a greater extent.

In Figure 3.1(b) two cases are shown where on changing the solvent initial and transition states are affected differently resulting in either (i) an increase or (ii) a decrease in \( \Delta^*G^\# \). Also the solutes A and B (equation 3.27) may be affected differently on going to a new solvent, e.g. one stabilised and the other destabilised. Therefore, an identification of the direction and magnitude of changes in the properties of initial and transition states is a pre-requisite to understanding the factors which control the dependence of kinetic parameters on solvent.

The analysis presented below applies to reactions in solution at constant temperature and ambient pressure, \( p(=p^\circ) \) in which the mechanism is well established. Consider the reaction represented by equation 3.27. The reference Gibbs function for activation, \( \Delta^*G^\#(c) \) is related to the reference chemical potentials of the chemical species A, B and (AB)* in solution by:

\[
\Delta^*G^\#(c) = \mu_{_{\text{A}}}^\#(c;\text{sln};T) - (\mu_{_{\text{A}}}^\#(c;\text{sln};T) + \mu_{_{\text{B}}}^\#(c;\text{sln};T)) \quad \text{.... (3.41)}
\]

where \( \mu_{_{\text{A}}}^\#(c;\text{sln};T) \), \( \mu_{_{\text{B}}}^\#(c;\text{sln};T) \) and \( \mu_{_{\text{AB}}}^\#(c;\text{sln};T) \) are the reference chemical potentials of the chemical species A, B and (AB)* respectively. Let the solvent for reaction (equation 3.27) be a mixture of liquids '1 + 2' at mole fraction \( x_2 \), (i.e. considering only description (II) of the system) and let the reference solvent be when \( x_2=0 \), then the change in \( \Delta^*G^\#(c) \) is calculated from the second order rate constants for reaction in the solvent at \( x_2=0 \) and at \( x_2>0 \) using equation 3.40. Equation 3.41 can be rewritten to yield;
\[
\Delta [(x_2=0) + x_2] \Delta \Delta G^\#(c) = \Delta [(x_2=0) + x_2] \mu^\#_+(c;\text{sln};T) - \Delta [(x_2=0) + x_2] [\mu^\#_A(c;\text{sln};T) + \mu^\#_B(c;\text{sln};T)] \quad \ldots \quad (3.42)
\]

If the reactants \(A\) and \(B\) are soluble in the reference solvent \((x_2=0)\) and in the solvent mixture \((x_2>0)\), the change in the reference chemical potential \(\Delta [(x_2=0) + x_2] \mu_j^\#(c;\text{sln};T)\) where \(j = A\) or \(B\) can be obtained from the dependence of the solubility of \(A\) and \(B\) on \(x_2\).

Consider a solution of solute \(A\), containing an excess of solid of pure \(A\);

\[
A_{\text{solid}} \rightleftharpoons A_{\text{solution}} \quad \ldots \quad (3.43)
\]

At equilibrium at constant \(T\) and ambient pressure, \(p(=p^e)\), the chemical potential of pure solid \(A\), \(\mu^*_A(s;T)\) is related to the chemical potential of solute \(A\) in solution by;

\[
\mu^*_A(s;T) = \mu^\text{eq}_A(s\text{ln};T) \quad \ldots \quad (3.44)
\]

Therefore it follows that;

\[
\mu^\text{eq}_A(s\text{ln};x_2=0;T) = \mu^\text{eq}_A(s\text{ln};x_2;T) \quad \ldots \quad (3.45)
\]

Assuming that all processes refer to the equilibrium mixture the superscript "eq" is omitted. Combining equations 3.9 at \(x_2=0\) and \(x_2>0\), and equation 3.45 yields;

\[
\Delta [(x_2=0) + x_2] \mu^\#_A(c;\text{sln};T) = -R.T. \ln \left( \frac{c_A(x_2) \cdot y_A(x_2)}{c_A(x_2=0) \cdot y_A(x_2=0)} \right) \quad \ldots \quad (3.46)
\]

In the limit of dilute solutions \(y_A(x_2=0)/y_A(x_2=0) = 1.0\), equation 3.46 becomes;

\[
\Delta [(x_2=0) + x_2] \mu^\#_A(c;\text{sln};T) = -R.T \ln \left( \frac{c_A(x_2)}{c_A(x_2=0)} \right) \quad \ldots \quad (3.47)
\]

where \(c_A(x_2)\) represents the equilibrium solubility of \(A\) in solvent \((x_2>0)\) and \(c_A(x_2=0)\) is the equilibrium solubility of \(A\) in solvent \((x_2=0)\).

An analogous equation is written for species \(B\). Therefore in equation 3.42 the term \(\Delta [(x_2=0) + x_2] [\mu^\#_A(c;\text{sln};T) + \mu^\#_B(c;\text{sln};T)]\) can be
calculated.

The transfer reference chemical potential for the transition state, (AB)$^+$, cannot be directly obtained. It is sometimes possible to measure the parameters for a solute in which the solvation characteristics resemble those of some postulated transition state. However, if $\Delta[(X_2 = 0) \rightarrow X_2] \Delta^{+} G^\circ(c)$ and $\Delta[(X_2 = 0) \rightarrow X_2] [\mu_A^\circ(c; \text{sln;} T) + \mu_B^\circ(c; \text{sln;} T)]$ are known, then the transfer reference chemical potential for the transition state can be directly calculated from equation 3.42. Similar expressions can be obtained on the m- and x-scales.

If A and B are ions calculation of $\Delta[(X_2 = 0) \rightarrow X_2] \mu_A^\circ(c; \text{sln;} T)$ and $\Delta[(X_2 = 0) \rightarrow X_2] \mu_B^\circ(c; \text{sln;} T)$ requires some independent estimates of single ion transfer parameters.

3.1.6 Calculation of Single Ion Transfer Parameters

Different sets of single ion transfer parameters from water to 'water + methanol' mixtures as reported by (i) C. F. Wells and (ii) M. H. Abraham differ quite markedly in some cases, even when the necessary conversions are made to allow for comparison on the same composition scales. Therefore, the basis of assignments of single ion parameters as used by these two authors is examined.

(i) Estimated Transfer Parameters according to Wells

The Born Equation (equation 3.48) provides a starting point for consideration of single ion transfer parameters;

$$\Delta(g + \text{sln}) \mu_j^\circ = \frac{-N(z_j e)^2}{8\pi r_j^2 \varepsilon_0} \left[ \frac{1}{\varepsilon_r} - 1 \right]$$

... (3.48)

where N is Avogadro's number, $z_j$ is the charge on ion, j, e is the electronic charge, $r_j$ is the radius of ion j, $\varepsilon_0$ is the permittivity of free space and $\varepsilon_r$ is the relative permittivity of the solvent in which ion, j, is dissolved. If the radius of a j-ion is independent
of solvent, the Born equation predicts that when a j-ion is transferred from one solvent to another solvent having a lower relative permittivity ($\varepsilon_r$), the ion is destabilised. On these grounds alone all ions are destabilised on going from an aqueous solution to a solution in 'monohydric alcohol + water' mixtures. The Born equation yields single ion transfer parameters on the concentration-scale. 4 This latter fact has prompted a recalculation 9 of single ion transfer parameters. 11

Consider an aqueous solution, at constant temperature and ambient pressure, $p(\approx p^\circ)$, prepared by adding one mole of $H^+X^-$ to $n_w$ moles of water. At equilibrium, the total Gibbs function, $G_1$, for the system is given by;

$$G_1 = n_w\mu_w + \mu_{H^+} + \mu_{X^-} \quad \ldots (3.49)$$

The $H^+$ ion can be considered as $H_3O^+$ ion. Therefore, for one mole of hydrogen ions, one mole of water molecules are associated with these ions and $(n_w-1)$ moles of water molecules are left as the solvent.

Equation 3.49 becomes;

$$G_1 = (n_w-1)\mu_w + \mu_{H_3O^+} + \mu_{X^-} \quad \ldots (3.50)$$

Wells 11 describes hydrogen ions as $H^+(H_2O)_n$ in aqueous solution, but this preference is not fundamental to the argument and, therefore, $H_3O^+$ is used in the following discussion.

Consider another solution consisting of one mole of $H^+X^-$ in a mixture of $n_w$ moles of water and $n_{ROH}$ moles of alcohol. Then at equilibrium;

$$G_2 = (n_w-1)\mu_w + n_{ROH}\mu_{ROH} + \mu_{H_3O^+} + \mu_{X^-} \quad \ldots (3.51)$$

Wells 11 postulates that at equilibrium one mole of hydrogen ions in this latter system is present as $\alpha$-moles of $ROH^+$ and $(1-\alpha)$ moles of $H_3O^+$. Therefore equation 3.51 becomes;
\[ G_2 = [n_w - (1 - \alpha)] \mu_w + (n_{\text{ROH}} - \alpha) \mu_{\text{ROH}} + (1 - \alpha) \mu_{H_3O^+} + \alpha \mu_{\text{ROH}^+} + \mu_X^- \]  

\[ \ldots \ldots \ ... (3.52) \]

If the system is very dilute in \( H^X^- \) then \( [n_w - (1 - \alpha)] \approx n_w \) and \( (n_{\text{ROH}} - \alpha) \approx n_{\text{ROH}} \).

In the system, described by equation 3.52, there is chemical equilibrium between \( H_3O^+ \) ions, \( \text{ROH}_2^+ \) ions, water and alcohol (ROH);

\[ H_3O^+ + \text{ROH} \rightleftharpoons \text{ROH}_2^+ + H_2O \]  

\[ \ldots \ldots \ ... (3.53) \]

At equilibrium;

\[ \mu_{H_3O^+} + \mu_{\text{ROH}} = \mu_{\text{ROH}_2^+} + \mu_{H_2O} \]  

\[ \ldots \ldots \ ... (3.54) \]

A description of the system is required at this stage (cf. Section 3.1.4, equation 3.30). The system is described as a solution of solutes \( H_3O^+ \), \( X^- \), \( \text{ROH}_2^+ \) in a solvent comprising a mixture of 'water + ROH' [i.e. description (II)]. If, \( V \), is the total volume of the system, then \( c_{\text{(ROH}_2^+)} = \frac{n_{\text{(ROH}_2^+)}}{V} \) and \( c_{(H_3O^+)} = \frac{n_{(H_3O^+)}}{V} \). From equation 3.52, \( c_{\text{(ROH}_2^+)} = \alpha/V \) and \( c_{(H_3O^+)} = (1-\alpha)/V \). Therefore, from equations 3.53, 3.9 and 3.6 for each species in equation 3.53 at constant \( T \) and ambient pressure, \( p(=p^*) \);

\[ \mu_{H_3O^+}^{\circ}(c) + R.T \cdot \ln \left( \frac{(1-\alpha)y_{H_3O^+}/(V \cdot c_r)}{\alpha y_{\text{ROH}_2^+}/(V \cdot c_r)} \right) + \mu_{\text{ROH}}^{\circ} + R.T \cdot \ln \left( x_{\text{ROH}} \cdot \xi_{\text{ROH}} \right) = \]

\[ \mu_{\text{ROH}_2^+}^{\circ}(c) + R.T \cdot \ln \left( \frac{\alpha y_{\text{ROH}_2^+}/(V \cdot c_r)}{(1-\alpha)y_{H_3O^+}/(V \cdot c_r)} \right) + \mu_{H_2O}^{\circ} + R.T \cdot \ln \left( x_{H_2O} \cdot \xi_{H_2O} \right) \]

\[ \ldots \ldots \ ... (3.55) \]

where \( \mu_{\text{ROH}}^{\circ} \) and \( \mu_{H_2O}^{\circ} \) are the chemical potentials of pure alcohol and water respectively at the same \( T \) and \( p \). By definition the change in Gibbs function for reaction, \( \Delta_r G^\circ(c) \) for equation 3.54 is given by;

\[ \Delta_r G^\circ(c) = -R.T \ln Q^\circ(c) = \mu_{\text{ROH}_2^+}^{\circ}(c) + \mu_{H_2O}^{\circ} - \mu_{H_3O^+}^{\circ}(c) - \mu_{\text{ROH}}^{\circ} \]

or

\[ \mu_{\text{ROH}_2^+}^{\circ}(c) - \mu_{H_3O^+}^{\circ}(c) = -R.T \ln Q^\circ(c) + (\mu_{\text{ROH}}^{\circ} - \mu_{H_2O}^{\circ}) \]  

\[ \ldots \ldots \ ... (3.56) \]

The left hand side of equation 3.56 describes the difference in the reference chemical potentials of solutes \( \text{ROH}_2^+ \) and \( H_3O^+ \) in a solvent.
mixture 'ROH + water' at mole fraction, $x_{ROH}$, when $c_j = 1.0$ and $y_j = 1.0$ ($j = H_3O^+$ or $ROH_2^+$) at the same temperature and standard pressure. This difference in $[\mu_{ROH}^*(c) - \mu_{H_3O^+}^*(c)]$ is related to the differences in chemical potentials of the two pure liquids ($\mu_{ROH}^* - \mu_{H_2O}^*$) and the equilibrium composition of the system described by $Q^#(c)$. From equation 3.33;

$$Q^#(c) = \frac{(\alpha \cdot y_{(ROH_2^+)}) \cdot [(1-x_{ROH}) \cdot f_{H_2O}]}{[(1-\alpha) \cdot y_{H_3O^+}] \cdot (x_{ROH} \cdot f_{ROH})} \quad \quad \quad (3.57)$$

The process of transferring one mole of hydrogen ions ($H_3O^+$) from pure water ($x_{ROH} = 0$) to a solvent mixture at $x_{ROH}$ is represented as follows;

$$H_3O^+(x_{ROH} = 0) \rightarrow [(1-\alpha) \cdot H_3O^+ + \alpha \cdot ROHz^+ (x_{ROH})] \quad \quad \quad (3.58)$$

In terms of chemical potentials;

$\mu_{H_3O^+}(c;x_{ROH}=0) = [(1-\alpha) \cdot \mu_{H_3O^+}(c;x_{ROH}) + \alpha \cdot \mu_{ROH_2^+}(c;x_{ROH})]$

or

$$\Delta [(x_{ROH}=0) \rightarrow x_{ROH}] \mu_{H_3O^+}^*(c) = [(1-\alpha) \cdot \mu_{H_3O^+}^*(c;x_{ROH}) + \alpha \cdot \mu_{ROH_2^+}^*(c;x_{ROH})] - \mu_{H_3O^+}^*(c;x_{ROH}=0)$$

or multiplying out the $(1-\alpha)$ term gives;

$$\Delta [(x_{ROH}=0) \rightarrow x_{ROH}] \mu_{H_3O^+}^*(c) = [\mu_{H_3O^+}^*(c;x_{ROH}) - \mu_{H_3O^+}^*(c;x_{ROH}=0)] + \alpha \left[ \mu_{ROH_2^+}^*(c;x_{ROH}) - \mu_{H_3O^+}^*(c;x_{ROH}) \right] \quad \quad \quad (3.59)$$

Combining equations 3.56 and 3.59 yields;

$$\Delta [(x_{ROH}=0) \rightarrow x_{ROH}] \mu_{H_3O^+}^*(c) = [\mu_{H_3O^+}^*(c;x_{ROH}) - \mu_{H_3O^+}^*(c;x_{ROH}=0)] - \alpha R.T. \ln Q^#(c) + \alpha \left[ \mu_{ROH}^* - \mu_{H_2O}^* \right] \quad \quad \quad (3.60)$$

In the absence of chemical complexity (equation 3.53), $\alpha$ is zero and the transfer parameter is given by the first bracket term on the right hand side of equation 3.59. Wells uses the Born equation to calculate this term. $\varepsilon_r$ of the mixture, "methanol + water" < $\varepsilon_r$ of water then...
According to the Born equation, hydrogen ions are destabilised on going from water to an aqueous mixture. Hence the reported stabilisation\textsuperscript{11} indicates that the second bracket term in equation 3.59 is very important.

Turning attention to equation 3.60, at this stage Wells makes a sweeping extrathermodynamic assumption although he does not draw attention to this step. In effect, Wells sets the difference $(\mu^*_\text{ROH} - \mu^*_\text{H}_2\text{O})$ equal to zero. Therefore, from equation 3.60 with $(\mu^*_\text{ROH} - \mu^*_\text{H}_2\text{O})$ equal to zero (cf. equation (8) in reference 11);

$$\Delta[(x^\text{ROH}=0) + x^\text{ROH}]\mu^*_\text{H}_2\text{O} \pm (c) = \Delta[(x^\text{H}_2\text{O}=0) + x^\text{ROH}]\mu^*(\text{H}_3\text{O}^+;\text{Born}) - \alpha \text{R.T.} \ln Q^*(c) \quad \ldots \quad (3.61)$$

The chemical potentials of pure liquids cannot be measured but the difference in the vapour pressures of water and methanol indicates that the extrathermodynamic assumption leading to equation 3.61 is poor. Even if the assumption is acceptable for 'water + methanol' mixtures,\textsuperscript{11-13} it is unlikely to be acceptable for binary aqueous mixtures where the organic co-solvents are iso-propanol,\textsuperscript{12} glycerol,\textsuperscript{12} ethylene glycol,\textsuperscript{14} t-buty1 alcohol,\textsuperscript{15} dioxan,\textsuperscript{16} DMSO\textsuperscript{17} and acetone.\textsuperscript{12,18} Abraham\textsuperscript{10} has noted a similar misunderstanding in connection with solubilities of various homologous series. According to the estimates given by Abraham,\textsuperscript{10} the difference between the chemical potentials of water and the organic liquids listed above, is of comparable magnitude to derived single ion transfer parameters.

If the extrathermodynamic assumption identified above is accepted, then from equation 3.61, $\alpha$ and $Q^*(c)$ have to be determined by experiment. Here Wells\textsuperscript{11} uses a spectrophotometric approach in a study of solutions containing $\text{H}^+\text{X}^-$, $\text{H}_2\text{O}$ and $\text{MeOH}$ together with a base, $\text{B}$, p-nitroaniline.

Consider, therefore, a system, $C$, which at time, $t=0$, contains $n_{\text{H}_2\text{O}}$, 

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n_{ROH}, n_{H^+_X^-} and n_B. The equilibrium composition of system, C, is controlled by two chemical equilibria; (cf. equations 3 and 4 of reference 11).

(i) \[ B + H_3O^+ \rightleftharpoons BH^+ + H_2O \] .... (3.62)

(ii) \[ B + ROH_2^+ \rightleftharpoons BH^+ + ROH \] .... (3.63)

Therefore at equilibrium (omitting superscript "eq") at fixed T and ambient pressure, p(\(\approx p^\circ\)), system C contains \(n_{H_3O^+}\), \(n_{ROH_2^+}\), \(n_B\), \(n_{BH^+}\), \(n_{X^-}\), \(n_{H_2O}\) and \(n_{ROH}\).

The equilibria in equations 3.62 and 3.63 are considered below in terms of descriptions (I) and (II) for system C, and using definitions on the concentration scale. Therefore, the term (c) for each term is omitted.

(a) Description (I) of system C

The equilibrium constant \(Q^*(i),(I)\) and \(Q^*(ii),(I)\) are given by;

\[
Q^*(i),(I) = \frac{C_{B\cdot H_3O^+}}{C_{BH^+\cdot H_2O}} \cdot \frac{y_{B\cdot H_3O^+}}{y_{BH^+\cdot H_2O}}
\] .... (3.64)

and

\[
Q^*(ii),(I) = \frac{C_{B\cdot ROH_2^+}}{C_{BH^+\cdot ROH}} \cdot \frac{y_{B\cdot ROH_2^+}}{y_{BH^+\cdot ROH}}
\] .... (3.65)

Quantities \(F[(i),(I)]\) and \(F[(ii),(I)]\) are defined in terms of the activity coefficients;

\[
F[(i),(I)] = \frac{y_{B\cdot H_3O^+}}{y_{BH^+\cdot H_2O}}
\] .... (3.66)

and

\[
F[(ii),(I)] = \frac{y_{B\cdot ROH_2^+}}{y_{BH^+\cdot ROH}}
\] .... (3.67)

(b) Description (II) of system C

The equilibrium constants \(Q^*(i),(II)\) and \(Q^*(ii),(II)\) are given by;

\[
Q^*(i),(II) = \frac{C_{B\cdot H_3O^+}}{C_{BH^+\cdot H_2O}} \cdot \frac{y_{B\cdot H_3O^+}}{y_{BH^+\cdot H_2O}}
\] .... (3.68)
where \( F[(i),II] = \frac{y_B(II) \cdot y_{H^3O^+}(II)}{y_{BH^+}(II) \cdot f_2} \) .... (3.69)

and \( Q^#[(ii),II] = \frac{C_{ROH}^+ \cdot x_{H^2O} \cdot y_{ROH^+}(II)}{C_{BH^+} \cdot x_{ROH} \cdot y_{BH^+}(II) \cdot f_{ROH}} \) .... (3.70)

where \( F[(ii),II] = \frac{y_B(II) \cdot y_{ROH^+}(II)}{y_{BH^+}(II) \cdot f_{ROH}} \) .... (3.71)

The ratio \( Q^#(ii)/Q^#(i) \), for the two descriptions of system, C, are given by:

**Description I:**

\[
\frac{Q^#[(ii),I]}{Q^#[(i),I]} = \frac{C_{ROH}^+ \cdot x_{H^2O} \cdot y_{ROH^+}(I) \cdot f_{H^2O}}{C_{BH^+} \cdot x_{ROH} \cdot y_{BH^+}(I) \cdot y_{H^3O^+}(I)} \] .... (3.72)

**Description II:**

\[
\frac{Q^#[(ii),II]}{Q^#[(i),II]} = \frac{C_{ROH}^+ \cdot x_{H^2O} \cdot y_{ROH^+}(II) \cdot f_{H^2O}}{x_{ROH} \cdot y_{ROH} \cdot f_{ROH} \cdot y_{H^3O^+}(II)} \] .... (3.73)

(cf. equation 3.57)

Wells\(^{1)}\) defines two quantities;

\[
F_1 = \frac{f(B) \cdot f(H^3O^+)}{f(BH^+) \cdot f(H_2O)} \] .... (3.74)

and \( F_2 = \frac{f(BH^+) \cdot f(ROH^+)}{f(ROH^+) \cdot f(ROH)} \) .... (3.75)

The ratio \( \frac{F_1}{F_2} = \frac{f(ROH) \cdot f(H^3O^+)}{f(H_2O) \cdot f(ROH^+)} \) .... (3.76)

Using description (I) of system, C, from equations 3.66 and 3.67 the ratio of activity coefficients, \( F(I) \), is given by;

\[
F(I) = \frac{F[(i);I]}{F[(ii);I]} = \frac{y_{H^3O^+}(I) \cdot y_{(ROH)^I}}{f(H_2O) \cdot y_{(ROH^+)^II}} \] .... (3.77)

Using description (II) of system, C, from equations 3.69 and 3.71;

\[
F(II) = \frac{F[(i);II]}{F[(ii);II]} = \frac{y_{H^3O^+}(II) \cdot f_{ROH}}{f_{H^2O} \cdot y_{ROH^+}(II)} \] .... (3.78)
Wells\textsuperscript{11} states that (i) $F_1 \approx 1.0$ at low $x_2$, and $F_2 \approx 1.0$ and (ii) $F_1/F_2$ remains unity at low $x_2$. These assumptions are consistent with equation 3.77. In a given system, the ratio $(y_{\text{H}_3\text{O}^+}/y_{\text{ROH}_2^+})$ are probably close to unity and in dilute aqueous solution $y_{\text{ROH}} \approx 1.0$ and $f_{\text{H}_2\text{O}} \approx 1.0$. Therefore assumptions used by Wells in connection with the activity coefficients indicate that the properties of the system are treated by Wells in terms of description (I) rather than description (II).

$F(II) \approx 1.0$ (equation 3.78) in dilute aqueous solution since $f_{\text{ROH}}$ at low $x_2$ would show strong deviations from ideal [i.e. Limit $(x_{\text{ROH}} \rightarrow 1.0)$, $f_{\text{ROH}} = 1.0$ at the same $T$ and $p$, cf. equation 3.6].

When a system is described in terms of description (I) (Section 3.1.4), $Q^\#(c)$ and $\Delta G^\#(c)$ are independent of the amount of ROH in the system, the changes in rate parameters being accounted for in terms of changes in activity coefficients defined by equation 3.77. Transfer chemical potentials, $\Delta [(x_2=0) + x_2] \mu_1^\#$, can only be estimated when description (II) is used for a system. Further at $x_{\text{ROH}} > 0.1$, $F(\text{I})$ can no longer approach unity, because $y_{\text{ROH}}$ is no longer close to unity.

Therefore it would seem that at a crucial stage in the analysis, Wells switches descriptions from the required description (II) (cf. equation 3.57) to the inappropriate description (I), and he assumes, in effect, that the properties of binary aqueous mixtures over the whole range of added $x_{\text{ROH}}$, are ideal. This latter assumption clearly cannot be valid.

An interesting point emerges from studies made by Koskikallio\textsuperscript{19} of proton transfer equilibria in 'methanol + water' mixtures. Koskikallio suggests that in 'methanol + water' mixtures containing more than 50% by weight of water, the concentration of the methoxonium ion is negligible (cf. equation 3.63). It is exactly in this 'methanol + water' range
that Wells reports his single ion transfer parameters.

Further criticism of the analysis presented by Wells concerns his definition of standard states. In the recent account, the equilibrium equation 3.53 is rewritten as follows;

\[ \text{H}_2\text{O}(\text{H}^+)\text{solv.} + \text{ROH}_{\text{solv.}} \rightleftharpoons [(\text{H}_2\text{O})_{x-1}\cdot\text{ROH}]_{\text{solv.}} + \text{H}_2\text{O} \] .... (3.79)

Wells states that "the standard states of all species (in equation 3.79) are defined on the molar scale as solutes in the mixture for i = 1 mol dm^-3 and y_i = 1.0 for y_i \to 1.0 and [i] \to 0". This cannot be correct - all the substances cannot be solutes; at least one substance must be the solvent.

A final flaw in the analysis presented by Wells, concerns the 'nature' of the proton being transferred from water to 'water + methanol' mixtures. In Figure 3 and Table 1 of reference 11 transfer chemical potentials of the proton, H^+, are reported yet the entire analysis section concerns the transfer chemical potential of the solvated proton, H^+(H_2O)_4. However, \[ \Delta[(x_2=0) \rightarrow x_2]\mu^\#(\text{H}^+) \] and \[ \Delta[(x_2=0) \rightarrow x_2]\mu^\#[\text{H}^+(\text{H}_2\text{O})_4] \] are not equal.

In conclusion, therefore, it is suggested that the method of calculating transfer parameters for ions suggested by Wells is flawed and the derived parameters incorrect.

(ii) Estimated transfer parameters according to Abraham

The transfer parameters reported by Abraham and co-workers are based on the extrathermodynamic assumption set out in equation 3.80, assuming constant temperature and ambient pressure, p(\approx p^\circ) and using the c-scale definitions;

\[ \Delta[(x_2=0) \rightarrow x_2]\mu^\#(\text{Ph}_4\text{P}^+) = \Delta[(x_2=0) \rightarrow x_2]\mu^\#(\text{Ph}_4\text{As}^+) \]
\[ = \Delta[(x_2=0) \rightarrow x_2]\mu^\#(\text{Ph}_4\text{B}^-) \] .... (3.80)

The origins of this assumption can be traced to empirical methods for
estimating single ion conductivities from the corresponding salt values for electrical conductivities of salt solutions;
e.g. \[ \Lambda^\circ(\text{Ph}_4\text{P}^+) = \Lambda^\circ(\text{Ph}_4\text{B}^-) = \frac{1}{2}[\Lambda^\circ(\text{Ph}_4\text{B}.\text{Ph}_4\text{As})] \]

Extension of these procedures to thermodynamic properties and hence to transfer parameters is a more recent development. Kim has subjected the \( \text{Ph}_4\text{As}^+/\text{Ph}_4\text{B}^- \) (tetraphenylarsonium/tetraphenyloboronate) assumption to critical analysis and has concluded that transfer parameters calculated on this basis are, at worst, in error by 7%. This uncertainty is acceptable in analysis of kinetic data, and recent applications support the view that the \( \text{Ph}_4\text{As}^+/\text{Ph}_4\text{B}^-/\text{Ph}_4\text{P}^- \) assumptions provide a valuable starting point for analysis of experimental data.

Before presenting the experimental section, comparison is drawn between the transfer chemical potentials of various salts from water to 'water + methanol' mixtures where the transfer parameter for the salt has been estimated by combining the appropriate single ion transfer parameters calculated by (i) Abraham and (ii) Wells [Figure 3.2 (a), (b) and (c)]. Included on the appropriate diagrams are transfer chemical potentials of potassium chloride and zinc chloride estimated from experimental e.m.f. data by (iii) Feakins and (iv) Lewandowski, and transfer parameters of potassium chloride from solubility and e.m.f. data by (v) Popovych et al.

There is some disagreement between the experimental transfer chemical potentials of potassium chloride at low mole fraction of methanol between values reported by Feakins and Lewandowski and the corresponding values reported by Popovych.

Unfortunately, no tables of single ion transfer parameters appear in the recent paper by Wells. It has therefore been necessary to inter-
\[ \Delta \left[ (x_2=0) \rightarrow x_2 \right] \mu_d^\#(\text{salt}) \text{ from water to } \] 
'MeOH + water' mixtures on the x-scale and c-scale for ZnCl\(_2\) and KCl. A, W, L, F and P refer to data obtained by Abraham, Wells, Lewandowski, Peakins and Popovych respectively. Included is the conversion factor

\[ \Delta \left[ (x_2=0) \rightarrow x_2 \right] \mu_d^\#(x) \rightarrow \Delta \left[ (x_2=0) \rightarrow x_2 \right] \mu_d^\#(c). \]
FIGURE 3.2(b)

$\Delta[(x_2=0) \rightarrow x_2] \mu^\circ (m)$ from water to 'MeOH + water' mixtures for ZnCl$_2$ after conversion of data by Abraham, Wells, Peake and Lewandowski.
plate data from enlarged graphs in reference 9. It is accepted that there may be a certain amount of inaccuracy in interpolation but, nevertheless, this could still not account for the large deviations in transfer parameters between the values reported by Abraham, Lewandowski and Feakins and the corresponding values reported by Wells (Figure 3.2). The conversion factor between single ion transfer parameters on the x-scale and c-scale is included in Figure 3.2(a).

It is clear from Figure 3.2 that even the consistency check,

\[ \Delta[(x_2=0)\rightarrow x_2] \mu^{\text{(salt)}} = v_+ \Delta[(x_2=0)\rightarrow x_2] \mu^+ + v_- \Delta[(x_2=0)\rightarrow x_2] \mu^- \]

is not satisfied by the single ion transfer parameters reported by Wells.

1.2 EXPERIMENTAL

Concentrated aqueous solutions containing Fe(gml)$_3$$^{2+}$ as the perchlorate salt were prepared. Kinetics of reaction of the iron complex with hydroxide ions were monitored in water and 20%, 40%, 60%, 80% (ideal volume) 'methanol + water' mixtures at constant ionic strength, \( I = 0.33 \text{ mol dm}^{-3} \) and at 298 K. Constant ionic strength was maintained by adding appropriate concentrations of sodium chloride to the reaction mixtures. In all systems the concentration of complex \(< 10^{-4} \text{ mol dm}^{-3} \) and the hydroxide ion concentration was \( \gg [\text{complex}] \). Reactions were monitored in solutions where \( 5 \times 10^{-3} < [\text{NaOH}] < 2 \times 10^{-2} \text{ mol dm}^{-3} \) at five different concentrations of sodium hydroxide.

Aqueous solutions of Fe(gml)$_3$$^{2+}$ are bright red with \( \lambda_{\text{max}} = 554 \text{ nm} \) and the extinction coefficient, \( \epsilon_{554} = 860 \text{ m}^2 \text{ mol}^{-1} \). No shift in \( \lambda_{\text{max}} \) was observed when the complex was dissolved in 'methanol + water' mixtures.

Kinetics of reaction were examined using an HP8451A diode array spectrophotometer (Chapter 2, Section 2.4.2). Repeat scans of the
dependence of absorbance on wavelength revealed that the dependence of absorbance on time followed first order kinetics. Kinetics of reaction were monitored at 554 nm and the data analysed in terms of first-order kinetics (Chapter 2, Sections 2.2 and 2.3).

Second order rate constants were calculated from the gradients of plots of first order rate constants as a function of sodium hydroxide concentration for each solvent mixture.

Solubility data \(^{36}\) for Fe(gmi)\(_3\) (ClO\(_4\))\(_2\) were obtained from the absorbances at \(\lambda_{\text{max}} = 554 \text{nm}\) of diluted samples taken from saturated solutions of the salt in the appropriate solvent mixture.

Solvent effects on initial and transition states for reaction of Fe(gmi)\(_3\)^{2+} with hydroxide ions were analysed using single ion transfer parameters reported by (i) Abraham\(^{10}\) and (ii) Wells.\(^9\) Conversions of single ion transfer parameters between molal, molar and mole-fraction scales (Figure 3.3 and Table 3.1) were made using equations 3.21, 3.22 and 3.23 and literature\(^37\) density data for 'water + methanol' mixtures (Figure 3.4).

Conversions of the proportion of methanol in "methanol + water" mixtures between mole-fraction (x), weight percent (w) and ideal volume percent \([v\% (\text{id})]\) of methanol were calculated using equations 3.81 and 3.82;

\[
X(\text{MeOH}) = \frac{(w(\text{MeOH})/M(\text{MeOH}))}{\left(\frac{w(\text{MeOH})}{M(\text{MeOH})} + \frac{w(H_2O)}{M(H_2O)}\right)} \quad \text{... (3.81)}
\]

\[
v\% (\text{id}; \text{MeOH}) = \frac{(w(\text{MeOH})/\rho(\text{MeOH}))}{(1/\rho_{\text{mixture}})} \quad \text{... (3.82)}
\]

Conversion quantities from (i) mole-fraction to weight percent of methanol and (ii) weight percent to ideal volume percent of methanol in the 'methanol + water' mixtures are shown graphically in Figures 3.5 and...
\[ \Delta \equiv \Delta \left( x_2 \rightarrow x_1 \right) \] for single ions

\[ \Delta \mu_1 = \Delta \mu_{(x)} = \Delta \mu_{(m)} = \Delta \mu_{(c)} \]

**FIGURE 3.3**

Conversions of single ion transfer parameters from water to methanol, mixtures between m-, c-, and x-scales.
FIGURE 3.4
Density data for 'water + methanol' mixtures vs. wt. % methanol.

FIGURES 3.5 & 3.6
Wt. % methanol vs. mol % in methanol for 'methanol + water' mixtures (top);
Wt. % methanol vs. x (methanol) for 'methanol + water' mixtures (bottom).
FIGURES 3.5 & 3.6
Wt. % methanol vs. vol. % (id) methanol for 'methanol + water' mixtures (top); Wt. % methanol vs. x(methanol) for 'methanol + water' mixtures (bottom).
3.3 RESULTS AND DISCUSSION

In aqueous solution and in 'methanol + water' mixtures the reactions of Fe(gmi)$_3^{2+}$ with hydroxide ions were first order in [complex]. Kinetic data are reported in Table 3.2. Each rate constant is the mean of at least three individual determinations, the reproducibility being, at worst (i.e. for the faster reactions), within 5%.

The rate of reaction between Fe(gmi)$_3^{2+}$ and hydroxide ions in aqueous solution is given by: (Chapter 1, Section 1.6.1)

$$-\frac{d[\text{complex}]}{dt} = (k_1 + k_2 [OH^-])[\text{complex}]$$

where $k_1$ is the first order rate constant for the aquation reaction and $k_2$ is a second order rate constant. For solutions where [NaOH] $\gg$ [complex], the first order rate constant, $k_{ob}$ = $k_1 + k_2 [OH^-]$. The dependence of $k_{ob}$ on sodium hydroxide concentration was fitted to this latter equation using a linear least squares procedure (Figure 3.7). The $k_1$-term was negligibly small and is not reported. The second order rate constants with standard errors are reported in Table 3.3.

The solubility data$^{36}$ for Fe(gmi)$_3$(ClO$_4$)$_2$ in water and "water + methanol" mixtures at 298 K are reported in Table 3.4, together with the transfer chemical potentials on the c-scale of the complex from water to "water + methanol" mixtures. These latter parameters were calculated using a modification of equation 3.47.

$$\Delta[(x_2=0) \rightarrow x_2] \mu^w(c;\text{sln};T;AB_2) = -3R.T.\ln \left[ \frac{C_{AB_2}(x_2)}{C_{AB_2}(x_2=0)} \right] \quad \ldots \quad (3.83)$$

From kinetic and solubility data the reactions of Fe(gmi)$_3^{2+}$ with hydroxide ions were analysed in terms of solvent effects on the initial- and transition-state using the method outlined in Section 3.1.5.
FIGURE 3.7
Dependence of first-order rate constants, $k_{obs}/s^{-1}$, on sodium hydroxide concentration for reactions of $\text{Fe(gmu)}_3^{2+}$ with hydroxide ions at 298 K in (a) pure water, (b) 20 vol. % (id) methanol + water, (c) 40 vol. % (id) methanol + water, (d) 60 vol. % (id) methanol + water, and (e) 80 vol. % (id) methanol + water.
In the first analysis (Table 3.5 and Figure 3.8) single ion transfer parameters (on the c-scale) reported by Abraham\textsuperscript{10} were used. In the second analysis (Table 3.6 and Figure 3.9) single ion transfer parameters (converted from x- to c-scale) reported by Wells\textsuperscript{9} were used.

3.4 CONCLUSION

Comparisons between Figure 3.8 and Figure 3.9 can only be made up to 60 v\% (id) methanol in the mixtures, because Wells\textsuperscript{9} does not report single ion transfer parameters at higher v\% of methanol.

Over the whole range of 'methanol + water' mixtures the rate of reaction of Fe(gmi)$_3^{2+}$ with hydroxide ions increases as the amount of methanol in the mixture increases, i.e. $\Delta[(x_2=0) \rightarrow x_2]A^\ddagger G^\ddagger(c)$ decreases with increasing methanol at fixed temperature and ambient pressure, $p(\neq p^\ddagger)$.

(i) Analysis A - Solvent effects on initial and transition states for the reaction using single ion transfer parameters reported by Abraham [ref. 10]

The decrease in $\Delta[(x_2=0) \rightarrow x_2]A^\ddagger G^\ddagger(c)$ with increasing concentration of methanol is dominated [Figure 3.8(b)] by the effect of the solvent on the transition state up to 60 v\% (id) methanol, i.e. the transition state is stabilised whereas the solvent has very little effect on the initial state, and shows only a small destabilisation (1.21 kJ mol$^{-1}$) at 60 v\% (id) methanol. The negligible solvent effect on the initial state up to 60 v\% (id) methanol stems from the small and similar solvent effects on hydroxide ions and Fe(gmi)$_3^{2+}$. At 20 v\% (id) methanol both hydroxide and Fe(gmi)$_3^{2+}$ ions are slightly stabilised relative to pure water, -0.12 and -0.67 kJ mol$^{-1}$ respectively. At 40 v\% (id) methanol Fe(gmi)$_3^{2+}$ is slightly stabilised (-1.27 kJ mol$^{-1}$) but there is virtually no effect on hydroxide ions (-0.02 kJ mol$^{-1}$). At 60 v\% (id) methanol the
FIGURE 3.8(a)
Dependence of the reference Gibbs function for activation, $\Delta^* G^\#(c)$, and related reference-state chemical potentials (c-scale) on vol. % (id) of added methanol for reactions of Fe(gml)$_2^{2+}$ with hydroxide ions at 298 K using single ion transfer parameters reported by Abraham.\textsuperscript{10}
FIGURE 3.8(b)
Dependence of the reference Gibbs function for activation, \( \Delta G^\#(c) \), and related reference-state chemical potentials (c-scale) on vol. % (id) of added methanol for reactions of Fe(gmi) \(^{2+}\) with hydroxide ions at 298 K using single ion transfer parameters reported by Abraham.\(^\text{16}\)
FIGURE 3.9(b)

Dependence of the reference Gibbs function for activation, $\Delta^+ G^\circ(c)$, and related reference-state chemical potentials (c-scale) on vol. % (id) of added methanol for reactions of Fe(gmi)$_3^{2+}$ with hydroxide ions at 298 K using single ion transfer parameters reported by Wells.
hydroxide ions are now slightly destabilised (1.44 kJ mol$^{-1}$) whereas there is virtually no effect on Fe(gmi)$_3^{2+}$ (-0.23 kJ mol$^{-1}$).

At 80 v% (id) methanol the decrease in $\Delta[(x_2=0) \rightarrow x_2] \Delta^\#G^\#(c)$ is now dominated by the large destabilisation of the initial state (10.25 kJ mol$^{-1}$), the transition state being only stabilised to a small extent (-1.88 kJ mol$^{-1}$). The large destabilisation of the initial state at 80 v% (id) methanol stems from destabilisation of both hydroxide (5.78 kJ mol$^{-1}$) and Fe(gmi)$_3^{2+}$ (4.47 kJ mol$^{-1}$) ions.

The picture presented above is consistent with what might be expected for reactions of Fe(gmi)$_3^{2+}$ with hydroxide ions as the methanol concentration is increased. Hydroxide ions are sufficiently hydrophilic to retain their hydration shell essentially intact up to even as high as 60 v% (id) methanol. At 80 v% (id) methanol the hydroxide ions are then greatly destabilised because there is insufficient water to maintain the hydration shell around these ions.

'gmi' is a small ligand and it is quite likely that these ligands are not sufficiently hydrophobic to dominate the hydration characteristics of Fe(gmi)$_3^{2+}$. The large destabilisation of Fe(gmi)$_3^{2+}$ ions at 80 v% (id) methanol is dominated by the positive charges on the complex cations.

Stabilisation of the transition state up to 60 v% (id) methanol is consistent with dispersal of charges on going from the initial- to the transition-state and hence transfer of the transition state to a less polar solvent will result in a stabilisation of the transition state. At 80 v% (id) methanol the transition state will be much less stabilised than at lower concentrations of methanol because the former solvent mixture is not sufficiently polar to accommodate the dispersed charges as adequately as at 60 v% (id) methanol.
(ii) Analysis W – Solvent effects on initial and transition states for the reaction using single ion transfer parameters reported by Wells [ref. 9]

The transition state is stabilised and still dominates [Figure 3.9(b)] the decrease in $\Delta[(x_2=0) \rightarrow x_2]^{\#}(c)$ as the concentration of methanol increases. However at 60 v% (id) methanol the transition state is stabilised to a much greater extent than in analysis A (cf. -13.75 kJ mol$^{-1}$ and -8.56 kJ mol$^{-1}$ respectively).

Increasing methanol concentration also stabilises the initial state but to a much smaller degree than the corresponding stabilisation of the transition state. In 60 v% (id) methanol $\Delta[(x_2=0) \rightarrow x_2]^{\#}(c)(I.S)$ is -3.98 kJ mol$^{-1}$ using analysis W and 1.21 kJ mol$^{-1}$ using analysis A, i.e. in analysis W the initial state is stabilised but in analysis A the initial state is destabilised.

Destabilisation of the initial state stems from almost equal and opposite solvent effects on hydroxide and Fe(gmi)$_3^{2+}$ ions. Hydroxide ions are progressively destabilised and Fe(gmi)$_3^{2+}$ ions are progressively stabilised with increasing methanol concentration. These latter effects suggest that hydroxide ions are unable to retain their hydration shell with increasing methanol concentration and that the hydration characteristics of Fe(gmi)$_3^{2+}$ ions are dominated by the 'gmi' ligands.

In other words, although solvent effects on the transition-state follow a similar pattern using either analysis A or analysis W, different conclusions emerge about the solvent effects on the initial state and the hydration characteristics of hydroxide and Fe(gmi)$_3^{2+}$ ions.

A further point to note is that the consistency check;

$\Delta[(x_2=0) \rightarrow x_2]^{\#}(c;\text{salt}) = \nu_+ \Delta[(x_2=0) \rightarrow x_2]^{\#}(c) + \nu_- \Delta[(x_2=0) \rightarrow x_2]^{\#}(c)$

for Fe(gmi)$_3$(OH)$_2$ fails, i.e. $\Delta[(x_2=0) \rightarrow x_2]^{\#}(c;\text{Fe(gmi)}_3(\text{OH})_2)$ at 60 v% (id) methanol is 2.65 kJ mol$^{-1}$ using single ion parameters reported by
Abraham$^{10}$ compared with -3.31 kJ mol$^{-1}$ using single ion parameters reported by Wells.$^{9}$ This latter inconsistency follows the pattern identified earlier where it was noted that transfer parameters for zinc chloride calculated using the data given by Wells$^{9}$ do not cross-check.

In this Chapter an attempt has been made to illustrate the conflicting conclusions that can be drawn when different single ion transfer parameters are used in conjunction with kinetic data to interpret solvent effects on initial- and transition-states in 'methanol + water' mixtures. The analysis is extended in Chapter 4 to 'acetone + water' and 'isopropanol + water' mixtures.
REFERENCES TO CHAPTER 3

CHAPTER 4

Solubilities of various salts and derived single ion parameters in 'acetone + water' and 'isopropanol + water' mixtures. Kinetics of reaction of iron(II) 1,10-phenanthroline with hydroxide ions and analysis of solvent effects on this reaction in 'isopropanol + water' mixtures.
4.1 INTRODUCTION

Solubility data at 298 K and calculated transfer parameters for a range of salts in 'acetone + water' mixtures are reported in this Chapter. Single ion transfer parameters are derived using the tetraphenylboronate/tetraphenylarsonium (Ph₄B⁻/Ph₄As⁺) assumption. The analysis is extended to include literature solubility data for various salts.

Solubility data at 298 K and calculated transfer parameters for several salts are also reported in 'isopropanol + water' mixtures, together with kinetic data for reactions of iron(II) 1,10-phenanthroline with hydroxide ions. The Ph₄As⁺/Ph₄B⁻ assumption is also used in this latter solvent to calculate single ion transfer parameters and these values are used in conjunction with kinetic data to analyse solvent effects on initial and transition states.

The necessary background to the analyses presented here is discussed in Chapter 3.

4.2 'ACETONE + WATER' MIXTURES

4.2.1 Experimental

Solubility data at 298 K were obtained from absorbances at appropriate λ_max of samples taken from saturated solutions of the salts in 0, 20, 40, 60, 80, 90 v% (id) 'acetone + water' mixtures. The samples were diluted where necessary. Solubility data were collected for the following salts: tetraphenylarsonium dichromate (Ph₄As)₂Cr₂O₇, potassium hexabromoplatinate K₂PtBr₆, rubidium dichromate Rb₂Cr₂O₇, and tetraphenylarsonium hexabromoplatinate (Ph₄As)₂PtBr₆.

λ_max for PtBr₆²⁻ ion is 305 nm. Acetone has an absorption band at 305 nm and hence solubility data for K₂PtBr₆ and (Ph₄As)₂PtBr₆ could
not be obtained from the absorbances of the saturated solutions at \( \lambda_{\text{max}} \) for PtBr\(_6\)\(^{2-} \). Fortunately, PtBr\(_6\)\(^{2-} \) ion has a smaller absorbance band (a shoulder) at 364 nm (Fig. 4.1) and thus solubility data were determined from the absorbances of the saturated samples at this latter wavelength.

The stability of K\(_2\)PtBr\(_6\) in water was investigated using the Unicam SP800 spectrophotometer. Repeat scans (Fig. 4.1) of the dependence of absorbance on time revealed that K\(_2\)PtBr\(_6\) was stable enough in water to allow solubility data to be monitored. This latter evidence was consistent with literature\(^5,6\) reports. The extinction coefficient at the shoulder absorbance, \( \varepsilon_{364} \), for PtBr\(_6\)\(^{2-} \) ions was calculated from absorbances of known concentrations of K\(_2\)PtBr\(_6\) in water and in 50 v\% (id) 'acetone + water' mixture using the Beer-Lambert Law (Chapter 2, equation 2.7).

The absorbance of (Ph\(_4\)As\(^+ \)) ions was investigated in the region of the shoulder absorbance (\( \lambda = 364 \) nm) of PtBr\(_6\)\(^{2-} \) ions and found to be negligible.

Solubilities of the dichromate salts were obtained using absorbance data at \( \lambda_{\text{max}} = 351 \) nm (i.e. \( \lambda_{\text{max}} \) for Cr\(_2\)O\(_7\)\(^{2-} \) ions). The extinction coefficient (\( \varepsilon_{\lambda_{\text{max}}} \)) at \( \lambda_{\text{max}} \) for Cr\(_2\)O\(_7\)\(^{2-} \) ions in water and in 50 v\% (id) 'acetone + water' mixture were obtained by analogous methods to those used for the determination of \( \varepsilon_{364} \) for PtBr\(_6\)\(^{2-} \) ions.

Single ion transfer parameters for the salts were obtained using Ph\(_4\)B\(^-\)/Ph\(_4\)As\(^+ \) assumption [Chapter 3, Section 3.1.6 (ii)] from the transfer parameters of Rb\(_2\)Cr\(_2\)O\(_7\), (Ph\(_4\)As\(_2\))Cr\(_2\)O\(_7\) and RbBPh\(_4\).

PtBr\(_6\)\(^{2-} \) salts could not be used as a basis for estimating single ion parameters because when (Ph\(_4\)As\(_2\))PtBr\(_6\) was present in excess in 'acetone + water' mixtures, the original yellow form of the salt changed to a red form on standing and solubilities of the two forms were different.

Solubility data for several salts reported\(^2-4\) by various authors
FIGURE 4.1
Dependence of absorbance on wavelength of K₂PtBr₆ in aqueous solution. Spectra repeated initially at 15 minute intervals. Time interval between spectra (a) and (b) is 24 hours.
were analysed and single ion transfer parameters were calculated.

4.2.2 Results

Figures 4.2, 4.3 and 4.4 show the changes in density, weight % vs volume % (id) (equation 3.82), and $\varepsilon_{354\text{nm}}$ of $\text{PtBr}_6^{2-}$ respectively as the concentration of acetone in 'acetone + water' mixtures is progressively increased.

Solubility data and transfer chemical potentials from water to 'water + acetone' mixtures on the concentration scale at 298 K of the salts: $\text{Rb}_2\text{Cr}_2\text{O}_7$, $(\text{Ph}_4\text{As})_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{PtBr}_6$ and $(\text{Ph}_4\text{As})_2\text{PtBr}_6$ are reported in Table 4.1. Included in Table 4.1 is the solubility data for $\text{RbBPh}_4$ in water obtained from reference 8, and solubility data for $\text{RbBPh}_4$ in 20, 40, 60, 80, 90 v% (id) 'acetone + water' mixtures from reference 1. Solubility of $\text{RbBPh}_4$ in 90 v% (id) 'acetone + water' mixture was interpolated using Figure 4.5. The reported transfer chemical potentials on the concentration scale for $\text{RbBPh}_4$ (Table 4.1) were calculated using solubility data presented in Table 4.1. Solubility of $\text{RbBPh}_4$ in water reported in reference 1 was not felt to be entirely satisfactory and, therefore, this latter value was obtained from reference 8.

Transfer chemical potentials of the salts from water to 'water + acetone' mixture were calculated as described in Chapter 3, Section 3.1.5, equation 3.47. The term '-RT ln{----}' in equation 3.47 was replaced by '-2RT ln{----}' for a 1:1 salt and by '-3RT ln{----}' for a 1:2 salt.

Solubility data at 298 K for a range of perchlorate salts and various silver salts in water and 'water + acetone' mixtures were analysed to yield transfer parameters on the concentration scale and in terms of v% (id) acetone in 'acetone + water' mixtures. Transfer chemical potentials of potassium chloride estimated from e.m.f. data,
FIGURE 4.2
Density data for 'water + acetone' mixtures vs. vol. % (id) acetone at 293 K.
FIGURE 4.3

Wt. % acetone vs. vol. % (id) acetone in 'acetone + water' mixtures.
FIGURE 4.4

$\Sigma_{364\text{nm}}(\text{PtBr}_6^{2-})/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ vs. vol. % (id) acetone in 'acetone + water' mixtures.
FIGURE 4.5

Solubility data\(^1\) (wt. %) of RbBPh\(_4\) in 80-100 vol. % (id) 'acetone + water' mixtures.
were converted from the molal to the concentration scale (Chapter 3, equation 3.21). Solubility data and transfer parameters, on the concentration scale, of the salts mentioned above are reported in Table 4.2.

Single ion transfer parameters were calculated using equation 4.1;

\[ \Delta[(x_2=0) \rightarrow x_2] \mu^\#(c; \text{Ph}_4\text{As}^+) = \Delta[(x_2=0) + x_2] \mu^\#(c; \text{Ph}_4\text{B}^-) = \Delta[(x_2=0) \rightarrow x_2] \mu^\#(c; (\text{Ph}_4\text{As})_2\text{Cr}_2\text{O}_7) + 2(\Delta[(x_2=0) \rightarrow x_2] \mu^\#(c; \text{RbBPh}_4)) - \Delta[(x_2=0) + x_2] \mu^\#(c; \text{Rb}_2\text{Cr}_2\text{O}_7) \]

From the transfer parameter for \( \text{Ph}_4\text{As}^+ / \text{Ph}_4\text{B}^- \), transfer parameters for all the other ions were calculated, e.g.

\[ \Delta[(x_2=0) \rightarrow x_2] \mu^\#(c; \text{Rb}^+) = \Delta[(x_2=0) + x_2] \mu^\#(c; \text{RbBPh}_4) - \Delta[(x_2=0) \rightarrow x_2] \mu^\#(c; \text{BPh}_4^-) \]

Single ion transfer parameters calculated as above are reported in Table 4.3 and Figure 4.6.

4.2.3 Discussion

\( \text{Ph}_4\text{As}^+ \) and \( \text{Ph}_4\text{B}^- \) ions are progressively stabilised as the concentration of acetone in 'acetone + water' mixtures is increased. Similarly, \( n\text{Pr}_4\text{N}^+ \) and \( n\text{Bu}_4\text{N}^+ \) ions are stabilised as the concentration of the organic co-solvent is increased. The hydration characteristics of these ions are dominated by the hydrophobic groups and hence transfer of these ions to a less polar solvent will result in stabilisation of the ions.

The cations \( \text{K}^+ \), \( \text{Rb}^+ \), \( \text{Cs}^+ \), \( \text{Ag}^+ \) and \( \text{Me}_4\text{N}^+ \) show a small but significant stabilisation as the concentration of acetone in the mixtures is increased. The transfer chemical potentials of these latter ions are similar and follow a similar pattern as the solvent mixture becomes less polar. At 60 v% (id) acetone the ions show a maximum stabilisation relative to water. Above 60 v% (id) acetone the ions become progressively less stabilised but even at 90 v% (id) acetone the transfer parameters are
FIGURE 4.6
Single ion transfer parameters (c-scale) from water to 'acetone + water' mixtures at 298 K using the Ph₄As⁺/Ph₄B⁻ assumption.
still slightly negative, e.g. $\Delta[(x_2=0) \times x_2] \mu^*(\text{c}) (\text{Rb}^+) \text{ is } -1.68 \text{ kJ mol}^{-1}$. Acetone is a good cationic solvating solvent because of the exposed lone pairs on the oxygen atom which can interact with the positive charges on the cations. This would explain the slight stabilisation of the cations as the concentration of acetone in the mixture increases even though the solvent is becoming less polar.

The anions in Figure 4.6 are all destabilised as the concentration of acetone is increased. The most dramatic effect is seen with the divalent Cr$_2$O$_7^{2-}$ ions. All the anions are hydrophilic and hence they become less stable as the solvent becomes progressively less polar. This effect can be seen clearly along the series Cl$^-$, Br$^-$ and I$^-$, i.e. as the anion becomes less hydrophilic so the extent of destabilisation decreases.

### 4.3 'ISOPROPANOL + WATER' MIXTURES

#### 4.3.1 Experimental

Concentrated aqueous solutions of Fe(phen)$_3^{2+}$ as the sulphate salt were used. Kinetics of reaction of the iron complex with hydroxide ions were monitored in 20, 40, 60, 80 v% (id) 'isopropanol + water' mixtures at constant ionic strength, $I = 0.0167 \text{ mol dm}^{-3}$, and at 298 K. Constant ionic strength was maintained by adding appropriate concentrations of sodium chloride to the reaction mixture. In all systems, $[\text{complex}] < 10^{-4} \text{ mol dm}^{-3}$ and $[\text{NaOH}] > [\text{complex}]$. Reactions were monitored between $3.3 \times 10^{-3} < [\text{NaOH}] < 1.67 \times 10^{-2} \text{ mol dm}^{-3}$ at five different concentrations of sodium hydroxide.

Kinetic data for the aquation reaction of Fe(phen)$_3^{2+}$ in 20 v% (id) 'isopropanol + water' mixture were also monitored.

The isopropanol used was 99+% spectrophotometric grade, gold label.
Aqueous solutions of Fe(phen)$_3^{2+}$ are bright red with $\lambda_{\text{max}} = 510$ nm. No shift in $\lambda_{\text{max}}$ was observed when the complexes were dissolved in 'isopropanol + water' mixtures. Repeat scans of the dependence of absorbance on wavelength, recorded on the Unicam SP800 spectrophotometer (Chapter 2, Section 2.4.1), revealed that the dependence of absorbance on time was first order. Kinetics of reactions were monitored at 510 nm using a Unicam SP1800 spectrophotometer (Chapter 2, Section 2.4.1). The computer was programmed to fit the absorbance data to a first order kinetic expression (Chapter 2, Section 2.3). Second order rate constants were calculated from the gradients of plots of first order rate constants as a function of sodium hydroxide concentration for each solvent mixture.

Solubility data at 298 K for (Ph$_4$As)$_2$Cr$_2$O$_7$ and Rb$_2$Cr$_2$O$_7$ were obtained from the absorbances at $\lambda_{\text{max}} = 351$ nm of diluted samples taken from saturated solutions of the salts in water and in 'isopropanol + water' mixtures.

Solubility data at 298 K in water and in 'water + isopropanol' mixtures for rubidium perchlorate (RbClO$_4$), iron(II) 1,10-phenanthroline perchlorate [Fe(phen)$_3$(ClO$_4$)$_2$], cobalt(III) ethylene diamine iodide and perchlorate [Co(en)$_3$I$_3$ and Co(en)$_3$(ClO$_4$)$_3$] were obtained from reference 10. Transfer parameters for RbBPh$_4$ from water to 'isopropanol + water' mixtures were obtained from a solubility analysis from reference 10.

4.3.2 Results and Discussion

In 'isopropanol + water' mixtures the reactions of Fe(phen)$_3^{2+}$ with hydroxide ions were first order in [complex]. Kinetic data are reported in Table 4.4, together with the corresponding data$^{11}$ for reaction in aqueous solution. Kinetic data for aquation reactions of Fe(phen)$_3^{2+}$ in 20 v% (id) 'isopropanol + water' mixtures are included in Table 4.4. Each value is the mean of at least three individual determinations, the
reproducibility being, at worst, within 5%.

Plots of first order rate constants against sodium hydroxide concentration are linear (Fig. 4.7). The intercept at 20 v% (id) 'isopropanol + water' mixture is equal to the rate constant for the aquation reaction of Fe(phen)$_3^{2+}$ in this latter solvent. At 40 v% (id) and 60 v% (id) isopropanol the intercept passes through the origin. At 80 v% (id) isopropanol the intercept is negligible.

The rate of reaction between Fe(phen)$_3^{2+}$ and hydroxide ions in aqueous solution is given by; [Chapter 1, Section 1.6.1]

\[- \frac{d [\text{complex}]}{dt} = \{k_1 + k_2 [OH^-]\} [\text{complex}]\]

For solutions where [NaOH] » [complex] the first order rate constant, $k_{obs} = k_1 + k_2 [OH^-]$. The dependence of $k_{obs}$ on sodium hydroxide concentration was fitted to this latter equation using a linear least squares procedure. At 40, 60 and 80 v% (id) isopropanol the $k_1$ term was negligibly small and is not reported. Second order rate constants with standard errors are reported in Table 4.5.

Solubility data for (Ph$_4$As)$_2$Cr$_2$O$_7$, Rb$_2$Cr$_2$O$_7$, RbClO$_4$, $^{10}$Fe(phen)$_3$ (ClO$_4$)$_2$, $^{10}$Co(en)$_3$I$_3$, $^{10}$Co(en)$_3$(ClO$_4$)$_3$ are reported in Table 4.6. Transfer chemical potentials from water to 'isopropanol + water' mixtures on the concentration scale, for these salts (Table 4.6) were obtained by analogous methods to those described in Section 4.2.2 for 'acetone + water' mixtures. Included in Table 4.6 are the transfer parameters (c-scale) for RbBPh$_4$ and hydrogen iodide. $^{12}$

Transfer parameters for hydrogen iodide are reported$^{12}$ on the mole-fraction scale and in terms of weight percent of isopropanol in the solvent mixture. Conversions of transfer parameters to the concentration scale (Table 4.7, Fig. 4.8) were made using equation 3.22. Conversions from weight percent to ideal volume percent isopropanol (Fig. 4.9) were
Dependence of first-order rate constants, $k_{obs}$, on sodium hydroxide concentration for reactions of $R(OH)_3^{+}$ with hydroxide ions at 298 K in: (a) 20 vol. % isopropanol + water and (b) 60 vol. % isopropanol + water.
FIGURE 4.8
Conversion of single ion transfer parameters from water to 'isopropanol + water' mixtures from the x-scale to the c-scale.

FIGURE 4.9
Wt. % isopropanol vs. vol. % (id) isopropanol for 'isopropanol + water' mixtures.
made using equation 3.82 and literature\textsuperscript{13} density data (Fig. 4.10). A
After conversion to the necessary scales a plot of transfer parameters (c-scale) as a function of ideal volume percent isopropanol was drawn (Fig. 4.11) and the transfer parameters for hydrogen iodide reported in Table 4.6 were interpolated from Figure 4.11.

Transfer parameters of (H\textsuperscript{+}OH\textsuperscript{-}) were calculated from pK\textsubscript{w}\textsuperscript{14} for water (Table 4.8) as set out below.

Consider description (II) of the system (Chapter 3), i.e. H\textsuperscript{+} and OH\textsuperscript{-} ions are solutes in the solvent mixture 'water + isopropanol', at fixed temperature, T and at ambient pressure, p(\approx p\textsuperscript{0}). Hydrogen and hydroxide ions in the system can be represented in terms of the equilibrium process;

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \hspace{1cm} \text{...(4.2)} \]

At equilibrium;

\[ \mu^{\text{eq}}(\text{H}_2\text{O}) = \mu^{\text{eq}}(\text{H}^+) + \mu^{\text{eq}}(\text{OH}^-) \hspace{1cm} \text{...(4.3)} \]

At mole fraction, \(x_2\), of isopropanol in the solvent mixture and assuming processes at equilibrium so that superscript "eq" is omitted the chemical potential of \(\text{H}_2\text{O}\) is given by;

\[ \mu(\text{H}_2\text{O}; x_2) = \mu^*(\ell) + RT \ln [x(\text{H}_2\text{O}); f(\text{H}_2\text{O})] \hspace{1cm} \text{...(4.4)} \]

Limit \([x(\text{H}_2\text{O}) \rightarrow 1] f(\text{H}_2\text{O}) \rightarrow 1\) at all \(T\) and \(p\), where \(\mu^*(\ell)\) is the chemical potential of pure water at the same temperature and ambient pressure and \(f(\text{H}_2\text{O})\) is the activity coefficient of water at mole fraction \(x_2\) of isopropanol. The chemical potential of (H\textsuperscript{+}OH\textsuperscript{-}) in the system at \(x_2\) of alcohol is given by;

\[ \mu(\text{H}^+\text{OH}^-; x_2) = \mu^*(\text{H}^+\text{OH}^-; x_2) + \text{R}. \text{T}. \ln \left[ \frac{c(\text{H}^+).c(\text{OH}^-).y(\text{H}^+;x_2).y(\text{OH}^-;x_2)}{c^2_r} \right] \hspace{1cm} \text{...(4.5)} \]

and

\[ y(\text{H}^+;x_2).y(\text{OH}^-;x_2) = y^2_+(x_2) \hspace{1cm} \text{...(4.6)} \]

Limit \([c(\text{H}^+).c(\text{OH}^-) \rightarrow 0] y_\pm(x_2) = 1\) at all \(T\) and \(p\).
Density data for isopropanol + water mixtures vs. wt. % isopropanol at 298 K.
FIGURE 4.11
$\Delta[(x_2=0) \rightarrow x_2] \mu^\#(c)$ from water to 'isopropanol + water' mixtures for HI and H\textsuperscript{+}OH\textsuperscript{-} vs. vol. % (id) isopropanol.
\[ \Delta G^\#(x_2) = -R.T. \ln K^\#(x_2) \]
\[ = \mu^\#(H^+;x_2) - \mu^\#(\ell;H_2O) \] \hspace{1cm} (4.7)

Then combining equations 4.3, 4.4, 4.5 and 4.7 yields;

\[ K^\#(x_2) = \frac{c(H^+) \cdot c(OH^-) \cdot y(H^+;x_2) \cdot y(OH^-;x_2)}{c_T^2 \cdot x(H_2O) \cdot f(H_2O)} \] \hspace{1cm} (4.8)

Similarly \[ \Delta G^\#(x_2=0) = -R.T. \ln K^\#(x_2=0) \]
\[ = \mu^\#(H^+;x_2=0) - \mu^\#(\ell;H_2O) \] \hspace{1cm} (4.9)

Combining equations 4.7 and 4.9 yields the transfer parameter from pure water to 'isopropanol + water' mixture at mole fraction, \( x_2 \) of alcohol for \( (H^+\text{OH}^-) \);

\[ \Delta[(x_2=0) + x_2] \mu^\#(H^+\text{OH}^-) = -R.T. \{ \ln K^\#(x_2) - \ln K^\#(x_2=0) \} \] \hspace{1cm} (4.10)

But \[ pK_w^\# = -\log_{10} K^\# \] \hspace{1cm} (4.11)

Combining equations 4.10 and 4.11 yield;

\[ \Delta[(x_2=0) + x_2] \mu^\#(H^+\text{OH}^-) = 2.303R.T. \{ pK_w^\#(x_2) - pK_w^\#(x_2=0) \} \] \hspace{1cm} (4.12)

Transfer parameters (c-scale) for \( H^+\text{OH}^- \) at 20, 40 and 60 v\% (id) isopropanol were interpolated from Figure 4.11.

Single ion transfer parameters (c-scale) for BPh^−/Ph_4As^+ were calculated using equation 4.1 and from these latter values the other single ion transfer parameters were estimated (Table 4.9, Fig. 4.12).

The kinetic data was used in conjunction with the solubility data to analyse the solvent effects on the initial and transition states for reaction of \( \text{Fe(phen)}_3^{2+} \) with hydroxide ions, using the method outlined in Chapter 3, Section 3.1.5 (Table 4.10, Fig. 4.13).

4.3.3 Conclusion

From Figure 4.12 it is clear that the hydrophobic ions (e.g. BPh^−, Ph_4As^+, \( \text{Fe(phen)}_3^{2+} \) and \( \text{Co(EN)}_3^{3+} \)) are stabilised as the solvent mixture becomes less polar, the more hydrophobic the ion the greater the stabilisation. With the exception of the hydrogen ion, the opposite is
FIGURE 4.12
Single ion transfer parameters (c-scale) from water to 'isopropanol + water' mixtures at 298 K using the Ph₄As⁺/Ph₄B⁻ assumption.
The effects of increasing the concentration of isopropanol in the solvent mixture become less polar. The initial state stabilisation at 40 and 60 vol% (id) isopropanol is due to the greater stabilisation of hydroxide ions than destabilisation of hydroxide ions at 20 vol% (id) isopropanol. At 40 and 60 vol% (id) isopropanol the decrease in $\Delta^c G^\circ(c)$ is due to the progressive greater stabilisation of the transition state with respect to the initial state for the reaction of Fe(phen)$_3^{2+}$ with hydroxide ions. The initial state stabilisation at 40 and 60 vol% (id) isopropanol can be accounted for by the dispersal of charges on going from the initial to the transition state and, therefore, the initial state is more stabilised than the initial state in the solvent mixture is more polar.

FIGURE 4.13
Dependence of $\Delta^c G^\circ(c)$ and related reference-state chemical potentials (c-scale) on vol. % (id) of added isopropanol for reactions of Fe(phen)$_3^{2+}$ with hydroxide ions at 298 K.
true of the hydrophilic ions, i.e. as the solvent becomes less polar the ions are destabilised.

Hydrogen ions are slightly more stabilised in 'isopropanol + water' mixtures up to 60 v% (id) isopropanol than in water (cf. at 60 v% (id) isopropanol, $\Delta[(x_2=0) \rightarrow x_2]\mu^\#(c)$ for $H^+$ is $-4.75$ kJ mol$^{-1}$).

Over the whole range of 'isopropanol + water' mixtures up to 80 v% (id) alcohol, the rate of reaction of $\text{Fe(phen)}_3^{2+}$ with hydroxide ions increases as the solvent becomes less polar (Table 4.10). This means that the Gibbs function for activation decreases as the solvent becomes more alcohol-rich, at fixed temperature and ambient pressure.

The decrease in $\Delta[(x_2=0) \rightarrow x_2]\Delta^\ast G^\#(c)$ at 20 v% (id) isopropanol (Fig. 4.13) is due to stabilisation of both the initial ($-4.36$ kJ mol$^{-1}$) and transition states ($-5.92$ kJ mol$^{-1}$) with the transition state being slightly more stabilised than the initial state. Stabilisation of the initial state arises from a greater stabilisation of $\text{Fe(phen)}_3^{2+}$ ions than destabilisation of hydroxide ions at 20 v% (id) isopropanol. At 40 and 60 v% (id) isopropanol in the solvent mixture the decrease in $\Delta[(x_2=0) \rightarrow x_2]\Delta^\ast G^\#(c)$ is due to the progressively greater stabilisation of the transition state with respect to the initial state as the solvent mixture becomes less polar. The initial state stabilisation at 40 and 60 v% (id) becomes constant as the destabilisation of hydroxide ions begins to mirror the corresponding stabilisation of $\text{Fe(phen)}_3^{2+}$ ions.

The effects of increasing the concentration of isopropanol in the solvent mixture, on the initial state for the reaction of $\text{Fe(phen)}_3^{2+}$ with hydroxide ions is consistent with the hydrophobic and hydrophilic nature respectively of the two ions. Stabilisation of the transition state up to 60 v% (id) isopropanol can be accounted for by the dispersal of charges on going from the initial to the transition state and, there-
fore, transfer of the transition state to a less polar solvent results in stabilisation of the transition state (cf. Chapter 3, Section 3.4).

In this and the previous chapter investigations were made into ionic systems. In the next chapter attention is turned to reactions involving neutral species.
REFERENCES TO CHAPTER 4


CHAPTER 5

Salt effects on the neutral hydrolysis of phenyl dichloroacetate in aqueous media
5.1 INTRODUCTION

In the preceding two chapters the effects of added organic co-solvent on rate constants for reaction between two ionic species were examined. The most unsatisfactory part of an analysis of kinetic data for reaction involving ionic species is the extrathermodynamic assumptions leading to single ion parameters. Estimates of single ion properties depend significantly on the type of extrathermodynamic assumption made and different assumptions can lead to different conclusions concerning trends in solvation of initial and transition states. In this Chapter attention is turned to reactions which involve neutral solutes. The dependence on salt of rate constants for hydrolysis of phenyl dichloroacetate in aqueous salt solutions at fixed ionic strength are reported. Trends in kinetic data are accounted for in terms of hydration properties of the added salt.

Kinetic data are also reported for hydrolysis of phenyl dichloroacetate as a function of added salt concentration for tetrabutylammonium bromide (n-Bu₄NBr) and potassium bromide.

Properties of aqueous salt solutions are determined by three main factors: (i) hydration characteristics of the individual ions; (ii) charge-charge interactions and (iii) interactions between cospheres of solvent surrounding the ions. Factors (i) and (ii) are discussed in Chapter 1, Section 1.3.5. Interactions between cospheres of solvent surrounding an ion and neutral solutes are examined below.

5.1.1 Solvent cosphere interactions

As noted in Chapter 1, Section 1.3.5, when the mean ionic activity coefficient, $\gamma_+^+$ for salt solutions at fixed molarity and temperature are examined as a function of the ion, several interesting patterns emerge. According to the Debye-Hückel Limiting Law, $\gamma_+^+$ should not depend on the
nature of the salt. These patterns and related trends can be understood in terms of the effect on $\gamma_2$ of overlapping solvent cospheres.

A solvent cosphere refers to solvent molecules surrounding a solute particle where the organisation differs from that of the pure solvent.

Consider two neutral solute particles, $i$ and $j$, in solution which approach so that their cospheres overlap (Fig. 5.1). Overlap of the cospheres results in one of two effects dependent on the compatibility of solvent structures in the cospheres: (i) mutually destructive interaction [Fig. 5.1(a)] or (ii) mutually constructive interaction [Fig. 5.2(c)].

![Diagram showing cosphere overlap and interaction types](image)

**FIGURE 5.1**

Diagrammatic representation of the process of co-sphere overlap as two solute species, $i$ and $j$, come together; (a) mutually destructive co-sphere interaction where the co-sphere of solute $j$ dominates the process leading to the solvent reaction shown in (b); in process (c) the interaction is mutually constructive, additional solvent being incorporated into the co-sphere as shown in reaction (d) assuming solute $j$ dominates (Friedman and Krishnan, 1973).
(i) **Mutually destructive interaction**

Organisation of solvent in the co-spheres is incompatible. Overlap leads to destabilisation causing some of the solvent in the 'overlap' region to be released into bulk solvent [Fig. 5.1(b)]. The total Gibbs function of the system increases with increase in co-sphere overlap, i.e. solutes i and j repel each other.

(ii) **Mutually constructive interaction**

Organisation of solvent in the co-spheres is compatible creating mutual re-enforcement and expansion of the two co-spheres. Some of the bulk solvent is incorporated into the overlap region [Fig. 5.1(d)]. Overlap leads to stabilisation. The total Gibbs function of the system decreases with increase in overlap of the co-spheres, i.e. solutes i and j attract each other.

Desnoyers' model can be summarised as follows:-

1) The influence of an ion on the structure of water is either as an "electrostrictive structure breaker" or an "electrostrictive structure former" (Chapter 1, Section 1.3.5).

2) The concentration effect of ions on water structure are due to overlap of ion solvent co-spheres.

3) Only two types of ions were considered:- hydrophilic and hydrophobic ions.

4) Two solutes attract each other if their influences on water structure are compatible and conversely two solutes repel each other if their influences on water structure are incompatible.

Using the model outlined above, the following predictions (Table 5.1) of the net effect on water structure due to overlap of two solvent co-spheres of solutes i and j were put forward.
The chemical potential, \( \mu_j \) of a salt in solution at constant temperature, \( T \) and pressure, \( p \), can be expressed as a sum of three contributions:

\[
\mu_j(sln; T; p) = \mu_j^\Theta(sln; id; T) + \mu_j(\text{coulombic}) + \mu_j(\text{co-sphere}) \tag{5.1}
\]

where \( \mu_j(\text{coulombic}) \) accounts for charge-charge interactions in terms of the D.H.L.L. and \( \mu_j(\text{co-sphere}) \) accounts for co-sphere-co-sphere interactions in real solutions. \( \mu_j^\Theta(sln; id; T) \) is the standard chemical potential of salt \( j \) in solution (Chapter 1, Section 1.3.1 and 1.3.5).

Deviations of \( \gamma_+ \) of salt \( j \) from the D.H.L.L. can be described for a 1:1 salt using equation 5.2;

\[
\log \gamma_+ = - S_Y \left( \frac{m_j}{m^\Theta} \right)^{1/2} + B \left( \frac{m_j}{m^\Theta} \right) \quad \text{...... (5.2)}
\]

where \( m_j \) is the molality of salt \( j \) \( (m_j = n_j/n_1M_1, \) where \( n_1, M_1 \) are the number of moles and molar mass of solvent 1, respectively); \( S_Y \) is a function of the solvent properties at the same \( T \) and \( p \) and charges on the ions; \( m^\Theta \) is the standard molality \( (1 \text{ mol kg}^{-1}) \); and \( B \) is a parameter which describes the deviations of \( \gamma_+ \) from the D.H.L.L. Equation 5.2 contains the first two terms in a power series in \( (m_j/m^\Theta)^{1/2} \). Equation 5.2 can be extended to the general equation;

\[
\log \gamma_+ = - S_Y \left( \frac{m_j}{m^\Theta} \right)^{1/2} + B_1 \left( \frac{m_j}{m^\Theta} \right) + B_2 \left( \frac{m_j}{m^\Theta} \right)^{3/2} + \ldots \quad \text{(5.3)}
\]

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Net effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic - hydrophobic</td>
<td>attraction - less structure making</td>
</tr>
<tr>
<td>Hydrophobic - hydrophilic</td>
<td>repulsion - less structure making</td>
</tr>
<tr>
<td>Hydrophilic - hydrophilic (opposite sign)</td>
<td>attraction - less structure breaking</td>
</tr>
<tr>
<td>Hydrophilic - hydrophilic (same sign)</td>
<td>repulsion - more structure breaking</td>
</tr>
</tbody>
</table>
For moderately concentrated solutions deviations from the D.H.L.L. are understood in terms of the linear coefficient $B_1$. Similarly, deviations in the apparent molar enthalpies, volumes and heat capacities from the D.H.L.L. can be expressed by analogous equations.

Desnoyers and co-workers,$^3,^6$ compared activity coefficient data of MX and R$_n$NX salts (where X = halide ions, M = alkali metal and R = methyl, ethyl, propyl and butyl) in aqueous solution at ambient pressure and 298 K (Fig. 5.2).$^3,^6$ The first term on the right-hand side of equation 5.3 was taken as $-0.512(m_j/m^0)^{1/2}$, and $m_j = 0.2$ mol kg$^{-1}$. Deviations of log $\gamma_1$ from the D.H.L.L. were explained entirely in terms of co-sphere-co-sphere interactions.

A small difference is apparent between the models suggested by (a) Desnoyers$^3,^4,^6$ and by (b) Friedman.$^2$ The Friedman$^2$ model in which interaction between solvent co-spheres is compatible results in mutual re-enforcement and expansion of the two co-spheres [Fig. 5.1(d)]. The net effect on the solvent is an increase in structure promotion. Desnoyers,$^3,^4,^6$ however, regards hydrophobic-hydrophobic co-sphere interaction (i.e. attraction between ions i and j) as a release of some of the solvent in the overlap region into the bulk solvent. The net effect on the solvent is a decrease in structure promotion. These differences reflect the contrasting models for hydrophobic bonding$^7$ in aqueous solution. Desnoyers,$^3,^4,^6$ models involving hydrophobic-hydrophilic, hydrophilic-hydrophilic (same sign and opposite sign) ions are consistent with the corresponding models put forward by Friedman.$^2$

In this Chapter all favourable cosphere-cosphere interactions will be treated in terms of Friedman's model.$^2$
FIGURE 5.2
Concentration dependence of activity coefficients in water at 298 K.
[Reprinted from Ref. 6]
5.1.2 Mechanism for reaction of the neutral hydrolysis of phenyl dichloroacetate

Phenyl dichloroacetate spontaneously hydrolyses in water (equation 5.4) to yield dichloroethanoic acid and phenol.

\[
\text{Cl}_2\text{CHC} = \text{O} \quad \text{H}_2\text{O} \quad \text{Cl}_2\text{CHC-OH} + \text{HO} \quad \text{PhOH} \quad \text{.... (5.4)}
\]

The mechanism for the above reaction involves rate-determining water-catalysed nucleophilic attack by water at the carbonyl carbon (equation 5.5).

\[
\text{Cl}_2\text{CHC} \quad \text{Cl}_2\text{CHC-OH} + \text{PhOH} \quad \text{.... (5.5)}
\]

No significant acid catalysis was observed for the hydrolysis of the p-nitro and p-methoxy derivatives. At acid (e.g. HCl(aq)) concentrations above 0.1 mol dm\(^{-3}\) hydrolysis of the derivatives was retarded. This latter feature was explained in terms of a salt effect. A comparable decrease in rate was observed for reaction in aqueous solution in the presence of similar concentrations of lithium chloride. At higher concentrations of acid, the probability that the hydrolysis may proceed via an acid-catalysed pathway was considered. However, the acid-catalysed pathway was overwhelmed by a negative salt effect. Acid catalysis apparently cannot compete with the rapid water-catalysed nucleophilic attack of water at the carbonyl moiety. The decrease in electron density in the carbonyl group due to the presence of chlorine atoms was regarded as being the reason for favouring water-catalysed rather than acid-catalysed nucleophilic attack.
Neutral hydrolysis of acyl-activated esters involves both a relatively simple mechanism and contribution from at least two water molecules to the transition state. One of the water molecules involved in the transition state, acts as a proton-transferring agent. It was anticipated\(^8,9\) that this type of hydrolysis reaction could be used to probe changes in water structure due to small amounts of added solutes and co-solvents. This hypothesis was confirmed for the p-methoxy and p-nitro derivatives of phenyl dichloroacetate. In the neutral hydrolysis of these latter two esters extrema in the standard molar enthalpy (\(\Delta^\circ H^\Theta\)) and standard molar entropy (\(\Delta^\circ S^\Theta\)) of activation were detected in the narrow concentration range (3-6 mol % of tertiary butyl alcohol [t-BuOH]), at which there is a maximum in solvent microheterogeneity. Therefore, neutral hydrolysis of these esters responds kinetically to a perturbation of water structure.

Effects of added n-Bu\(_4\)NBr and potassium bromide on \(\Delta^\circ H^\Theta\) and \(\Delta^\circ S^\Theta\) for the neutral hydrolysis of the p-nitro ester derivative were also investigated.\(^8,9\) In the concentration range 0.0 < [n-Bu\(_4\)NBr] < 0.35 mol dm\(^{-3}\), the variation of \(\Delta^\circ H^\Theta\) and \(\Delta^\circ S^\Theta\) resembled the corresponding variation in 't-BuOH + water' mixtures, in the range 0.95 < \(n_{(H_2O)}\) < 1.00. This latter observation suggested that the effect of n-Bu\(_4\)NBr on water structure was the predominant influence on the neutral ester hydrolysis reaction and electrostatic considerations were inadequate to account for the kinetic response of the system. n-Bu\(_4\)NBr is considered a hydrophobic water structure-former (Chapter 1, Section 1.3.5) which is consistent with the trends in \(\Delta^\circ H^\Theta\) and \(\Delta^\circ S^\Theta\) observed above. At [n-Bu\(_4\)NBr] > 0.35 mol dm\(^{-3}\) both \(\Delta^\circ H^\Theta\) and \(\Delta^\circ S^\Theta\) are larger than for reaction in water. This latter trend was accounted for in terms of overlap of hydration cospheres of n-Bu\(_4\)NBr resulting in a gradual decrease of water structure promotion.
Addition of potassium bromide, an electrostrictive water structure-breaking salt, retarded the rate of hydrolysis of p-nitrophenyl dichloroacetate, but to a much lesser extent than added n-Bu₄NBr. Addition of potassium bromide also caused an increase in $\Delta^\Phi H^\Phi$ but this was not totally compensated by the accompanying increase in $\Delta^\Phi S^\Phi$. Extrema in the standard molar activation parameters were found to occur at $[\text{KBr}] \approx 0.75$ mol dm$^{-3}$.

Additional support for the contention that the salt effect on the hydrolysis reaction of the p-nitro ester derivative is a result of water-structure perturbation was found in the small changes in $\Delta^\Phi H^\Phi$ and $\Delta^\Phi S^\Phi$ induced by sodium perchlorate (NaClO₄). In the concentration range examined, sodium perchlorate alters water-structure only slightly.

The above is a short resume of the work by Engberts and co-workers which prompted the investigations presented in this Chapter.

5.2 EXPERIMENTAL

Concentrated solutions of phenyldichloroacetate (PDCA) in acetonitrile were prepared. Kinetics of the water-catalysed hydrolysis reaction of PDCA at 298 K were monitored in water and aqueous solutions containing 0.9 mol dm$^{-3}$ electrolyte. The electrolytes were MX (where X = fluoride, chloride, bromide and M = lithium, sodium, potassium, rubidium, caesium) and R₄NX (where R = methyl, ethyl, propyl, butyl). All solutions used in kinetic experiments contained $10^{-2}$ mol dm$^{-3}$ hydrochloric acid to suppress any possible catalysis by hydroxide ions.

Kinetics of the hydrolysis reaction of PDCA in aqueous solution at 298 K at $0.1 \leq [\text{n-Bu}_4\text{NBr}] \leq 0.9$ mol dm$^{-3}$ and $0.1 \leq [\text{KBr}] \leq 1.0$ mol dm$^{-3}$ at five and four different salt concentrations respectively were also monitored.
In all systems reaction was initiated by adding one or two drops of a concentrated solution of PDCA in acetonitrile to the reagents in a 1 cm³ quartz cell. Any hydration effects of the one or two drops of acetonitrile in 3 cm³ aqueous solvent were considered negligible. In all systems PDCA < 10⁻⁴ mol dm⁻³ and [H₂O] ≫ [complex].

Aqueous solutions of PDCA are colourless and kinetics of the hydrolysis reaction were monitored by measuring the appearance of the phenol at λ_max = 272 nm.

Kinetics of the hydrolysis reaction in aqueous solution with 0.9 mol dm⁻³ iodide salts could not be monitored because iodide ions absorb intensely in the region of the phenol absorbance and irradiation of iodide ions within the spectrophotometer produces I₃⁻ ions. These latter ions also absorb in the region of the phenol absorbance.

Kinetics of reaction were examined using an HP8451A diode array spectrophotometer (Chapter 2, Section 2.4.2). Repeat scans of the dependence of absorbance on wavelength revealed that the dependence of absorbance on time followed first order kinetics. From the plots of absorbance data as a function of time [Fig. 5.3(a)], it was evident that if the reaction was monitored for more than 2.5 half-lives further complicated reactions of the phenol ensued [last fifteen data points in Fig. 5.3(a)]. These reactions were attributed to oxidation of the phenol by dissolved oxygen in the solutions. Degassing of solutions and flushing with nitrogen did not entirely eliminate these undesirable side-reactions. Nevertheless, from the absorbance-time plots it was relatively simple to deduce when the hydrolysis reaction of PDCA was complete and any data points which were due to oxidation of the phenol were dropped before analysing the remaining data in terms of first order kinetics. Figure 5.3(b) is a first order plot, for the neutral hydrolysis of PDCA
FIGURE 5.3

(a) Dependence of absorbance on time at \( \lambda_{\text{max}} = 272 \text{ nm} \) for the neutral hydrolysis of phenyl dichloroacetate in 0.9 mol dm\(^{-3}\) aqueous CsBr solution (aqueous solution also contains \( 10^{-2} \) mol dm\(^{-3}\) hydrochloric acid);
(b) Dependence of \( \ln \frac{[P_0-P_\infty]}{[P_0-P_t]} \) on time at \( \lambda_{\text{max}} = 272 \text{ nm} \) for the neutral hydrolysis of phenyl dichloroacetate in 0.9 mol dm\(^{-3}\) aqueous CsBr solution.
in 0.9 mol dm$^{-3}$ aqueous, acidic, caesium bromide solution, in which the last fifteen data points in Figure 5.3(a) have not been included in the analysis. Dropping a specified number of data points at the end of a reaction was another option offered by the program written for the minicomputer within the spectrophotometer.

### 5.3 RESULTS AND DISCUSSION

In aqueous solution and in solutions containing a known concentration of the electrolytes MX or R$_n$NX, the neutral hydrolyses of PDCA were first order in [ester]. Kinetic data are reported in Table 5.2 together with $\log_{10}(k_1/k_0)$ where $k_1$ is the first order rate constant for reaction in aqueous salt solutions and $k_0$ is the first order rate constant for reaction in aqueous solution.

Each rate constant is the mean of at least three individual determinations, the reproducibility being at worst within 5%. In aqueous solutions of 0.9 mol dm$^{-3}$ n-Bu$_n$NF the reproducibility of the rate constants for reaction was only within 15% due to the very hygroscopic nature of this salt and the impurities still present in the samples.

Aqueous salt solutions of constant ionic strength, $I = 0.9$ mol dm$^{-3}$ were chosen to investigate trends in $\log(k_1/k_0)$ as a function of the added anion, because at this concentration, the rate constant for the hydrolysis of PDCA in the presence of MX, showed an appreciable change with respect to the corresponding rate constant in water.

Figure 5.4 shows the concentration dependence of $\log_{10}(k_1/k_0)$ with added n-Bu$_n$NBr and potassium bromide in aqueous solution at 298 K. Both n-Bu$_n$NBr and potassium bromide retard the rate of hydrolysis of PDCA relative to the corresponding rate in water. The rate of reaction decreases as the concentration of the added salt increases, but the
FIGURE 5.4
Dependence of \( \log_{10}(k/k_0) \) on salt concentration for the neutral hydrolysis of phenyl dichloroacetate in aqueous solution at 298 K. \( k_0 \) is the first-order rate constant in the absence of added salt. \( k \) is the first-order rate constant in aqueous salt solution.
relationship between $\log_{10} (k_1/k_0)$ and salt concentration is not linear. $\log_{10} (k_1/k_0)$ decreases progressively more rapidly as the salt concentration increases. Further $n$-Bu$_4$NBr has a more dramatic retardation effect on the rate of reaction than potassium bromide.

Plots of $\log_{10} (k_1/k_0)$ as a function of the anions, fluoride, chloride and bromide (Fig. 5.5) and the corresponding plots of $\ln(y)$ as a function of the anions (Fig. 5.6) were drawn. Data for $\gamma$ of the MX and R$_n$NX salts in aqueous solution at [salt] = 0.9 mol dm$^{-3}$ were collected from reference 5 for MCI, MBr, NaF, KF; reference 10 for RbF, CsF; reference 11 for R$_n$NCl, R$_n$NBr and reference 12 for R$_n$NF.

$\log(k_1/k_0)$ for MX and R$_n$NX salt solutions, where X = chloride and bromide, is negative, i.e. the rate of hydrolysis reaction of PDCA in 0.9 mol dm$^{-3}$ salt solutions is decreased relative to the corresponding rate in water. The most dramatic effect is seen in n-Bu$_4$NBr solutions. As the length of the alkyl chain decreases so the retardation effect of the bromide and chloride R$_n$NX salt solutions on the rate of reaction decreases, i.e. the decrease in rate of reaction relative to the corresponding rate in water is in the order n-Bu$_4$N$^+ >$ Pr$_4$N$^+ >$ Et$_4$N$^+ >$ Me$_4$N$^+$. R$_n$NBr salt solutions retard the reaction more than R$_n$NCl solutions.

In salt solutions of R$_n$NBr and R$_n$NCl, $\log_{10} (k_1/k_0)$ is more negative than in the corresponding MBr and MCI salt solutions. In the latter salt solutions all the M$^+$ ions display a small and similar rate retardation on the PDCA hydrolysis reaction. The decrease in rate of reaction in MBr solutions relative to the corresponding rate in water is in the order $K^+ >$ Li$^+ >$ Na$^+ >$ Cs$^+ >$ Rb$^+$ and in MCI solutions is in the order Li$^+ \sim$ Na$^+ >$ K$^+ >$ Rb$^+ >$ Cs$^+$. The effect on the rate of reaction of added MCI for M$^+$ = Li$^+$, Na$^+$, Rb$^+$ and Cs$^+$ is marginally greater than the
FIGURE 5.5
$\log_{10}(k/k_0)$ vs. the anion $X^-$ (where $X^-=F^-, Cl^-, Br^-$) for $M^+$ and $Rb^+$ for the neutral hydrolysis of phenyl dichloroacetate in aqueous solution at 298 K where [salt] = 0.9 mol dm$^{-3}$.
FIGURE 5.6

ln $\gamma_+$ vs. the anions $X^-$ (where $X^-$ = $F^-$, $Cl^-$, $Br^-$) for the $M^+$ and $Rb^+$ salts in aqueous solution at 298 K where [salt] = 0.9 mol dm$^{-3}$. 

Also the total Gibbs function of PME. Also the total Gibbs function of PME.
corresponding bromides but KBr has a slightly greater effect than KCl.

In contrast \( \log_{10} (k_1/k_0) \) for the series of fluoride salt solutions is positive, i.e. the rate of reaction is accelerated in fluoride salt solutions relative to the corresponding rate in water. The increase in rate of reaction in fluoride salt solutions is in the order \( \text{Et}_4\text{N}^+ > \text{Me}_4\text{N}^+ > K^+ > \text{Cs}^+ > \text{Rb}^+ > \text{n-Bu}_4\text{N}^+ > \text{Na}^+ \). The position of \( \text{n-Bu}_4\text{N}^+ \) in this series is surprising. The unsatisfactory quality of \( \text{n-Bu}_4\text{NF} \) samples could explain the rather low value of \( \log_{10} (k_1/k_0) \) in this latter salt solution.

Nevertheless, the increase in rate of reaction in \( \text{n-Bu}_4\text{NF} \) solutions relative to the corresponding rate in \( \text{n-Bu}_4\text{NCl} \) and \( \text{n-Bu}_4\text{NBr} \) solutions is the most dramatic out of the whole series of salt solutions investigated here.

Comparison of Figures 5.5 and 5.6 reveals a similar pattern for \( \text{M}^+ \) and \( \text{R}_4\text{N}^+ \) ions of the fluoride, chloride and bromide salts.

5.4 CONCLUSION

The similarity between Figures 5.5 and 5.6 suggests that trends in \( \log_{10} (k_1/k_0) \) as a function of the salt are due to solute co-sphere-co-sphere interactions.

In \( \text{n-Bu}_4\text{NBr} \) solutions cation-cation co-sphere (i.e. \( \text{n-Bu}_4\text{N}^+ - \text{n-Bu}_4\text{N}^+ \)) interactions dominate the hydration characteristics of the salt because \( \text{n-Bu}_4\text{N}^+ \) is a hydrophobic cation and \( \text{Br}^- \) is a weaker hydrophilic ion than \( \text{F}^- \) and \( \text{Cl}^- \) ions. Therefore, \( \ln \gamma_+ \) for \( \text{n-Bu}_4\text{NBr} \) has the largest negative deviations from the D.H.L.L. in this series of salts (Fig. 5.6).

Attraction between hydrophobic \( \text{n-Bu}_4\text{N}^+ \) co-spheres results in some of the bulk water being incorporated into the overlap region between the co-spheres [Fig. 5.1(d)] and, therefore, less bulk water is available for the neutral hydrolysis of PDCA. Also the total Gibbs function of the
system is less than in the corresponding pure aqueous solvent. These
two effects lead to retardation of the rate of the water-catalysed
reaction.

The hydrophobic nature of R in R₄N⁺ ions decreases in the order
n-Bu₄N⁺ > Pr₄N⁺ > Et₄N⁺ > Me₄N⁺ and, therefore, the hydrophobic cation
co-sphere interactions will dominate the hydration characteristics of
the salts to a progressively lesser degree across this series. The
overall effect is a progressive decrease in negative deviations of lnγ±
from D.H.L.L. (Fig. 5.6) and a decrease in the retardation of the rate
of reaction along the series (Fig. 5.5).

The MBr salts have a very small and similar retardation effect on
the rate of reaction. This suggests that the total Gibbs function of
these latter salt solutions is only slightly less than the pure aqueous
solvent. A balance is struck between hydrophilic-hydrophilic (same
sign) co-sphere interactions and hydrophilic-hydrophilic (opposite sign)
co-sphere interactions. Attraction between co-spheres of oppositely
charged ions, leading to a lowering of the total Gibbs function of the
system, slightly dominates the ion co-sphere interactions of MBr aqueous
salt solutions.

Trends in lnγ± and log₁₀(k₁/k₀) for MCl and R₄NCl salt solutions are
similar but less significant than for the corresponding bromide salts,
which is consistent with the solute co-sphere-co-sphere interaction
model.

In complete contrast the total Gibbs function of MF and R₄NF
solutions is greater than in the pure aqueous solvent. This is reflected
by positive deviations of lnγ± from the D.H.L.L. (Fig. 5.6) and an
acceleration in the rate of hydrolysis of PDCA (Fig. 5.5). Hydration
characteristics of the fluoride salt solutions are dominated by repulsion
between solute co-spheres, i.e. hydrophobic-hydrophilic co-sphere interactions for $R_n N F$ salt solutions ($R_n N^+ F^-$ interactions); and hydrophilic-hydrophilic (same sign) co-sphere interactions for MF salt solutions ($M^+ M^+$ and $F^- F^-$ interactions).

The patterns identified in this investigation are a striking indication of the importance of co-sphere effects.

In this Chapter the water-catalysed neutral hydrolysis of PDCA has been used as a probe to investigate changes in water structure due to addition of various electrolytes. In subsequent chapters attention is turned to more complicated microemulsion systems in which the kinetics of a number of inorganic and organic reactions are used as a probe to investigate the structure of these latter systems.
REFERENCES TO CHAPTER 5


CHAPTER 6

Structure and Properties of Microemulsions
6.1 INTRODUCTION

Numerous types of systems are formed when one phase is dispersed in another. In liquid systems the dispersed phase can at one extreme comprise molecules and at the other extreme comprise aggregates of many molecules. For aqueous systems an important class concerns systems formed by surfactants. The latter term describe molecules containing a hydrocarbon (hydrophobic) chain and a polar head group. The structure and size distribution of aggregates formed by surfactants are quite different in water and non-polar solvents.

Properties of aqueous solutions undergo an abrupt change over a narrow range of concentrations when the surfactant concentration increases. The concentration at the sharp transition is called the critical micelle concentration (c.m.c). Micelles are aggregates of surfactants formed via a strongly cooperative process.

In contrast the physical properties of non-aqueous solutions change gradually as the surfactant concentration is increased.

In this Chapter properties of systems containing water, a surfactant and another non-aqueous component are examined. Properties of systems change dramatically when oil is added to a solution of a surfactant in water. Under such conditions oil and water solubilize one another. When oil is solubilized in water the solubilized molecules are incorporated between the hydrocarbon chains in the micelle. Solubilization occurs above the c.m.c. Water dissolved in oil probably facilitates aggregation of surfactant molecules as swollen inverse micelles in which the polar head groups are embedded in aqueous domains.

Molecular motion within a micelle (translational, reorientation, chain flexibility) is almost as rapid as in a liquid hydrocarbon. In the water-continuous phase, water molecules and counter ions are highly
mobile. A rather distinct spatial separation between hydrophilic and hydrophobic domains is a feature of many surfactant-water systems. Under these conditions passage of a species between different regions is an improbable event. The reverse situation applies for a system which is oil-continuous but water-discontinuous. A bicontinuous phase (i.e. both oil and water continuous) gives rapid diffusion of all components. Concentration dependence of the various self-diffusion coefficients, shows characteristic features. For a water-continuous system diffusion coefficients of hydrophilic and hydrophobic species both decrease with increasing oil concentration. The mobility of hydrophilic species decreases due to an obstruction effect arising from an increasing volume fraction of aggregates while that of hydrophobic species decreases due to increasing inter-aggregate interactions. For an oil-continuous system diffusion coefficients of hydrophilic and hydrophobic species both decrease with increasing water concentration. For a bicontinuous system or a system which lacks distinct internal interfaces, the mobility of hydrophiles decreases with increasing oil content while that of hydrophobes increases.

Rather different systems are formed by surfactants in water in the presence of a medium chain length alcohol - a cosurfactant. A large oil-water interface is generated as a result of formation of many globules of one phase in the other. This kind of dispersion is similar to an emulsion but because the globules are smaller the systems are called microemulsions. Figure 5.1^2 is a schematic representation of micelles, solubilized micelles and microemulsions.

Large quantities of oil can be dissolved in microemulsions. For this reason microemulsions are extensively used commercially as, for example, water soluble waxes, cutting oils, wetting agents, herbicides and
FIGURE 6.1
Schematic representation of pure micelles, micelles containing solubilizates and microemulsions.
pesticides, synthetic blood and tertiary oil recovery. Since the
discovery of microemulsions by Schulman and coworkers in 1943 much
attention has been paid to these systems because of their commercial
importance.

For both water-in-oil (w.o.) and oil-in-water (o.w.) systems
Danielsson and Lindman have defined a microemulsion as "a system of
water, oil and surfactant which is a single optically isotropic
thermodynamically stable liquid solution".

6.2 STRUCTURES OF MICROEMULSIONS

Considerable controversy surrounds microemulsions and many measure-
ments have been reported with the intention of gaining a greater insight
into their structure. Lindman and Wennerström observed that many
molecular properties remain practically unchanged at the transition from
one type of aggregate to another. Much information concerning micro-
emulsions has emerged from studies of diffusion in these systems.

Studies on a "typical" ionic surfactant microemulsion, sodium octyl-
benzenesulfonate-decane-pentanol-sodium chloride-water, revealed that
over wide composition ranges, diffusion of water, hydrocarbon and counter
ion was rapid. Therefore this microemulsion is both oil and water-
continuous (bicontinuous) and the internal interfaces are easily deform-
able or not well-defined. The conclusion was reached that in the typical
microemulsion region there is:–

(i) polydispersity in 'aggregate' size,
(ii) polydispersity in 'aggregate' shape,
(iii) relatively low order at the polar-apolar 'interface',
(iv) rapid changes in aggregate size and shape,
(v) at either the water-rich region or oil-rich region there occurs
Studies on microemulsions of three, non-ionic surfactant-hydrocarbon-water, systems revealed that self-diffusion coefficients of both hydrocarbon and surfactant are quite low at high water concentrations and have about the same value. The following conclusions were drawn:

(a) the solutions contain micelles, (b) the hydrocarbon is solubilized in the micelles and (c) the concentration of monomeric surfactant is very low. The mobility of water was shown to be very high in the water-rich regions and to decrease with decreasing water content. Retardation of water mobility was explained as an obstruction effect from the micelles and hydration water bound to the polar head groups of the surfactant. The mobility of water in the oil-rich phase was expected to be extremely low, which would be compatible with the presence of reversed micelles (i.e. closed water droplets in an oil continuum). However, this conclusion was not confirmed experimentally. It was therefore concluded that over wide concentration ranges there is no marked separation into distinct hydrophilic and hydrophobic domains separated by a well-organised interface. The solutions probably comprise very labile and flexible aggregates. Typical micelles with solubilized oil are formed at the highest water contents and reversed micelles with closed water cores are indicated in the oil-rich region.

Zana and Lang examined six different microemulsion systems. Their properties were accounted for in terms of bicontinuous structures in the intermediate zone between water-rich and oil-rich phases. The bicontinuous zones are formed by interconnected oil/water droplets forming large transient clusters. Transition between oil-in-water and water-in-oil microemulsions is progressive and dependent on the nature of the microemulsion. Continual exchange of alcohol and surfactant
occurs between the interfacial film and the continuous phase. Important changes in these exchange processes occur upon phase inversion.

Multicomponent self-diffusion coefficient measurements \(^7\) in seven different microemulsions prompted the following conclusions;

(a) 'Classical' microemulsions (i.e. Anionic surfactant(s) - short-chain alcohol-hydrocarbon-water microemulsions) contain an abundance of small aggregates. Any internal interfaces have either a quite limited spatial extension or are very dynamic and flexible and break-up and reform at a high rate. There is no distinct separation into hydrophobic and hydrophilic domains and no evidence for extended aggregates. Presence of closed oil or water droplets with well-organised surfaces or extended bicontinuous structures was considered unlikely. The hydrophobicity of the alcohol in this type of microemulsion had a small but significant effect on the diffusion coefficients because of its preference for being solubilized in surfactant aggregates rather than in the aqueous regions. Nevertheless the structure of the microemulsions was consistent with the above model.

(b) Non-ionic surfactant (of the polyethylene oxide type) - hydrocarbon-water microemulsions showed similar trends in self-diffusion coefficients to those observed for 'classical' microemulsions and it was concluded that their structures were similar.

(c) Quaternary long-chain alcohol microemulsions and three component ionic surfactant (Aerosol OT) microemulsions showed different trends in self-diffusion coefficients and it was considered likely that rather distinct water droplets in a hydrophobic medium may occur in these latter systems.

Talmon and Prager \(^8\) treated the structure of microemulsions as a random geometry of interspersed oil and water domains generated by a
Voronoi tesselation, Figure 6.2, with the surfactant adsorbed at the boundary. In a later paper the Voronoi model was extended to provide a description of the interfacial region.

Kaler and coworkers presented evidence for bicontinuous structures in microemulsions over a broad range of compositions, describing the regions using a Voronoi model of a random interspersion of oil and water.

Biais and coworkers measured the vapour pressure of oil and alcohol

![Voronoi Polyhedron](image)

**FIGURE 6.2**

(a) Voronoi polyhedron.  
(b) Oil (shaded) and water (unshaded) domains generated by the Voronoi process.  
[Heavy lines denote the surfactant monolayer.]

[Reprinted from Ref. 8]
for several microemulsions containing water–toluene–sodium dodecyl-
sulphate–n-butanol. It was concluded that a microemulsion consists of
three domains – water domain, membrane domain and oil domain – which
behave as separate phases, pseudophases, in equilibrium. [The model
fails when there is more than 80% water in the microemulsion.] The
structure of the microemulsion and partitioning of components between
the pseudophases is such that the vapour pressure of toluene and butanol
are high even when the total concentrations of these components are low.
It was assumed that the water phase contained only water and alcohol,
the oil phase contained only oil, water and alcohol and the membrane
phase contained the surfactant and some alcohol.

Studies\textsuperscript{12} involving microemulsions of sodium octylbenzene sulphonate–
pentanol–decane–water (with 0.3% sodium chloride), identified zones
with reversed micelles or water droplets in an oil-rich continuum and
direct micelles in the water-rich region.

A major factor determining the size of microemulsion droplets is the
tendency of the surfactant layer adsorbed at the drop surface to 'bend'.
A detailed investigation\textsuperscript{13} was made into the behaviour of microemulsions
that have a distinctive dispersed phase (in particular, spherical drops)
and in which 'bending' of the surfactant layer, long-range Van der Waals'
attraction between droplets, electrostatic repulsions caused by formation
of electrical double layers on the surface of droplets, and/or the
increase in entropy accompanying dispersion of drops play important
rôles. These microemulsions were considered to be intermediate between
those which contained oil (water) droplets in a water (oil)-rich
continuum and the middle-phase (bicontinuous) microemulsions. This
study used a theory proposed by Winsor\textsuperscript{14} that bending of a surfactant
is closely related to the ratio of surfactant/oil interaction energy $E_{SO}$.
to the surfactant/water interaction energy, $E_{gw}$. According to this approach when $(E_{so}/E_{gw}) \ll 1$, bending of the surfactant layer favours formation of small oil drops in water. Thus this type of microemulsion has water as its continuous phase and will co-exist with an excess oil phase. When $(E_{so}/E_{gw}) \gg 1$, water drops form in oil and the microemulsion co-exists with an excess water phase. As the ratio approaches unity, bending of the surfactant layer decreases and the relative importance of other factors, mentioned above, increases. The spherical geometry of the drops may not be maintained and identification of the continuous and dispersed phase becomes more difficult.

Two likely causes for bending of the surfactant layer were identified. On the water (or brine) side, electrostatic repulsion by the ionic heads of surfactant molecules stretches the hydrophilic portion of the interfacial layer. On the oil side, stretching of the hydrophobic portion of the interfacial layer occurs because the hydrophobic chains "push" each other to attain lower configurational entropy.

The enthalpy of mixing between the oil and surfactant also affects the bending tendency because curving of the interface causes a change in the surfactant-oil ratio near the interface. An imbalance in the extent of "stretching" on the water and oil sides appears to cause the bending tendency.

For volume fractions of the dispersed phase $(V_{\text{dispersed}}/V_{\text{continuous}})$ of up to approximately 0.3, interactions between dispersed microemulsion drops are negligible. For volume ratios $>0.3$ interactions between drops become increasingly important. Interactions between microemulsion drops are mainly 'hard-sphere' repulsion even though Van der Waals' attraction may make a substantial contribution. Electrostatic repulsion from the electrical double layer around drops and steric repulsion by surfactant
hydrophobic chains make only minor contributions.

In the case of surfactant/oil and surfactant/water balanced interaction microemulsions that co-exist with excess oil and brine, it is thought that the mean curvature of the surfactant layer adsorbed between water-rich and oil-rich phases is zero.

On the basis of the evidence cited in this Chapter, the following conclusions can be drawn about the structure of microemulsions. There is, of course, a wealth of information concerning microemulsion structures that has not been included but, nevertheless, a general overview can be offered.

When the volume fraction, $\phi$, of the dispersed phase is not too large, the single-phase microemulsion contains spherical droplets almost uniform in size. When $\phi$ is sufficiently large, microemulsions have very flexible internal interfaces that open and reform on a short timescale. Microemulsions have unusual phase behaviour which is illustrated by what happens when the concentration of salt is increased, at fixed concentrations of oil, water, surfactant and co-surfactant.

At relatively low concentrations of salt, an oil in water microemulsion co-exists with excess oil. At sufficiently high salt content a water in oil microemulsion is in thermodynamic equilibrium with excess water. At intermediate salinities a (middle-phase) microemulsion co-exists with both oil and water excess phases. In these latter systems thermal fluctuations may produce changes from one type of microemulsion to the other in the vicinity of the inversion point, and a constantly changing mosaic of regions exists of both kinds of microemulsions. Middle-phase microemulsions are birefringent (i.e. they scatter light because the particle sizes are of the order of the wavelength of visible light).

A large fraction of the surfactant and co-surfactant is adsorbed on
the large interface formed between the two media of the microemulsion and the rest is distributed between the phases. Concentrations of surfactant and co-surfactant in the bulk of the globules appear to be the same as those in the excess dispersed phase.

6.3 QUALITATIVE THERMODYNAMIC CONSIDERATIONS OF MICROEMULSIONS

The thermodynamic stability of microemulsions can be understood by defining a reference state in which water and oil are not dispersed and surfactant and co-surfactant are distributed at equilibrium between the two liquids. One phase is then dispersed in the other in the form of globules. This leads to an increase in entropy of the system and adsorption of surfactant and co-surfactant on the large interfacial area thus created. Adsorption decreases the interfacial tension between water and oil phases, and decreases the concentrations of surfactant and co-surfactant. The latter effect produces a decrease in the chemical potentials of surfactant and co-surfactant relative to the corresponding values in the reference state. 'Dilution' of the bulk phases leads to a decrease in the total Gibbs function of the system (dilution effect). When the decrease in the total Gibbs function of the system, associated both with the entropy of dispersion and with the dilution effect, overcomes the positive product of the low interfacial tension and the large interfacial area, dispersions that are thermodynamically stable are generated.

Since concentrations of surfactant and co-surfactant in the bulk of the globules appear to be the same as those in the excess dispersed phase, phase separation cannot be caused by the concentration dependence of the chemical potentials of various components. Therefore, mechanical equilibrium remains the only possible explanation for the unusual phase
behaviour of microemulsions.

A globule has its own internal pressure, \( p_2 \), and \( p_1 \) is the pressure near the globule in the continuous phase. \( p_1 \) and \( p_2 \) are called micropressures to emphasize the fact that they are defined on the scale of globules and to contrast them to the macro- (thermodynamic) pressure of the entire microemulsion. The thermodynamic pressure equals the pressure, \( p \), of the environment. Each of the micropressures when augmented by contributions from the collective behaviour, must equal the thermodynamic pressure. For one globule at the interface between microemulsion and environment, the condition for the globule to stay in the microemulsion is that the micropressure (inside the globule), \( p_2 < p \). The mechanical equilibrium condition is still satisfied because of the additional contribution to the thermodynamic pressure provided by the collective behaviour. When \( p_2 = p \) or the contribution of the collective behaviour to the thermodynamic pressure is zero, an excess dispersed phase in equilibrium with the microemulsion appears.

When the micropressure (near the globules in the continuous phase), \( p_1 = p \) an excess continuous phase appears. When \( p_2 = p_1 = p \) a three-phase system composed of both excess phases and a microemulsion form. However when \( p_2 = p_1 \) no spherical globules exist and a change in structure is expected to occur. At \( p_2 = p_1 \) the spherical interface between the two media of the microemulsion becomes unstable to thermal perturbations and thus fluctuates. This results in a chaotic structure. This latter behaviour is similar to that occurring near a critical point.

The interfacial tension, \( \gamma \), between a microemulsion and the excess dispersed phase is given by:

\[
\gamma \propto \frac{k_BT}{r^2}
\]
where $T$ is the temperature, $k_B$ the Boltzmann constant and $r$ the radius of the globules. The proportionality constant has a value between three and four and is weakly dependent on the radius of the droplets.

The interfacial tension at the surface of a globule has been shown\(^2\) to be almost inversely proportional to $r^2$ with a proportionality constant of about $4k_BT$. The latter is weakly dependent on $r$, and the volume fraction, $\phi$, of the dispersed phase. Therefore the interfacial tension decreases as $r$ increases. The radius of the globules varies between $10^{-3}$ and $10^{-7}$ m and for these values of $r$, the interfacial tension varies between $10^{-4}$ and $10^{-6}$ N m$^{-2}$. At relatively low concentrations of salt, $r$ increases with increasing salt concentration while at high concentrations of salt $r$ decreases with increasing salt concentration.

Fluctuations within a microemulsion have an effect on the interfacial tensions.\(^2\) At the interface between a microemulsion and an excess dispersed phase fluctuations may result in two similar media being brought into contact and this will result in lowering the interfacial tension. Similarly at the interface with the excess continuous phase, fluctuations cause some contact between two dissimilar media and the interfacial tension is greater than that in the absence of fluctuations. These fluctuations cause the interfacial tensions for the two pairs of phases in contact to be equal at the inversion point. This happens because the volume fraction, $\phi$, of the dispersed phase is approximately half at the inversion point. Therefore the probability of having oil or water at any point of either interface is also half.

6.4 EFFECT OF SALINITY ON MICROEMULSION STRUCTURE

For fixed amounts of oil, water, surfactant and co-surfactant, the
interfacial tension between the microemulsion and the excess dispersed phase decreases with increasing salinity at relatively low concentrations of salt (oil in water microemulsion $\Rightarrow$ excess oil), passes through a minimum value (excess water $\Rightarrow$ middle phase microemulsion $\Rightarrow$ excess oil), and then increases with increase in salt concentration (water in oil microemulsion $\Rightarrow$ excess water). Ruckenstein\textsuperscript{2} presented a possible explanation for the occurrence of the minimum in the interfacial tension.

At low salt content, surfactant molecules accumulate at the interface, where the hydrocarbon chains are immersed in the oil and the polar head groups interact favourably with water. At higher salt content organisation of water molecules induced by ions (for structure-making ions) is more extensive and favourable interactions between the polar head groups and water are diminished. Consequently surfactant molecules are salted out as micelles in the water phase and as individual molecules in the oil phase. Salting out to oil will dominate when the favourable interactions of the head groups with water are outweighed by the larger entropy available in the oil phase.

At very high salt concentrations, water is so strongly organised that the surfactant is completely salted out to the oil phase resulting in negative adsorption. As soon as negative adsorption occurs, the interfacial tension, $\gamma$, increases with increasing salinity. Thus a minimum in $\gamma$ is observed.

An alternative explanation may be provided by negative adsorption of the salt. Distribution of ions near the interface will be such that their distance from the oil phase is greater than the range of ion-dipole interactions in water. The corresponding increase in interfacial tension, though small, may well be comparable to the magnitude of the interfacial tension itself.
6.5 EFFECT OF TEMPERATURE ON MICROEMULSION STRUCTURE

The temperature dependence of the size and polydispersity of the water core in a pure water in oil, three-component microemulsion was investigated. A linear increase in the radius of the water droplets with increasing temperature was observed. The extrapolated radius at zero water concentration was non-zero, indicating substantial water penetration into the charged head group region of the inverted micelle.

Polydispersity in size of the water droplets was found to be appreciable even at room temperature and increased steadily as the temperature increased.

Microemulsions separate into phases at the cloud point (critical) temperature upon heating. In a later communication investigations were reported on the same water-in-oil microemulsion near the critical temperature. It was concluded that clusters were formed with fixed size and polydispersity. The average droplet size and distribution in droplet size was found to exhibit little temperature dependence.

6.6 MICROEMULSIONS IN WHICH KINETICS OF ORGANIC AND INORGANIC REACTIONS WERE STUDIED

Three main microemulsions were selected to study their effects on the kinetics of various organic and inorganic reactions (Chapters 7, 9, 10 and Appendix 1). In this section, phase diagrams and relevant background material of the three microemulsions are presented. The three microemulsions were:

MEA - 60 mol % 2-butoxyethanol (2BE), 20 mol % decane, 20 mol % water (18),
MEB - 45 mol % 2-propanol (2PrOH), 40 mol % hexane, 15 mol % water (19),
MEC - sodium dodecylsulphate (SDS), 30 mass % n-butanol, 5 mass % toluene, 65 mass % water, where SDS:n-butanol is 1:2 (20,21).
6.6.1 2BE-decane-water microemulsion

The phase diagram at 298 K is shown in Figure 6.3. Investigations into this microemulsion by Desnoyers and coworkers arose primarily from their systematic studies of the thermodynamic properties of aqueous organic mixtures and of electrolytes in mixed solvents. Of particular interest was the discovery that the partial molar heat capacities \( (C_{p_2}) \) of certain hydrophobic alcohols, alkoxyethanols and amines undergo drastic changes in the water-rich region, especially at lower temperatures. It was concluded that in these binary systems there is some kind of microphase separation which could be analogous to micellization and structures are locally not too different from those of microemulsions (Chapter 8 - water-rich '2BE + water' mixtures). Addition of surface active molecules stabilized the pseudo-phases, making transitions sharper and occurring at lower concentrations.

In the context of developing a new approach to the problem of tertiary oil recovery an interesting feature of '2BE + water' mixtures is its tendency to un-mix at higher temperatures. '2BE + water' mixture has a lower critical solution temperature at 322 K. This binary system could therefore be used to dissolve the oil at low temperatures and then recover the oil simply by raising the temperature. The idea was based on the assumption that at high temperatures, the ternary system would also separate into two phases, one of which would be very rich in oil. It was expected that such a technique would be especially useful for the lighter oils. Decane was chosen as a typical oil.

Phase diagrams of the 2BE-decane-water system were determined by the cloud point technique. At a constant temperature, '2BE + water' mixtures were titrated with decane until a slight cloudiness appeared, corresponding to formation of two or more phases. For temperature
FIGURE 6.3
Phase diagram of decane + 2-butoxyethanol + water at 298 K. All mole fractions are expressed relative to the other two components. [Y = M.E. comp. used for kinetics.]
[Reprinted from Ref. 18]

FIGURE 6.4
Phase diagram of hexane + propan-2-ol + water at 298 K. All mole fractions are expressed relative to the other two components. [Y = M.E. comp. used for kinetics.]
[Reprinted from Ref. 19]
studies, the temperature of a known mixture of '2BE + decane + water' was varied until a cloud point was observed.

In the water-rich region the solubility of decane is low. Three phases often appeared when excess decane was added. The upper phase contains mostly decane and the lower one mostly water. The co-existence of three phases is typical of many microemulsions. In the decane-rich region the phase diagram was too complex to fix unambiguously. Figure 6.3 shows only cloud points corresponding to the initial un-mixing.

The cloud point technique is useful for estimating the initial concentration or temperature when un-mixing begins but is not suitable to distinguish between the co-existence of two phases and three phases. If the addition of the third component is continued beyond the cloud point three distinct phases appear. The three-phase region depends quite critically on temperature.

It was found that the microemulsion un-mixes at low and high temperatures.

Addition of SDS increases the miscibility range of the oil in water. It was concluded that the surfactant probably stabilises the microstructures which are already present in the ternary system and decreases the quantity of 2BE needed to solubilize decane. A surfactant was considered useful but not essential to the stability of microemulsions.

The apparent molar heat capacity of decane was measured in '2BE + water' mixtures and these measurements indicated that decane essentially comes into contact with the non-aqueous component only.

6.6.2 2-Propanol-hexane-water

The ternary pseudo-phase diagram for the microemulsion at 298 K (Fig. 6.4) was constructed using the physical properties of various compositions of the constituents. Regions were identified as follows.
Ternary compositions from region A are turbid macroemulsions when freshly prepared or agitated; upon standing they eventually separate into two phases. Solutions from region B are stable, transparent microemulsions, consisting of water-rich droplets dispersed in a hexane-rich continuous phase. Solutions assigned to regions C and D are transparent single-phase solutions. Region C contains hydrogen-bonded aggregates of water and alcohol. Region D encompasses "true" ternary solutions which have no microheterogeneity. Thus while the C/D boundary is not a phase boundary, it does make a distinction between regions of different characteristics.

When sodium chloride was added to the ternary mixtures the microemulsion (region B) was stabilised (cf. Chapter 7, where addition of SDS or CTAB stabilises the microemulsion). The following model was proposed to explain this stabilisation.

Formation of microemulsions in the absence of surfactant requires that the transient interfacial tension ($\gamma_1$) reaches zero at some point consistent with the equation;

$$\gamma_1 = \gamma_{(w/o)a} - \pi$$

where $\gamma_{(w/o)a}$ is the interfacial tension between the oil and water in the presence of an alcohol and $\pi$ is the two-dimensional lateral pressure within the film which encompasses the droplet of the dispersed phase. 2-Propanol does not support large values of $\pi$, so the interfacial pressure, $\gamma_{(o/w)a}$, must be sufficiently lowered to allow $\gamma_1$ to approach zero. This is accomplished by partitioning of the alcohol between the oil, water and interface. As the alcohol content is increased, two phenomena occur simultaneously. Small amounts of water are gradually transferred from the dispersed droplets into the continuous phase. Generally, this is accomplished by hydrogen-bonding between water and
2-propanol. As a result of redistribution of water, $Y_{o/w}^a$ changes and the droplet size decreases until a new equilibrium state is reached.

Addition of salt to the system disrupts hydrogen-bonding in the small aggregate region. Therefore it also disrupts hydrogen-bonding in the microemulsion region. Disruption of hydrogen-bonding results in a retardation of the transfer of dispersed water from the droplet into the continuous phase, which serves to stabilise the microemulsion.

If a ternary microemulsion in the absence of a surfactant (detergent-less microemulsions) is to be used as a solvent for a reaction involving inorganic salts, the nature of the total system in the presence of reactants needs to be carefully examined because the region boundaries of the phase diagram of the system shift on addition of salt. In other words, while the system may be a microemulsion before addition of reactants, afterward it may not be.

6.6.3 SDS-n-butanol-toluene-water

Investigations into the structures of the single-phase microemulsion existing in the quaternary system were made by A. Viallard and coworkers. The phase diagram at 298 K is shown in Figure 6.5.

Using toluene as a molecular probe, variations of its apparent molar volume as a function of concentration were studied. It was assumed that any change in environment of toluene molecules would be reflected by a difference between the apparent molar volume and the molar volume of pure toluene.

In the very water-rich region toluene is solubilized in an aliphatic medium, which corresponds to a maximum in structure of the mixed micelle and maximum stabilisation. When the concentration of the 'surfactant + co-surfactant' mixture is increased, the micelles in which toluene is
FIGURE 6.5
Phase diagram of SDS + n-butanol + toluene + water. Straight lines T represent the dilution lines by toluene. U is the solubility curve and L is the demixtion line. Concentrations are in mass percentages. The non-hatched zone shows the single phase microemulsion region.
[Y = M.E. used for kinetics.]
[Reprinted from Ref. 21]

solubilized are more and more structured until a maximum of organisation is reached around 20 mass % of 'surfactant + co-surfactant'.

In the water-rich region there are still oil in water direct micelles. Their number and volume increases as the percentage of 'SDS + n-butanol' increases. It would appear that as the micelles become larger they become less structured. It was postulated that between zero and 30 mass % 'SDS + n-butanol' the concentration of 'n-butanol + SDS' in the aqueous part is small, approximately 1 mass % and 0.1 mass % respectively.
Practically all the 'n-butanol + SDS' is in the interfacial region in the form of micelles between the oil and water phases.

In the oil-rich region the microemulsion mainly consists of reversed water in oil micelles. In this region toluene is practically in a pure toluene environment. Thus toluene was not a suitable probe for this latter solution and using water as the probe would be more appropriate.

In the intermediate zones between oil-rich and water-rich regions the apparent molar volume of toluene changed gradually from its value in one type of structure to that in the other type. The exact limits of these zones could not be accurately established because there was no sharp transition in the apparent volumetric property of toluene. The indication was that in the intermediate zones there is a progressive change between the two types of structure and the microstructure in this region is not well established.

Heat capacity measurements using toluene again as the probe, revealed analogous results. The idea of a bicontinuous structure in the intermediate zone was favoured.
REFERENCES TO CHAPTER 6


CHAPTER 7

Aquation reactions of three low-spin iron(II) di-imine complexes and reactions with hydroxide and cyanide ions in neutral water-in-oil microemulsions
7.1 INTRODUCTION

In Chapters 3, 4 and 5 effects on kinetics of reaction of changing the solvent composition in binary aqueous mixtures and aqueous salt solutions were investigated. In this Chapter kinetics of reaction of iron(II)-1,10-phenanthroline \([\text{Fe(phen)}]^2+\), iron(II) 5-nitro-1,10-phenanthroline \([\text{Fe(5-NO_2phen)}]^2+\) and iron(II) hexadentate Schiff base \([\text{Fe(hxsbH)}]^2+\) with acid, hydroxide and cyanide ions are reported in two neutral water-in-oil microemulsions. Formulae (I) and (II) show the 5-nitro-1,10-phenanthroline ligand and the hexadentate Schiff base ligand respectively.

\[
\text{(I)} \quad \text{5-NO}_2\text{phen}-\text{ligand}
\]

\[
\text{(II)} \quad \text{(hxsbH)}-\text{ligand}
\]

\(\text{Fe(hxsbH)}^2+\) contains only one ligand which is hexa-coordinated around the iron through six iron-nitrogen bonds. Molecular models (Fig. 7.1) and the X-ray structure\(^1\) of the thiocyanate salt show that the iron is close to the surface of the complex cation. Such a structure allows water molecules and small nucleophiles such as hydroxide and cyanide ions to approach quite closely to the iron atom.

General kinetic features of the aquation reactions of low spin iron(II) complexes and reactions with hydroxide and cyanide ions in aqueous solutions are presented in Chapter 1, Section 1.6.1. Ligand substituted transient intermediates in the latter reactions have been proposed\(^2\) (Chapter 1, Sections 1.6.1 and 1.7). The exact form of these intermediates is still uncertain.
FIGURE 7.1
Molecular model of Fe(hxsbH)²⁺ ion.
Nucleophilic attack can take place either at the central metal atom or at some position on the coordinated ligand. A possible structure of the transient intermediate resulting from the latter mechanism is:

\[
\begin{align*}
\text{(phen)}_2\text{Fe}^+ \\
\text{Nu} \\
\text{H}
\end{align*}
\]

where Nu is the nucleophile. Electron-withdrawing substituents such as the nitro and sulphonato groups favour the formation of such intermediates in this class of reactions. In reactions of \(\text{Fe}(5\text{-NO}_2\text{phen})_3^{2+}\) with hydroxide ions and ferrozine \([\text{Fe}(\text{ppsa})_3]^{-}\); \(\text{ppsa} = 3\text{-}(2\text{-pyridyl})\text{-5,6-bis}(4\text{-sulphophenyl}-1,2,4\text{-triazine})\) with hydroxide ions in aqueous solvent rapid appearance of a new spectrum was detected corresponding to formation of an intermediate. A solid product which was thought to be of type (III) was obtained from the reaction of \(\text{Fe}(5\text{-NO}_2\text{phen})_3^{2+}\) with cyanide ions. Evidence for formation of a long-lived intermediate in the reactions of \(\text{Fe}(\text{hxsBH})^{2+}\) with hydroxide ions in two neutral water-in-oil microemulsions is reported in this Chapter.

Effects on rates of reaction of \(\text{Fe(phen)}_3^{2+}\) with hydroxide ions, of adding ionic surfactants, SDS and CTAB to the neutral w/o microemulsion are investigated. Kinetic data are also reported for aquation reactions of \(\text{Fe}(\text{hxsBH})^{2+}\) in aqueous acidic solution.

7.2 EXPERIMENTAL

(i) \(\text{Fe(phen)}_3^{2+}\) and \(\text{Fe}(5\text{-NO}_2\text{phen})_3^{2+}\)

\(\text{Fe(phen)}_3^{2+}\) and \(\text{Fe}(5\text{-NO}_2\text{phen})_3^{2+}\) solutions were prepared as the
sulphate salt solutions by adding the appropriate ligand (in slight excess, to avoid mono- or bis-complex formation), to iron(II) ammonium sulphate solution of the required concentration.

Kinetics of reaction of the two complexes were monitored in two neutral w/o microemulsions:-

Microemulsion A (MEA): 60 mol % 2-butoxyethanol (2BE); 20 mol % decane and 20 mol % water (Chapter 6, Section 6.6.1).

Microemulsion B (MEB): 45 mol % 2-propanol; 40 mol % hexane; 15 mol % water (Chapter 6, Section 6.6.2).

Reactions in MEA and MEB were monitored at 298 K. In all systems concentration of complex $< 10^{-4}$ mol dm$^{-3}$ and [nucleophile]$>>$[complex]. Fresh microemulsion solutions were prepared for each kinetic study because stock solutions containing hydroxide ions rapidly decomposed to form carbonates. Constant ionic strength was not maintained because the phase diagrams of microemulsions are very sensitive to concentrations of added salt (Chapter 6). In all systems reaction was initiated by adding one or two drops of a concentrated solution of complex in water to the reagents in a 1 cm$^3$ quartz cell.

Aqueous solutions of both complexes are bright red with $\lambda_{\text{max}} = 510$ nm. No shift in $\lambda_{\text{max}}$ was observed when the complexes were dissolved in the microemulsions.

Rates of aquation reactions of Fe(phen)$_3^{2+}$ and Fe(SNO$_2$phen)$_3^{2+}$ in MEA and MEB were monitored. The microemulsions were made acidic for these reactions by addition of known concentrations of sulphuric acid. Reactions were monitored at three different acid concentrations between the limits $1.49 \times 10^{-2} \leq [\text{sulphuric acid}] \leq 5.94 \times 10^{-2}$ mol dm$^{-3}$. At acid concentrations $< 1.49 \times 10^{-2}$ mol dm$^{-3}$ the aquation reactions did not go to completion because there was insufficient acid to protonate the
phenanthroline ligands and prevent recombination of the iron complex.

Reactions of Fe(phen)$_3^{2+}$ with hydroxide ions in MEA and MEB were monitored at several different concentrations of sodium hydroxide. In MEB the sodium hydroxide concentration was kept between the limits $3 \times 10^{-4} \leq [\text{sodium hydroxide}] \leq 3 \times 10^{-3}$ mol dm$^{-3}$. If $[\text{sodium hydroxide}] < 3 \times 10^{-4}$ mol dm$^{-3}$ there was little or no reaction; if $[\text{sodium hydroxide}] > 3 \times 10^{-3}$ mol dm$^{-3}$ the solutions were cloudy.

Repeat scans of the dependence of absorbance on wavelength (Unicam SP800 spectrophotometer, Chapter 2, Section 2.4.1), revealed that the dependence of absorbance on time was first order. Kinetics of reaction were monitored at 510 nm (Unicam SP1800 spectrophotometer, Chapter 2, Section 2.4.1). The computer was programmed to fit the absorbance data to a first order kinetic expression (Chapter 2, Section 2.3).

Kinetics of reaction of Fe(phen)$_3^{2+}$ with hydroxide ions were also measured in a microemulsion comprising 40 mol % 2BE, 50 mol % decane and 10 mol % water. These experiments probed a possible relationship between the amount of water in the microemulsion and the rate of reaction. Similarly, kinetics of aquation reactions of Fe(5-NO$_2$phen)$_3^{2+}$ were monitored in a range of microemulsions containing progressively less water.

Reactions of Fe(5-NO$_2$phen)$_3^{2+}$ with hydroxide ions in MEA where $[\text{sodium hydroxide}] = 2.97 \times 10^{-3}$ mol dm$^{-3}$ and reactions of both complexes with cyanide ions in MEA where $[\text{potassium cyanide}] = 2.97 \times 10^{-3}$ mol dm$^{-3}$ were too fast to be able to monitor kinetic data. However, the qualitative observations proved useful (Section 7.4). When cyanide ions were added to MEB the solution turned cloudy. Therefore, a kinetic study of the reactions involving the iron complexes was not possible. Nevertheless, qualitative observations gave useful insight into the system.
Addition of SDS or CTAB to MEB allowed the system to retain its microheterogeneity when \([\text{sodium hydroxide}] > 3 \times 10^{-3} \ \text{mol dm}^{-3}\). Kinetics of reaction of \(\text{Fe(phen)}_3^{2+}\) with hydroxide ions were monitored in these latter microemulsions where \(0.012 < [\text{surfactant}] < 0.046 \ \text{mol dm}^{-3}\) and at several different concentrations of sodium hydroxide between \(1.5 \times 10^{-3} < [\text{sodium hydroxide}] < 3.01 \times 10^{-2} \ \text{mol dm}^{-3}\).

\((ii) \ \text{Fe(hxsbH)}^{2+}\)

Concentrated aqueous solutions of \(\text{Fe(hxsbH)}^{2+}\) as the chloride salt were prepared. The solutions were deep blue-purple with \(\lambda_{\text{max}} = 612 \ \text{nm}\) and \(\varepsilon_{612} = 614 \ \text{m}^2 \ \text{mol}^{-1}\). No shift in \(\lambda_{\text{max}}\) was observed when the complex was dissolved in either MEA or MEB.

Reactions in MEA and MEB were monitored at 298 K. In all systems \([\text{complex}] < 10^{-4} \ \text{mol dm}^{-3}\) and \([\text{nucleophile}] \gg [\text{complex}].\)

Rates of aquation reactions of \(\text{Fe(hxsbH)}^{2+}\) in aqueous acidic solvent were monitored where \(0.2 < [\text{sulphuric acid}] < 2 \ \text{mol dm}^{-3}\) at eight different concentrations of sulphuric acid. In MEB rates of aquation of \(\text{Fe(hxsbH)}^{2+}\) were monitored where \(3 \times 10^{-3} < [\text{sulphuric acid}] < 6 \times 10^{-2} \ \text{mol dm}^{-3}\) and where \(3 \times 10^{-3} < [\text{hydrochloric acid}] < 3 \times 10^{-2} \ \text{mol dm}^{-3}\) at several different concentrations of each acid.

Kinetic data for reactions of \(\text{Fe(hxsbH)}^{2+}\) with cyanide ions in MEA were collected at several different concentrations of potassium cyanide between the limits \(2.97 \times 10^{-3} < [\text{potassium cyanide}] < 2.97 \times 10^{-2} \ \text{mol dm}^{-3}\).

For kinetic systems of \(\text{Fe(hxsbH)}^{2+}\) mentioned above repeat scans of the dependence of absorbance on wavelength (Unicam SP1800 spectrophotometer - Chapter 2, Section 2.4.1), revealed that the dependence of absorbance on time was first order. Kinetic data for reactions were monitored at 612 nm (Unicam SP1800 spectrophotometer - Chapter 2, Section 2.4.1). The absorb-
ance data were fitted to first order expressions.

In MEA aquation reactions of Fe(hxsbH)²⁺ were monitored using (a) hydrochloric acid, (b) sulphuric acid and (c) p-toluene sulphonic acid to make the solutions acidic. Kinetics of reaction were monitored at three different acid concentrations for each acid between the limits $2.97 \times 10^{-3} \leq [\text{acid}] \leq 2.97 \times 10^{-2}$ mol dm⁻³.

Repeat scans in all three systems revealed that at fixed time intervals there was a regular decrease in absorbance at $\lambda_{\text{max}}$ (Fig. 7.2), i.e. the dependence of absorbance on time was not first order. Various kinetic schemes were examined to account for the complexity and new programs developed for the HP9825A minicomputer. Logging procedures of absorbance as a function of time for these reactions were designed to record a pre-set number of data points at specified time intervals. In each experiment absorbance–time data were logged until the reaction was essentially complete in order to fully characterise the reaction.

When data logging was complete various options were offered by the computer for analysing the dependence of absorbance on time. Comparison between the observed absorbances, $P_{\text{obs}}$, and the calculated absorbances, $P_{\text{calc}}$, were aided by presenting the output on the HP7245A plotter.

Kinetic data for reactions of Fe(hxsbH)²⁺ with hydroxide ions in MEA and MEB were monitored but the kinetics were complicated and no satisfactory analysis was developed. Complexities arose because addition of Fe(hxsbH)²⁺ to the reaction media resulted in a relatively rapid change of colour from deep blue-purple to green, followed by slow disappearance of the green colour.

7.3 ANALYSIS

Presentation of the results and discussion of their significance are
FIGURE 7.2
Dependence of absorbance on wavenumber at time intervals of a 100s in ME.A, where [hydrochloric acid] = $2.97 \times 10^{-3}$ mol dm$^{-3}$.
facilitated if four kinetic schemes are considered at this stage.
Attention is concentrated on accounting for the dependence on time of
the absorbance characteristic of the metal complex at fixed wavelength.

(i) Scheme I

Consider a first order reaction involving a metal complex M;
(Chapter 2, Section 2.3).

\[ M \xrightarrow{k_1} \text{products} \quad \ldots \quad (I) \]

The dependence of absorbance, \( P \) on time, \( t \), is given by equation
7.1; (Chapter 2, Section 2.3).

\[ P = (P_0 - P_\infty) \exp(-k_1 t) + P_\infty \quad \ldots \quad (7.1) \]

The analysis uses the Non-Linear Least Squares method suggested by
Moore,\(^\text{16}\) to fit the first order dependence of absorbance, \( P \) on time,
\( t \) (Chapter 2, Section 2.3).

(ii) Scheme II

Let the reaction between metal complex, \( M \) and reactant, \( X \), proceed
in two stages via an intermediate, \( I \);

\[ M + X \xrightarrow{k_{2'}} I \xrightarrow{k_3} \text{products (Z)} \quad \ldots \quad (IIa) \]

In the limit that \([X] \gg [M] \), and \( k_2 = k_2'[X] \), scheme IIa can be
simplified;

\[ M \xrightarrow{k_2} I \xrightarrow{k_3} \text{products (Z)} \quad \ldots \quad (IIb) \]

Then;

\[ \frac{dM}{dt} = -k_2 M + k_3 I \quad \ldots \quad (7.2) \]
\[ \frac{dI}{dt} = k_2 M - (k_3 + k_4) I \quad \ldots \quad (7.3) \]
\[ \frac{dZ}{dt} = k_4 I \quad \ldots \quad (7.4) \]

IIb is a classic kinetic scheme which has attracted considerable atten-
tion.\(^\text{17}\) The concentration dependences of the reactant, \([M]\), and product,
\([Z]\) on time are not first order;\(^\text{17,18}\) this scheme is developed further in
Chapters 9 and 10.

However, if the steady state assumption is applied to intermediate I,\textsuperscript{17,18,19} i.e. $\frac{dI}{dt} = 0$, then;

$$k_2 \cdot M = (k_3 + k_4) \cdot I \quad \ldots \quad (7.5)$$

Combining equations 7.4 and 7.5 yields;

$$\frac{dZ}{dt} = \frac{k_4 \cdot k_2}{(k_3 + k_4)} \cdot M \quad \ldots \quad (7.6)$$

Then, $k_{\text{obs}} = \frac{k_4 \cdot k_2}{(k_3 + k_4)}$

or $k_{\text{obs}} = \frac{k_2}{(1 + \alpha)} \quad \ldots \quad (7.7)$

where $\alpha = \frac{k_3}{k_4}$.

The dependence of the absorbance of the metal complex, M, on time is therefore first order and indistinguishable in form from that required by Scheme (I).

(iii) Scheme III

Consider a chemical reaction in a system which comprises two phases,\textsuperscript{20,21} $\alpha$ and $\beta$, where the reactions in both phases follow first order kinetics;

$$\begin{align*}
\text{\textit{$\alpha$-phase}} & \quad M_{\alpha} \xrightarrow{k_5} \text{products, Z} \\
\text{\textit{$\beta$-phase}} & \quad M_{\beta} \xrightarrow{k_6} \text{products, Z}
\end{align*} \quad \ldots \quad (\text{III})$$

If $M_\alpha$ and $M_\beta$ are in equilibrium at all stages of the reaction, the equilibrium is characterised by a distribution coefficient, $K_d$. If there are $\alpha$-moles of M in the $\beta$-phase, and $(1-\alpha)$ moles of M in the $\alpha$-phase and assuming $M_\alpha$ and $M_\beta$ are ideal solutes, then;

$$K_d = \frac{M_\beta}{M_\alpha} = \frac{\alpha M}{(1-\alpha)M}$$

or $\alpha = \frac{K_d}{(1 + K_d)} \quad \ldots \quad (7.8)$
\[
dM/dt = -k_5 \, M_a - k_6 \, M_b
\]
or
\[
dM/dt = -k_5 (1-a) \, M - k_6 \, a \, M
\]
or
\[
dM/dt = -[k_5 (1-a) + k_6 \, a] \, M
\]

Equation 7.9 is called Holtermann's equation, and \( k_{\text{obs}} \) is given by:

\[
k_{\text{obs}} = k_5 (1-a) + k_6 \, a
\]

Combining equations 7.10 and 7.8;

\[
k_{\text{obs}} = k_5 \left[ 1 - \frac{K_d}{1 + K_d} \right] + \frac{k_6 \, K_d}{1 + K_d}
\]

\[
k_{\text{obs}} = k_5 + k_5 K_d - k_5 K_d + k_6 K_d
\]

or
\[
k_{\text{obs}} = (k_5 + k_6 K_d)/(1 + K_d)
\]

The rate of disappearance of \( M \) from the system follows first order kinetics and, therefore, the dependence of absorbance, \( P \), on time is identical to that required by Scheme I.

(iv) Scheme IV

This scheme is a development of Scheme III. Phase \( \beta \) is dispersed in the form of microscopic drops in phase \( \alpha \). An interface \( \alpha \beta \) is formed at which solute \( M \) can be adsorbed. For a system containing a proportionally small amount of \( \beta \), a given volume of the total system contains a concentration of sites [C], at which \( M \) can be adsorbed. The scheme for chemical reaction is represented by;

\[
M + C \xrightarrow{k_7} MC
\]

\[
MC + X \xrightarrow{k_9} C + \text{products, } Z
\]

IVb represents attack by \( X \) (from either \( \alpha \)- or \( \beta \)- phases) on \( M \) adsorbed at \( C \). Then;

\[
\frac{d[MC]}{dt} = k_7 [M] [C] - (k_8 + k_9 [X]) [MC]
\]
If desorption and production of vacant site, C, is rapid, the steady state hypothesis can be applied, i.e. $d[M\cdot C]/dt = 0$ and $[M\cdot C]$ is given by;

$$[M\cdot C] = \frac{k_7\cdot[M]\cdot[C]}{k_8 + k_9\cdot[X]}$$  \hspace{1cm} (7.13)

In the absence of reactants and products $[C] = [C_0]$. Therefore, in the reacting solution;

$$[C_0] = [C] + [M\cdot C]$$  \hspace{1cm} (7.14)

Combining equations 7.13 and 7.14 yields;

$$[C_0] = [C] + \left[\frac{[k_7\cdot[M]\cdot[C]}{k_8 + k_9\cdot[X]}\right]$$

or

$$[C_0] = [C] \left[1 + \frac{[k_7\cdot[M]}{k_8 + k_9\cdot[X]}\right]$$  \hspace{1cm} (7.15)

Combining equations 7.15 and 7.13, yields;

$$[M\cdot C] = \frac{k_7\cdot[M]\cdot[C_0]}{k_8 + k_9\cdot[X] + k_7\cdot[M]}$$  \hspace{1cm} (7.16)

But;

$$\frac{d\cdot[M]}{dt} = k_9\cdot[M]\cdot[C\cdot q]\cdot[X]$$  \hspace{1cm} (7.19)

and under the steady state hypothesis;

$$-\frac{d[M]}{dt} = \frac{d\cdot[Z]}{dt}$$  \hspace{1cm} (7.18)

Then combining equations 7.17, 7.18 and 7.16 yields;

$$\frac{d[M]}{dt} = -\frac{k_9\cdot k_7\cdot[M]\cdot[C_0]\cdot[X]}{k_8 + k_9\cdot[X] + k_7\cdot[M]}$$  \hspace{1cm} (7.19)

In all systems $[X] \gg [M]$. If $[M] = a$ and;

$$\theta_1 = k_7\cdot k_9\cdot[C_0]\cdot[X]$$  \hspace{1cm} (7.20)

$$\theta_2 = k_8 + k_9\cdot[X]$$  \hspace{1cm} (7.21)

$$\theta_3 = k_7$$  \hspace{1cm} (7.22)

Combining equations 7.19, 7.20, 7.21 and 7.22 yields;

$$-\frac{da}{\theta_2 + \theta_3 a} = -\frac{\theta_1}{(\theta_2 + \theta_3 a)}\cdot a$$  \hspace{1cm} (7.23)
For systems where $\theta_2 > (\theta_1.a)$ the reaction will follow first-order kinetics:

$$\frac{-da}{dt} = k_{obs}.a$$

where

$$k_{obs} = (\theta_1/\theta_2)$$

For systems where $(\theta_3.a) > \theta_2$ the reaction will follow zero-order kinetics:

$$\frac{-da}{dt} = (\theta_1/\theta_3)$$

The zero-order condition, $(\theta_3.a) > \theta_2$, will be favoured near the start of the reaction and by a low concentration of X. The first-order condition, $\theta_2 > (\theta_3.a)$, will be favoured near the end of the reaction and by a high concentration of X.

Integration of equation 7.23 between the limits, $a=a$ at time, $t$, and $a=a_0$ at $t=0$, yields;

$$t = -\int_0^t \frac{\theta_2}{\theta_1} \ln\left(\frac{a}{a_0}\right) \, da$$

or

$$t = -\left(\frac{\theta_2}{\theta_1}\right) \ln\left(\frac{a}{a_0}\right) - \left(\frac{\theta_3}{\theta_1}\right) (a-a_0)$$

The concentration term, $a$, was monitored by measuring the absorbance $P$ of the solute at wavelength, $\lambda_{max}$, and extinction coefficient, $\Sigma_{\lambda_{max}}$ in a cell of path-length, $\ell$. From Beer's Law, $P = a.\Sigma_{\lambda_{max}}.\ell$ and equation 7.27;

$$t = -\beta_1.\ln\left(\frac{P-P_\infty}{P_0-P_\infty}\right) - \beta_2.(P-P_0)$$

where

$$\beta_1 = \theta_2/\theta_1$$

and

$$\beta_2 = \theta_3/(\theta_1.\Sigma_{\lambda_{max}}.\ell)$$

Both reaction constants $\beta_1$ and $\beta_2$ have units of time. The term 
"$\beta_1.\ln((P-P_\infty)/(P_0-P_\infty))$" in equation 7.28 describes a first-order depend-
ence of absorbance on time. The term "β₂ (P-P₀)" describes a zero-order dependence of absorbance on time. Units for θ₁, θ₂ and θ₃ are s⁻², s⁻¹ and dm³ mol⁻¹ s⁻¹ respectively. Therefore, β₁ (=θ₂/θ₁) and β₂ (=θ₃/(θ₁·Λₘₐₓ·l)) have different units and comparison is not straightforward.

The two terms in equation 7.28 cannot be separated when describing a reaction following Scheme IV. Equation 7.28 is a total description of the kinetics of reaction and both terms contribute to a greater or lesser extent in the total reaction scheme.

Usually, kinetic equations (e.g. equation 7.1) express the dependence of the observable, i.e. absorbance on time. Statistical analysis then seeks to fit the dependence of absorbance on time using one or more rate constants. Time, t, is assumed to be without error and a least squares analysis seeks to minimise ∑(P₀bs-P₀calc)² over n data points (Chapter 2, Section 2.3). From equation 7.28 it is clear that such a method could not be used in this case. The opposite procedure was therefore adopted, i.e. the absorbance, P, was assumed to be without error and a least squares analysis sought to minimise ∑(t₀bs-t₀calc)² over n data points.

From equation 7.28, t, at fixed, P, is a function of β₁, β₂, P₀ and P∞;

$$t = t [β₁, β₂, P₀, P∞] \quad \ldots \quad (7.31)$$

The general differential of equation 7.31 is given by;

$$dt = \frac{∂t}{∂β₁} . dβ₁ + \frac{∂t}{∂β₂} . dβ₂ + \frac{∂t}{∂P₀} . dP₀ + \frac{∂t}{∂P∞} . dP∞ \quad \ldots \quad (7.32)$$

Hence from equation 7.28;

$$\frac{∂t}{∂β₁} = - \ln \left( \frac{P-P∞}{P₀-P∞} \right) \quad \ldots \quad (7.33)$$
Starting from estimated values of \( P_0, P_\infty, \beta_1 \) and \( \beta_2 \), the four derivatives (i.e. equations 7.33, 7.34, 7.35 and 7.36) were calculated at each absorbance, \( P \). A linear least squares procedure (Chapter 2, Section 2.3) calculated the correctors \( d\beta_1, d\beta_2, dP_0 \) and \( dP_\infty \) and an iterative calculation refined the values of \( \beta_1, \beta_2, P_0 \) and \( P_\infty \).

In a further step, the fraction \( \gamma \) of sites \( C \) occupied by \( M \) was calculated at regular stages of the reaction:

\[
\gamma = \frac{[MC]}{[C]_0} \tag{7.37}
\]

Combining equations 7.16 and 7.37 yields:

\[
\gamma = \frac{k_7[M]}{k_8 + k_9[X] + k_7[M]} \tag{7.38}
\]

Combining Beer's Law, \([M] = P/\Lambda_{\text{max}} \ell\) and equation 7.38;

\[
\gamma = \frac{(k_7.P)/(\Lambda_{\text{max}} \ell)}{k_8 + k_9[X] + (k_7.P)/(\Lambda_{\text{max}} \ell)} \tag{7.39}
\]

and combining equations 7.21, 7.22 and 7.39 yields;

\[
\gamma = \frac{\theta_3 (P/(\Lambda_{\text{max}} \ell))}{\theta_2 + \theta_3 (P/(\Lambda_{\text{max}} \ell))}
\]

or

\[
\gamma = \frac{P/(\Lambda_{\text{max}} \ell)}{(\theta_2/\theta_3) + P/(\Lambda_{\text{max}} \ell)}
\]

But

\[
\beta_1/\beta_2 = \left(\frac{\theta_2}{\theta_3}\right) \cdot \Lambda_{\text{max}} \ell
\]

Then

\[
\gamma = \frac{P}{\{(\beta_1/\beta_2) + P\}} \tag{7.40}
\]
The derived parameters were used to calculate the dependence of $\gamma$ on $(P-P_0)$, the latter being proportional to $[M]$. The analysis to find $\gamma$, turned out to be the most informative in displaying the extent of the zero-order contribution to the total kinetics of reaction.

7.4 RESULTS AND DISCUSSION

Each rate constant reported in this Chapter is the mean of at least three individual determinations, the reproducibility of first-order rate constants being at worst (i.e. for the fastest reactions) within 5%.

7.4.1 Aquation reactions and reactions with cyanide ions of Fe(phen)$_3^{2+}$

Aquation reactions of Fe(phen)$_3^{2+}$ in MEA and MEB were first-order in [complex]. Kinetic data for aquation and reaction with cyanide ions together with the corresponding data$^{22,4}$ in aqueous solution are reported in Table 7.1. First-order rate constants for aquation reactions were independent of sulphuric acid concentration, suggesting a similar dissociative mechanism to that in aqueous solution (Chapter 1, Section 1.6.1). The purpose of the acid in these reactions is to protonate the ligands and prevent recombination with the iron. Indeed, if the acid concentration was $< 1.49 \times 10^{-2}$ mol dm$^{-3}$ the aquation reactions of Fe(phen)$_3^{2+}$ did not go to completion. The rate constants for aquation in MEA and MEB were similar (i.e. $2.17 \times 10^{-4}$ s$^{-1}$ and $2.33 \times 10^{-4}$ s$^{-1}$ respectively) and reflected an increase of a factor of approximately 3 over the corresponding rate constant$^{22}$ in water (i.e. $7.33 \times 10^{-5}$ s$^{-1}$).

For reactions of Fe(phen)$_3^{2+}$ with cyanide ions in MEA a dramatic acceleration in rate relative to the corresponding rate of reaction in water was observed. Indeed, kinetic data for this latter reaction could not be monitored because the reaction was complete within a second or two of mixing the reagents.
Addition of cyanide ions to MEB caused the solution to become cloudy. Nevertheless, addition of Fe(phen)$_3$ to this system resulted in immediate disappearance of the bright red colour of the iron complex.

From these qualitative observations it was concluded that the rates of reaction of Fe(phen)$_3$ with cyanide ions in MEA and MEB were accelerated by a factor of $>10^3$ relative to the corresponding rate of reaction in water.

**7.4.2 Reactions of Fe(phen)$_3$ with hydroxide ions**

The reactions followed first-order kinetics in [complex] in all systems. Kinetic data are reported in Table 7.2. In aqueous solution the second-order rate constant for reaction is $1.08 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$. Therefore, in aqueous solution where [NaOH] = $2 \times 10^{-3}$ mol dm$^{-3}$, the predicted first-order rate constant is $2.16 \times 10^{-5}$ s$^{-1}$. In MEA where [NaOH] = $2 \times 10^{-3}$ mol dm$^{-3}$, the first-order rate constant was $8.99 \times 10^{-2}$ s$^{-1}$, corresponding to an increase by a factor of $4 \times 10^3$ over the corresponding rate constant in water. The dependence of the first-order rate constant on sodium hydroxide concentration was non-linear (Fig. 7.3). Initially as [sodium hydroxide] increased the first-order rate constant increased rapidly; when [NaOH] $>10^{-2}$ mol dm$^{-3}$, the rate constant was independent of sodium hydroxide concentration.

In an analogous microemulsion to MEA, containing 40 mol % 2BE, 50 mol % decane and 10 mol % water, where [NaOH] = $1.18 \times 10^{-2}$ mol dm$^{-3}$, the rate constant was $1.43 \times 10^{-1}$ s$^{-1}$. In MEA where [NaOH] = $1.19 \times 10^{-2}$ mol dm$^{-3}$, the rate constant was $1.75 \times 10^{-1}$ s$^{-1}$, i.e. the rate constant for reaction in both microemulsions is similar.

In MEB, where [NaOH] = $2.72 \times 10^{-3}$ mol dm$^{-3}$ the rate constant for reaction was $2.84 \times 10^{-1}$ s$^{-1}$. In aqueous solution where [NaOH] = $2.72 \times 10^{-3}$ mol dm$^{-3}$, the predicted first-order rate constant is $2.93 \times 10^{-5}$ s$^{-1}$. 
Therefore the acceleration in rate of reaction in MEB relative to the corresponding rate in water is a factor of $9.7 \times 10^3$. The dependence of the rate constant on sodium hydroxide concentration is illustrated in Figure 7.4, i.e. the rate constant for reaction increased rapidly with increase in $[\text{NaOH}]$. When $[\text{NaOH}] > 3 \times 10^{-3}$ mol dm$^{-3}$ the solution turns cloudy and, therefore, kinetic data for reaction could not be monitored. However, at the upper limit of sodium hydroxide concentration, the rate constant for reaction is beginning to be independent of alkali concentration (Fig. 7.4).
FIGURE 7.4
Dependence of first-order rate constants on [sodium hydroxide] concentration for reactions of Fe(phen)$_3^{2+}$ with hydroxide ions at 298 K in (a) ME.B. (Δ), (b) ME.B. with $2.3 \times 10^{-2}$ mol dm$^{-3}$ CTAB (○) and (c) ME.B. with $2.3 \times 10^{-2}$ mol dm$^{-3}$ SDS (○).
Kinetic trends for reaction of Fe(phen)$_2^{2+}$ with hydroxide ions were investigated when sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide (CTAB) were added to MEB. Kinetic data are reported in Table 7.3. The dependences of rate constants for reaction on sodium hydroxide concentration are illustrated in Figure 7.4. When $[\text{NaOH}] = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ in MEB;

(i) $k_{\text{obs}} = 2.64 \times 10^{-1} \text{ s}^{-1}$

(ii) when $[\text{SDS}] = 0.012 \text{ mol dm}^{-3}$; $k_{\text{obs}} = 5.92 \times 10^{-3} \text{ s}^{-1}$

(iii) when $[\text{SDS}] = 0.023 \text{ mol dm}^{-3}$; $k_{\text{obs}} = 2.65 \times 10^{-3} \text{ s}^{-1}$

(iv) when $[\text{CTAB}] = 0.023 \text{ mol dm}^{-3}$; $k_{\text{obs}} = 9.03 \times 10^{-3} \text{ s}^{-1}$

(v) when $[\text{CTAB}] = 0.046 \text{ mol dm}^{-3}$; $k_{\text{obs}} = 4.20 \times 10^{-3} \text{ s}^{-1}$.

Therefore relative to the rate of reaction in MEB, the following decelerations in rate were observed on addition of ionic surfactant;

(i) $[\text{SDS}] = 0.012 \text{ mol dm}^{-3}$; a factor of $4.5 \times 10$

(ii) $[\text{SDS}] = 0.023 \text{ mol dm}^{-3}$; a factor of $10^2$

(iii) $[\text{CTAB}] = 0.023 \text{ mol dm}^{-3}$; a factor of $3 \times 10$

(iv) $[\text{CTAB}] = 0.046 \text{ mol dm}^{-3}$; a factor of $6.3 \times 10$.

SDS is more effective in slowing the reaction rate in MEB than CTAB. SDS forms anionic micelles and CTAB forms cationic micelles. If the surfactant concentration is doubled the reaction rate is also slowed down by a factor of approximately 2. When $[\text{surfactant}] = 2.3 \times 10^{-2} \text{ mol dm}^{-3}$ the dependence of the rate constant on sodium hydroxide concentration is non-linear (Fig. 7.4); with increase in $[\text{sodium hydroxide}]$, the rate constant increased initially and, in the presence of SDS, when $[\text{NaOH}] > 7.4 \times 10^{-3} \text{ mol dm}^{-3}$ the rate constant was independent of $[\text{NaOH}]$. In the presence of CTAB when $[\text{NaOH}] > 1.43 \times 10^{-2} \text{ mol dm}^{-3}$, the dependence of the rate constant on $[\text{NaOH}]$ was complicated.
7.4.3 Reactions of Fe(5-NO₂phen)₃²⁺

Aquation reactions of Fe(5-NO₂phen)₃²⁺ were first-order in [complex] in MEA and MEB and in two further microemulsions, which were analogous to MEA but with smaller concentrations of the aqueous component;

MEB: 40 mol % 2BE, 50 mol % decane and 10 mol % water
MED: 40 mol % 2BE, 55 mol % decane and 5 mol % water.

Kinetic data are reported in Table 7.4. The rate constants for aquation reactions were independent of sulphuric acid concentration in all systems.

The rate constant for aquation reactions in MEB is a factor of approximately 10 faster than in aqueous solution. In MEA and its analogues rate constants for aquation reactions are enhanced by a factor of approximately 5 relative to that in water.

Reducing the amount of water in MEA had little effect on the rates of aquation reactions of Fe(5-NO₂phen)₃²⁺.

The reaction of Fe(5-NO₂phen)₃²⁺ with hydroxide ions in aqueous solution is slightly faster than the corresponding reaction involving Fe(phen)₃²⁺, i.e. the second-order rate constant for Fe(phen)₃²⁺ is 1.08 × 10⁻² dm³ mol⁻¹ s⁻¹, cf. second-order rate constant for Fe(5-NO₂phen)₃²⁺ is 9.3 × 10⁻² dm³ mol⁻¹ s⁻¹. The rates of reaction of Fe(5-NO₂phen)₃²⁺ with hydroxide ions in MEA and MEB showed an acceleration as dramatic as that for Fe(phen)₃²⁺. However, the reactions were too fast to be able to monitor kinetic data, being complete within a second or so of mixing the reagents.

Similarly, rates of reaction of Fe(5-NO₂phen)₃²⁺ with cyanide ions in MEA and MEB were too fast to measure, but from the qualitative observations it was concluded that the rates of reaction of Fe(5-NO₂phen)₃²⁺ with cyanide ions in MEA and MEB were accelerated by a factor of >10³.
relative to the corresponding rate of reaction⁵ in water.

7.4.4 Aquation reactions of Fe(hxsbH)²⁺

Aquation reactions of Fe(hxsbH)²⁺ in aqueous solution were first-order in [complex]. Kinetic data are reported in Table 7.5. The dependence of first-order rate constants on sulphuric acid concentration were non-linear (Fig. 7.5). The rate constant increased with increase in acid concentration but when [H₂SO₄] > 1 mol dm⁻³, the rate constant was independent of acid concentration.

Rate constants for aquation reactions of Fe(hxsbH)²⁺ when [acid] < 0.3 mol dm⁻³ are already reported²³ and the dependence of the rate constants on [acid] are consistent with data presented here.

The dependence of rate constants for aquation of Fe(hxsbH)²⁺ on [acid], between 0.2 < [acid] < 2 mol dm⁻³, identified as above, is similar to the corresponding dependence observed for iron(II)-2,2'-bipyridyl [Fe(bipy)]₃²⁺.²⁴ Rate constants for aquation of this latter complex are also independent of [acid], when [acid] > 1.0 mol dm⁻³. The following mechanism was proposed;

```
(LL)₂Fe²⁺ + (LL)₂Fe²⁺ \xrightarrow{k₁} (LL)₂Fe²⁺ \xrightarrow{k₃} (LL)₂Fe²⁺ + N^-
```

Applying the steady state approximation for concentrations of the partly dissociated species, the observed rate constant, kₐₜₜ, is given by;

$$k_{obs} = k₁ \frac{k₃}{(k₂ + k₃ + k₄[H^+])} \quad \ldots \quad (7.41)$$
FIGURE 7.5
Dependence of first-order rate constants on [sulphuric acid] for aquation reactions of Fe(hxsbh)$^{2+}$ in aqueous solution at 298 K.
At high acidities, \( k_2 \) and \( k_3 \ll k_4 [H^+] \) and \( k_{\text{obs}} = k_1 \). At low acidities \([H^+]\) is negligible and \( k_{\text{obs}} = k_1 (k_3/(k_2 + k_3)) \). Such a mechanism is applicable to iron complexes with flexible bi- and multidentate ligands such as (bipy) and (hxsbH), [i.e. not for (phen) because phen is a rigid ligand]. If such a ligand is removed by a dissociation mechanism, the process probably involves a number of such steps. Each step would be reversible because the coordinating atom remains close to the metal atom.

In MEB aquation reactions of Fe(hxsbH)\(^{2+}\) with (a) sulphuric acid and (b) hydrochloric acid were first-order in complex. Kinetic data are reported in Table 7.6. The dependence of first-order rate constants on [acid] (Fig. 7.6) showed a pattern similar to that observed for the corresponding aquation in aqueous solvent. The rate constant was independent of [acid] at much lower concentrations of acid in MEB than in water, i.e. in MEB in the presence of sulphuric acid, the rate constant is independent of [acid], when \([H_2SO_4] = 5 \times 10^{-2} \text{ mol dm}^{-3}\).

Assuming a linear dependence of \( k_{\text{obs}} \) on [acid] when \([H_2SO_4] < 1 \text{ mol dm}^{-3}\) in aqueous solvent, then when \([H_2SO_4] = 0.03 \text{ mol dm}^{-3}\) the estimated first-order rate constant is \( 1.02 \times 10^{-3} \text{ s}^{-1} \). In MEB when \([H_2SO_4] = 0.03 \text{ mol dm}^{-3}\), the first-order rate constant is \( 4.52 \times 10^{-3} \text{ s}^{-1} \) corresponding to an acceleration in rate of reaction by a factor of approximately 4.5, relative to the rate of reaction in water. The increase in the rate constant for aquation of Fe(hxsbH)\(^{2+}\) in MEB relative to the rate constant in water is consistent with the corresponding results observed for Fe(phen)\(^{2+}\) and Fe(5-NO\(_2\)phen)\(^{2+}\). However, in aqueous solvent, when \( k_{\text{obs}} \) is independent of [acid], the rate constant for aquation is \( 2.53 \times 10^{-2} \text{ s}^{-1} \), cf. \( 5.46 \times 10^{-3} \) in MEB, i.e. a decrease in rate constant relative to water by a factor of approximately 4.5. This latter observation can be explained on the basis of a local saturation effect analogous to that
FIGURE 7.6
Dependence of first-order rate constants on [acid] for aquation reactions of Fe(hxesbH)⁴⁺ in ME.B.
observed for Fe(phen)$_3^{2+}$ with hydroxide ions in the microemulsions.

In MEA, the aquation reactions of Fe(hxsbH)$_2^{2+}$ were not first-order in [complex]. Plots of absorbance at $\lambda_{\text{max}}$ against time were linear for a considerable time of the total reaction. The extent of this latter feature was dependent on the concentration of acid. As the acid concentration was increased, the time taken for complete reaction decreased. The dependence of absorbance on time towards the end of the reaction approached that expected for a first order reaction. The kinetic analysis in Scheme IV was developed to account for these observations.

The dependence of time, t, on absorbance, P, (equation 7.28) was used to obtain estimates of $P_0$, $P_\infty$, $\beta_1$ and $\beta_2$. The standard error on each run was better than ±0.05s. Using these values the dependence of $\gamma$ on $(P-P_\infty)$ was calculated (equation 7.40). Kinetic data are reported in Table 7.7 and a typical set of experimental plots of absorbance viz. time are illustrated in Figs. 7.7. On these latter plots the full line represents the calculated curve. Also included are the two components, the 'first' and 'zero' order parts of equation 7.28. These lines show the calculated dependence when (a) $\beta_1 \neq 0$, $\beta_2 = 0$ and (b) $\beta_1 = 0$, $\beta_2 \neq 0$.

The trend in $\gamma$ is more informative than comparison of the separate trends in $\beta_1$ and $\beta_2$, because $\gamma$ is a function of both $\beta$ quantities. A high $\gamma$ at $t = 0$ and $P = P_0$, indicates that the reaction has considerable zero-order character, whereas a low $\gamma$ at $t = 0$ and $P = P_\infty$ is associated with a reaction having significant first-order contribution.

As the concentration of acid is decreased (Table 7.7 and Figs. 7.7) the zero-order character of the reaction increases, which is consistent with the predictions made on the basis of Scheme IV. At high acid concentration the zero-order contribution to the total reaction, using p-toluene sulphonic acid, is approximately double than when hydrochloric
Dependence of absorbance, $P$, on time, $t$ and $y$ on $(P-P_{\infty})$ at $\lambda_{\text{max}} = 512 \text{nm}$ (equation 7.26) for aquation reactions of Fe$(\text{hnsb})_{2}^{2+}$ in MEA at 298 K containing different concentrations of acid. The full line represents the calculated curve using equation 7.28. (---) represents the 'zero' order contribution in the event $B_{1}=0$ and $B_{2}=0$ and (-----) represents the 'first' order contribution in the event $B_{1}=0$ and $B_{2}=0$.

(a) [p-toluenesulphonic acid] = $2.97 \times 10^{-3}$ mol dm$^{-3}$
(b) [p-toluenesulphonic acid] = $1.49 \times 10^{-2}$ mol dm$^{-3}$
(c) [p-toluenesulphonic acid] = $2.97 \times 10^{-2}$ mol dm$^{-3}$
(d) [hydrochloric acid] = $2.97 \times 10^{-1}$ mol dm$^{-3}$
FIGURE 7.7 (c)
... acid is used. Therefore, the first-order/slow-order balance is dependent on the nature of the acid.

Similar trends were observed when sulphuric acid was used in MEA, but an slight cloudiness towards the end of the reaction produced unreliable values. The cloudiness was probably due to formation of an insoluble sulphate.

Reactions of Fe(NH₄)₆³⁺ with cyanide and cyanide ions

Reactions of Fe(NH₄)₆³⁺ with cyanide ions in MEA were accompanied by a blue coloration (complex). Kinetic data are reported in Table 7.8. The reaction was dramatically accelerated, i.e. by a factor of 10⁳ relative to the corresponding reaction in aqueous solvent. When [MEB] = 2.5 x 10⁻³ mol dm⁻³, the first-order rate constant, k₁, for the reaction in MEA is 5.2 x 10⁻⁵ dm³ mol⁻¹ s⁻¹ at the same potassium cyanide concentration in water.

The first-order rate constant for reaction increased initially with increase in [potassium cyanide] and then became independent of cyanide concentration (Fig. 7.8).

Kinetic data for reaction of Fe(NH₄)₆³⁺ with cyanide ions could not be monitored in MEA because the solution was cloudy. When the addition of Fe(NH₄)₆³⁺ to the reagents in MEA was blue color of the complex faded extremely rapidly, indicating that the acceleration in this reaction relative to the corresponding reaction in water.

Addition of Fe(NH₄)₆³⁺ to reagents in MEA containing cyanide resulted in a change of color from blue to green. The addition of a reducing agent then changed the green to colourless. Changes in color with time were very complicated and no satisfactory kinetic analysis was developed.
acid is used. Therefore, the first-order/zero-order balance is dependent
on the nature of the acid.

Similar trends were observed when sulphuric acid was used in MEA, but
a slight cloudiness towards the end of the reaction produced unreliable
P values. The cloudiness was probably due to formation of an insoluble
sulphate.

7.4.5 Reactions of Fe(hxsbH)\textsuperscript{2+} with hydroxide and cyanide ions

Reactions of Fe(hxsbH)\textsuperscript{2+} with cyanide ions in MEA were first-order
in [complex]. Kinetic data are reported in Table 7.8. The reaction was
dramatically accelerated, i.e. by a factor of 10\textsuperscript{3} relative to the
 corresponding reaction in aqueous solvent. When [KCN] = 2.23 \times 10\textsuperscript{-2} mol
 dm\textsuperscript{-3}, the first-order rate constant was 4.9 \times 10\textsuperscript{-2} s\textsuperscript{-1}, cf. 4.7 \times 10\textsuperscript{-5} s\textsuperscript{-1}
 at the same potassium cyanide concentration in water.\textsuperscript{15}

The first-order rate constant for reaction increased initially with
increase in [potassium cyanide] and then became independent of cyanide
concentration (Fig. 7.8).

Kinetic data for reaction of Fe(hxsbH)\textsuperscript{2+} with cyanide ions could not
be monitored in MEB because the solution was cloudy. However, on
addition of Fe(hxsbH)\textsuperscript{2+} to the reagents in MEB, the blue colour of the
complex faded extremely rapidly, indicating a similar dramatic accelerat­
ion in this reaction relative to the corresponding reaction in water.

Addition of Fe(hxsbH)\textsuperscript{2+} to either MEA or MEB containing hydroxide
ions, resulted in a rapid change of colour from blue to green. The
green of the solution then faded slowly to colourless. Changes in
absorption spectra with time were very complicated and no satisfactory
kinetic analysis was developed.
FIGURE 7.8
Dependence of first-order rate constants on [potassium cyanide] for reactions of Fe(hxsBH)²⁺ with cyanide ions in MEA at 298 K.
7.5 CONCLUSION

One of the most important observations reported in this Chapter was that the form of the dependence of absorbance on time for reactions involving some metal complexes changed on going from a solution in water to a solution in a microemulsion. Zero-order kinetics are indicative of complexity where some new factor controls the reaction rate. The following model is proposed to account for the observations cited above.

MEA and MEB are water-in-oil microemulsions, i.e. the water is dispersed as microscopic droplets in an oil-rich continuum, with a large proportion of the co-surfactant being concentrated in the interfacial region between oil and water phases (Chapter 6).

The structure of the metal complexes have the characteristics of a surfactant, i.e. a large hydrophobic moiety and a hydrophilic charge-bearing atom. A large proportion of the total substrate concentration is, therefore, situated between water-rich and hydrocarbon-rich domains, i.e. in the interfacial region (Chapter 6) with the co-surfactant 2BE in MEA and 2-propanol in MEB. Indeed, evidence supporting this model is illustrated by molybdenum tetracarbonyl 1,10-phenanthroline [Mo(CO)₄phen] and molybdenum tetracarbonyl 2,2'-bipyridyl [Mo(CO)₄bipy] (Appendix 1). The solvatochromic nature of these latter two complexes made it possible to assess their environment in a microemulsion of n-butanol, SDS, toluene and water (Chapter 6, Section 6.6.3). The results (Appendix 1) indicate that the complexes are in an alcohol-rich environment, i.e. in the interfacial region between oil and water phases.

Scheme IV (Section 7.3) applies to kinetics of reaction involving either aquation in acidic medium or reaction of the iron complexes with hydroxide or cyanide ions. For those reactions where no zero-order contribution to the overall kinetics was detected, the kinetics of
reaction can be understood in terms of equation 7.28, where the $\beta_2$ term is very small.

The hydroxide and cyanide ions in the microemulsions are localised in the water droplets, rather than in the hydrocarbon continuous phase. A very high local concentration of these latter ions is produced within the diffuse double layer of counter ions adjacent to the complex ions in the interfacial region;

Further the hydroxide and cyanide ions are probably greatly destabilised (Chapters 3 and 4) in the microemulsion relative to aqueous solvent because of the small concentrations of water present in MEA and MEB. These two factors result in the dramatic accelerations in reaction rates of the iron complexes with hydroxide or cyanide ions observed in MEA and MEB relative to the corresponding reaction rates in water.

The dependence of the rate constant for reaction on nucleophile concentration in the microemulsions can be understood in terms of a local concentration saturation. The droplets are small ($\approx 10^{-8} \text{m}$) and reaction occurs at the surface of the water droplets. Therefore, there is a limit to the number of hydroxide or cyanide ions which can conglomerate
at the surface at any given instant.

SDS and CTAB stabilise the microemulsion by being adsorbed at the interface. However, these surfactants displace the complex ions and hence reduce the amount of reaction occurring at the surface, i.e. the overall rate of reaction falls. The anionic micelles of SDS will slow the reaction down more than the cationic micelles of CTAB because of electrostatic repulsion between the anionic micelles and the nucleophilic ions.

The rate of aquation reactions of the metal complexes show only a modest acceleration relative to the corresponding reaction in water. The rate determining step for aquation of Fe(phen)$_3^{2+}$ is loss of the first ligand followed by subsequent protonation of the ligand to prevent recombination (Chapter 1, Section 1.6.1). The proton must therefore approach the complex in order to protonate the ligand as it dissociates from the metal ion. Approach of a similarly charged hydrogen ion to the complex ion in the interface is more difficult than for oppositely charged ions such as hydroxide or cyanide ions.

In describing Scheme IV an assumption was made that desorption and production of a vacant site at the interface was rapid. Situations must arise where the product of reaction or an intermediate remains in the interface. The appearance of a persistent green colour in the reaction between hydroxide ions and Fe(hxsblH)$_2^{2+}$ in MEA and MEB can be explained by attack of hydroxide ions at the coordinated ligand to form an intermediate of type III (Section 7.1) (i.e. the green complex). In aqueous solution intramolecular movement of the hydroxide ion to the central metal ion and simultaneous dissociation of the ligand from the metal is rapid, only electron withdrawing substituents being able to increase the lifetime of the intermediate. However, in MEA and MEB the
lifetime of the intermediate is greatly increased because desorption of this latter species from the interface is slow;
REFERENCES TO CHAPTER 7

CHAPTER 8

Aquation reactions of iron(II) hexadentate Schiff base in water-rich '2-n-butoxyethanol + water' mixtures and reactions of iron(II) 1,10-phenanthroline in the 2-n-butoxyethanol-rich region
8.1 INTRODUCTION

Kinetic evidence for microheterogeneity in water-rich '2-n-butoxy-ethanol (2BE) + water' mixtures is examined in this Chapter. By way of introduction a short resume is presented of the properties of water-rich aqueous mixtures.

8.1.1 Critical Solution Temperatures

Conditions for phase separation of a binary aqueous mixture at a critical temperature can be explained in terms of the excess functions of mixing. The mixing of typically aqueous mixtures is entropy controlled (Chapter 1, Section 1.3), and the importance of $S_m^E$ for these solutions explains why many of these systems phase separate at a lower critical solution temperature (L.C.S.T.). For a binary mixture at constant temperature, $T$, and pressure, $p$, the criteria for a L.C.S.T. are;

$$\left(\frac{\partial^2 G_m^E}{\partial x_2^2}\right)_{T; p} + R \cdot T = 0 \quad \ldots \quad (8.1)$$

$$\left(\frac{\partial^2 H_m^E}{\partial x_2^2}\right)_{T; p} > 0 \quad \ldots \quad (8.2)$$

$$\left(\frac{\partial^2 S_m^E}{\partial x_2^2}\right)_{T; p} > \frac{R}{x_1 x_2} \quad \ldots \quad (8.3)$$

and $G_m^E > 0$, $H_m^E < 0$, $S_m^E < 0$, where $x_1$ is mole fraction of component 1 (i.e. water) and $x_2$ is mole fraction of component 2 (i.e. added cosolvent). Thus for $G_m^E$ to be positive $|T \cdot S_m^E| > |H_m^E|$.

For a binary solution to display an upper critical solution temperature, an important condition is;

$$\left(\frac{\partial^2 H_m^E}{\partial x_2^2}\right)_{T; p} < 0 \quad \ldots \quad (8.4)$$

Therefore, the enthalpy of mixing is the key to a binary solution
displaying an U.C.S.T.

Generally at an U.C.S.T., the excess molar isobaric heat capacity of mixing, $C_p^E < 0$ and the excess molar volume of mixing, $V_m^E > 0$. At a L.C.S.T., $C_p^E > 0$ and $V_m^E < 0$. If $C_p^E$ is negative at an L.C.S.T. and remains so as the temperature rises, then $S_m^E$ and $H_m^E$ may change in such a way that the conditions for an U.C.S.T. are met. Such systems show a closed solubility loop. '2BE + water' mixtures display this latter behaviour (Fig. 8.1).^2

FIGURE 8.1
Phase diagram for '2-butoxyethanol + water' mixtures.
[Reprinted from Ref. 2]
8.1.2 Volumetric Properties of binary typically aqueous mixtures

For typically aqueous (T.A.) mixtures $V_m^E$ is negative and plots of $V_m^E$ against $x_2$ have a point of inflexion in water-rich mixtures. Therefore, the partial molar volume, $V_2$, of an organic cosolvent has a minimum in water-rich regions.

Many properties of T.A. mixtures show extrema in the water-rich regions. Hayduk\(^3\) and co-workers report a careful study of the properties of 'tetrahydrofuran (THF) + water' mixtures. In the water-rich region at $x(\text{THF}) \approx 0.15$, the viscosity of the mixture has a sharp maximum at 298 K. Further studies\(^4\) into this latter solvent system led to the proposal that at low mole fractions of THF, strong hydrogen-bonding between water molecules causes the water to exist as a separate phase.

Arnaud et al.\(^5\) estimated the excess molar heat capacities ($C_{pm}^E$) of various hydro-organic mixtures at 298 K and ambient pressure. Plots of $C_{pm}^E$ against mole fraction, $x_2$, of organic cosolvent show maxima in the water-rich regions;\(^5\)

<table>
<thead>
<tr>
<th>Organic Cosolvent</th>
<th>$C_{pm}^E$ (max) / J mol(^{-1}) K(^{-1})</th>
<th>$x_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>7.0</td>
<td>0.194</td>
</tr>
<tr>
<td>ethanol</td>
<td>16.8</td>
<td>0.281</td>
</tr>
<tr>
<td>isopropanol</td>
<td>16.4</td>
<td>0.09</td>
</tr>
<tr>
<td>tertiary butyl alcohol</td>
<td>15.4</td>
<td>0.0749</td>
</tr>
<tr>
<td>acetone</td>
<td>9.1</td>
<td>0.237</td>
</tr>
</tbody>
</table>

Macdonald\(^6\) et al. calculated thermal pressures [(\(9P/9T\))\(_T\)] and internal pressures [(\(9U/9V\))\(_T\)] for 'methanol + water' and 'tertiary butyl alcohol + water' mixtures at several temperatures between 292 K and 328 K using the relationship $T(\partial P/\partial T)_T = (\partial U/\partial V)_T$. The internal pressures have maxima at $x_2(\text{MeOH}) = 0.3$-0.4 and $x(t-\text{BuOH}) = 0.1$. The latter are consistent with the average intermolecular distance passing through a minimum in both systems at the corresponding mole fractions of cosolvent. The
maximum in \(\frac{\partial \alpha}{\partial V} \) indicates minimum intermolecular separations.

A comprehensive study\(^7\) of the ultrasonic absorption properties of aqueous mixtures shows that the dependence of \(\frac{\alpha_A}{v^2}\) (where \(\alpha_A\) is the amplitude absorption coefficient and \(v\) is the frequency of the sound wave), on mole fraction, \(x_2\) of organic cosolvent passes through a maximum in the water-rich regions. \(\frac{\alpha_A}{v^2}\) is a maximum at a mole fraction characteristic of a given binary mixture. Two main composition regions were identified;

(i) a plateau region where \(\frac{\alpha_A}{v^2}\) is relatively insensitive to added cosolvent,

(ii) a region where \(\frac{\alpha_A}{v^2}\) rises rapidly to a maximum at a characteristic \(x_2\), which is called the peak sound absorption composition (P.S.A.C.).

With increase in hydrophobic character of added cosolvent the P.S.A.C. decreases and \((\frac{\alpha_A}{v^2})_{\text{max}}\) increases (i.e. in the order ethanol < isopropanol < tertiary butyl alcohol). The shape of the plot of \(\frac{\alpha_A}{v^2}\) against \(x_2\) provides a useful qualitative indicator for the hydrophobic/hydrophilic character of an organic cosolvent.

A close link was observed between the P.S.A.C. and the mole fraction, \(x_2\), at which small angle X-ray scattering passes through a maximum. Further the shapes of the two graphs are similar. X-ray scattering is large when clustering produces large density fluctuations. Therefore, the link between maxima in light scattering and sound absorption led to the development of a model based on a treatment of concentration fluctuations within the solvent mixture.

As the mole-fraction, \(x_2\), of the added cosolvent increases, a point is reached where the cosolvent can no longer be accommodated by water molecules linked by the short bond form of hydrogen bonds (Chapter 1, Section 1.2). The larger the hydrophobic group(s) of the cosolvent, the
lower the $x_2$ at which the latter can no longer be accommodated. At this mole fraction interference between solvent cospheres (Chapter 5, Section 5.1.1) produces a structure-breaking effect. Organisation of water and cosolvent in this region can be understood in terms of component clustering to form microscopic heterogeneities, i.e. regions which are either water-rich or cosolvent-rich. Water molecules endeavour to maintain local networks of the short bond hydrogen-bonded molecules by ejecting excess cosolvent. In the limit such behaviour leads to phase separation at an L.C.S.T., at mole fraction, $x_2^*$, but even for completely miscible systems there is a strong tendency to immiscibility at mole fractions close to $x_2^*$. As $x_2$ increases further, the mixture becomes rich in cosolvent. There is insufficient water to maintain a network of hydrogen-bonded molecules. The properties of the mixture now resemble a mixture of more conventional polar molecules. The extent of microheterogeneity decreases.

8.1.3 Thermodynamic Properties of '2BE + water' mixtures

Properties of '2-n-alkoxyethanol + water' mixtures including 2BE have been studied at 277, 283, 298, 313 and 328 K. The excess molar functions for the mixtures showed no anomalous behaviour even though plots of the excess molar functions against mole-fraction of added cosolvent displayed pronounced asymmetry. However, the apparent or partial molar properties showed spectacular changes in the water-rich region, indicating that important structural features were present. The latter feature was especially apparent in systems containing long-chain homologues and at low temperatures.

The dependence of apparent partial molar volumes, $\tilde{\nu}$, on mole-fraction, $x_{BE}$, for '2BE + water' mixtures is typical of most aqueous organic
mixtures (Fig. 8.2), i.e. $f_V$ passes through a minimum and then levels off with increase in $x_{BE}$. The depth of the minimum decreases with increasing temperature.

The dependence of the apparent partial molar heat capacity $f(C_{p2})$ on $x_{BE}$ passes through a minimum followed by a sharp maximum (Fig. 8.2). Changes in $f(C_{p2})$ in the water-rich region are shown more clearly in Figure 8.3. The maximum in $f(C_{p2})$ is most intense at low temperatures and vanishes completely at high temperatures. These features are even more spectacular when the partial molar heat capacity of 2BE, $C_{p2}$, is plotted against $x_{BE}$. At $x_{BE} > 0.1$, $C_{p2}$ showed little concentration dependence. Trends in $f(C_{p})$ and $C_{p2}$ are analogous to those for ionic surfactants in water. For the latter systems a sharp increase in $C_{p2}$ is observed just before the critical micelle concentration, followed by a very large decrease during micellisation, a shallow minimum and a constant $C_{p2}$ in the post-micellar region.

The dependence of $C_{p2}$ on $x_{BE}$, therefore, indicates that at $x_{BE}$, at which $C_{p2}$ is a maximum (i.e. $x_{BE} = 0.02$) (Fig. 8.4), a microphase transition occurs and beyond the transition 2BE exists as microphases or aggregates. This clustering persists up to high temperatures although the maximum in $f(C_{p2})$ or $C_{p2}$ for aggregation is less sharp at high temperatures. No simple pattern is observed between systems showing a L.C.S.T. and other systems whose properties are dominated by microheterogeneity.

The apparent partial molar expansibility, $[d(f_V)/dT]_p$, of 2BE also passed through a maximum at low mole fraction of 2BE.

Holtermann and Engberts examined the standard molar enthalpies, entropies and heat capacities of activation ($\Delta^*H^\circ$, $\Delta^*S^\circ$ and $\Delta^*C_p^\circ$ respectively, assuming ambient pressure [atm]) for the neutral hydrolysis
FIGURE 8.2
Excess apparent molar heat capacities and volumes of '2-butoxyethanol + water' mixtures at 298 K.

[Reprinted from Ref. 9]

(a) \( \Phi_v - \Phi_v^0 \)

(b) \( \Phi_c - \Phi_c^0 \)
FIGURE 8.3
Excess apparent molar heat capacities of '2-butoxy-ethanol + water' mixtures in the water-rich region at 298 K.

[Reprinted from Ref. 9]
FIGURE 8.4
Phase diagram of '2-butoxyethanol + water' mixtures in the water-rich region.

[Reprinted from Ref. 9]
of two acyl activated esters in water-rich '2BE + water' mixtures. At
\( x_{BE} = 0.02 \), \( \Delta^*Cp^\circ \) was derived by fitting the data to the Valentiner
equation using a least squares procedure;

\[
\ln k_{obs} = \frac{A}{T} + B \ln T + C \quad \ldots \ (8.4)
\]

Hence

\[
\frac{\Delta^*H^\circ}{R} = -A + (B \cdot T) - T \quad \ldots \ (8.5)
\]

Also

\[
\Delta^*Cp^\circ = (B-1) \cdot R \quad \ldots \ (8.6)
\]

The analytical method outlined above was used because at \( x_{BE} = 0.02 \)
plots of \( \ln(k_{obs}/T) \) vs \( (1/T) \) showed strong curvature. At \( x_2 = 0 \) and
0.05 the latter plots were linear with slope \( (\Delta^*H^\circ/R) \). \( \Delta^*Cp^\circ \) was large
and positive with a maximum at \( x_{BE} = 0.02 \), and this contrasts sharply
with the negative extrema in \( \Delta^*Cp^\circ \) associated with solvolyses of
neutral substrates in typically aqueous mixtures. \( \Delta^*G^\circ \) increased
continuously with increasing \( x_{BE} \), but \( \Delta^*H^\circ \) and \( T\Delta^*S^\circ \) exhibited mirror-
image behaviour, passing through extrema near \( x_{BE} = 0.02 \) (cf. Chapter 5,
Section 5.1.2).

Comparison \(^{11,12}\) with the neutral hydrolysis of tertiary butyl chloride
(t-BuCl), in water-rich '2BE + water' mixtures at \( x_{BE} = 0.02 \) revealed
that plots of \( \ln(k_{obs}/T) \) vs \( (1/T) \) deviated significantly from linearity.
\( \Delta^*Cp^\circ \), obtained from fitting the kinetic data to the Valentiner equation,
were negative between 283 and 303 K, but nevertheless showed a positive
increase with respect to the corresponding values in pure water. This
trend is in direct contrast to that observed for hydrolysis of t-BuCl
in water-rich 't-BuOH + water' mixtures. In the latter system at
\( x_{t-BuOH} = 0.05 \), \( \Delta^*Cp^\circ \) decreases relative to the corresponding value in
pure water. These latter results provide direct support that positive
\( \Delta^*Cp^\circ \) for the neutral hydrolysis of the two acyl esters are caused by
specific effects in the solvent system.

Activation parameters $\Delta^+X^\Phi$ (where $X = H, S, G$ and $Cp$) for the neutral hydrolysis of the two acyl esters were dissected$^{12}$ into initial-state/transition-state contributions. Solvent effects on $\Delta^+X^\Phi$ for the initial-state were estimated from solubility data of model substrates (cf. Chapter 3). The standard molar enthalpy and entropy of transfer, $[\Delta([x_2=0] \rightarrow x_2)H^\Phi$ and $\Delta([x_2=0] \rightarrow x_2)S^\Phi]$ from water to '2BE + water' mixtures at $x_{BE} = 0.02$, increased and a positive partial molar heat capacity of transfer, $[\Delta([x_2=0] \rightarrow x_2)Cp_2^\Phi]$, was obtained. The following pseudo-phase separation model was proposed.

In the region $x_{BE} = 0.02$, the '2BE + water' mixture begins to form water-rich and 2BE-rich microphases (cf. reference 13). The microphases were not considered as separate phases but as aggregates of the hydrophobic cosolvent. Estimates were made for rate constants and $\Delta^+H^\Phi$ for reaction in each microphase. The large positive $\Delta^+Cp^\Phi$ at $x_{BE} = 0.02$ could be explained by a temperature dependent partitioning of the substrate between the two microphases.

This theory is consistent with the observations that large, positive $\Delta^+Cp^\Phi$ were not detected at other mole fractions of 2BE. At $x_{BE} = 0.005$, there is insufficient 2BE to form 2BE-rich microphases. $\Delta^+H^\Phi$ and $\Delta^+S^\Phi$ are smaller than the corresponding values in water, as a result of hydrophobic interactions between the substrate and 2BE.

At $x_{BE} = 0.05$ to 0.10, all the substrate is dissolved in 2BE, which results in no deviations from a linear plot of $\ln(k_{obs}/T)$ vs $(1/T)$. The above theory also explains why the magnitude of $\Delta^+Cp^\Phi$ is related to substrate hydrophobicity.

Kanerva and Euranto$^{14}$ reported large positive $\Delta^+Cp^\Phi$ for the water-catalyzed hydrolysis of chloromethyldichloroacetate in '2BE + water'
mixtures at \( x_{BE} = 0.02 \) in the temperature range 298 to 313 K. The plot of \( \ln(k_{obs}/T) \) vs \( (1/T) \) was S-shaped at low temperatures, which resulted in positive \( \Delta^\circ Cp^\circ \) at high temperatures (298-313 K) changing to negative \( \Delta^\circ Cp^\circ \) at low temperatures (275.5 - 298 K). Holtermann and Engberts\(^{12}\) rationalised these observations in terms of their pseudo-phase separation model. At low temperatures phase separation would start at higher mole-fractions of 2BE. Therefore, at \( x_{BE} = 0.02 \) at low temperatures there would be hardly any 2BE-rich microphases, which would result in no apparent positive contribution to the negative \( \Delta^\circ Cp^\circ \). At \( x_{BE} = 0.025 \), the plot of \( \ln(k_{obs}/T) \) vs \( (1/T) \) is also S-shaped. The change from negative \( \Delta^\circ Cp^\circ \) to positive \( \Delta^\circ Cp^\circ \) occurred at 280.5 K in this latter system. This latter pattern is consistent with the pseudo-phase separation model, i.e. at 280.5 K the concentration of 2BE-rich microphases at \( x_{BE} = 0.025 \) is significant.

Further kinetic evidence for the pseudo-phase separation model in water-rich '2BE + water' mixtures is presented in this Chapter. The evidence is based on data for aquation of Fe(hxsbH)\(^{2+}\) in '2BE + water' mixtures in the range \( x_{BE} = 0.002 \) to 0.1. Also kinetic data for aquation of Fe(phen)\(_3\)\(^{2+}\) and reactions with hydroxide and cyanide ions are reported in '2BE + water' mixtures at \( x_{BE} = 0.8 \) and 0.9.

Kinetics for aquation of Fe(hxsbH)\(^{2+}\) in 'ethanol + water' mixtures and 't-BuOH + water' mixtures at \( x_2 = 0.05 \) and 0.1 are examined. These data allow a comparison to be made between kinetics of reaction in the latter systems and in water-rich '2BE + water' mixtures.

8.2 EXPERIMENTAL

(1) Fe(hxsbH)\(^{2+}\)

Concentrated aqueous solutions of Fe(hxsbH)\(^{2+}\) as the chloride salt
were prepared. Rates of aquation reactions of Fe(hxsH)\textsuperscript{2+} were monitored in water-rich '2BE + water' mixtures where x\textsubscript{BE} = 0.002, 0.006, 0.01, 0.016, 0.025, 0.05, 0.075 and 0.1. Aquation reactions were monitored in solutions containing high and low concentrations of sulphuric acid, 6.29 \times 10^{-3} \leq \text{[sulphuric acid]} \leq 0.553 \text{ mol dm}^{-3}. In all systems \text{[complex]} \leq 10^{-4} \text{ mol dm}^{-3} and the sulphuric acid concentration was sufficient to protonate the Schiff base ligand and prevent recombination of the iron complex (i.e. in all systems the aquation reactions went to completion).

In all systems kinetic data for aquation reactions were monitored at 298 K. In mixtures where x\textsubscript{BE} = 0.025, kinetic data were also monitored at 308 K and 316 K, and in mixtures where x\textsubscript{BE} = 0.05, kinetic data were also monitored at 316 K.

An aqueous solution of Fe(hxsH)\textsuperscript{2+} is deep blue-purple with \( \lambda_{\text{max}} = 612 \text{ nm} \) and \( \varepsilon_{612} = 614 \text{ m}^2 \text{ mol}^{-1} \). No shift in \( \lambda_{\text{max}} \) was observed when the complex was dissolved in '2BE + water' mixtures.

Repeat scans of the dependence of absorbance on wavelength (Unicam SP800 spectrophotometer - Chapter 2, Section 2.4.1), revealed that in certain '2BE + water' mixtures the absorbance decreased regularly with time (Fig. 8.5), indicating zero-order kinetics. In other '2BE + water' mixtures the dependence of absorbance on time followed a pattern consistent with first-order kinetics.

Kinetics of reaction were monitored at 612 nm (Unicam SP1800 spectrophotometer - Chapter 2, Section 2.4.1). Logging procedures of absorbance as a function of time recorded a pre-set number of data points at specified time intervals. In each experiment absorbance-time data were logged until the reaction was essentially complete in order to fully characterise the reaction. When data logging was complete, the data
FIGURE 8.5
Dependence of absorbance on wavenumber at time intervals of 200s for aquation reactions of Fe(hxshb)²⁺ in '2-butoxyethanol + water' mixtures where $X_{2BE} = 0.05$ and [sulphuric acid] = $7.2 \times 10^{-3}$ mol dm⁻³ at 298 K.
were analysed either in terms of first-order expressions (Chapter 2, Section 2.3) or in terms of Scheme (IV) (Chapter 7, Section 7.3(iv), equation 7.28 and 7.40). Comparison between the observed absorbances, $P_{\text{obs}}$, and the calculated absorbances, $P_{\text{calc}}$, was aided by presenting the output on the HP7245A plotter.

Kinetics of aquation reactions of Fe(hxsbH)$^{2+}$ at 298 K in 't-BuOH + water' mixtures and 'EtOH + water' mixtures where $x_2 = 0.05$ and 0.1 and $8.54 \times 10^{-3} \leq [\text{H}_2\text{SO}_4] \leq 8.54 \times 10^{-2}$ mol dm$^{-3}$ were monitored in analogous fashion.

(i) Fe(phen)$_3$$^{2+}$

Concentrated aqueous solutions of Fe(phen)$_3$$^{2+}$ as the sulphate salt were prepared [Chapter 7, Section 7.2(i)].

Kinetics of aquation reactions of the complex were monitored in '2BE + water' mixtures where $x_{2BE} = 0.8$ and [sulphuric acid] = $1.66 \times 10^{-2}$ mol dm$^{-3}$. Kinetics of reactions of the complex with hydroxide ions were monitored in mixtures where $x_{2BE} = 0.8$ and 0.9 and $1.5 \times 10^{-3} \leq [\text{sodium hydroxide}] \leq 3.3 \times 10^{-2}$ mol dm$^{-3}$. For reactions of Fe(phen)$_3$$^{2+}$ with cyanide ions in mixtures where $x_{2BE} = 0.8$ and 0.9 and [potassium cyanide] = $3.3 \times 10^{-3}$ mol dm$^{-3}$, no kinetic data could be obtained because the reaction was complete within a second or two of mixing the reagents.

Kinetic data in all systems were monitored at 298 K where [Fe(phen)$_3$$^{2+}$] $\ll 10^{-4}$ mol dm$^{-3}$ and [nucleophile] $\gg$ [complex]. Repeat scans of the dependence of absorbance on wavelength (Unicam SP800 spectrophotometer - Chapter 2, Section 2.4.1) revealed that, in all systems, the dependence of absorbance on time was first-order. Kinetics of reaction were monitored at $\lambda_{\text{max}} = 510$ nm (Unicam SP1800 spectrophotometer - Chapter 2, Section 2.4.1) and the absorbance data were fitted to a first-order kinetic expression (Chapter 2, Section 2.3).
8.3 RESULTS AND DISCUSSION

8.3.1 Aquation reactions of Fe(hxsH)$^{2+}$

Kinetic data for aquation reactions in water-rich '2BE + water', 'EtOH + water' and 't-BuOH + water' mixtures are reported in Table 8.1. Reactions for which kinetic data could be satisfactorily described by a first-order rate constant (Chapter 2, Section 2.3) are reported in Table 8.1(i). Reactions for which kinetic data were fitted satisfactorily using Scheme IV (Chapter 7, Section 7.3(iv), equations 7.28 and 7.40) are reported in Table 8.1(ii).

Each kinetic parameter reported in Table 8.1 is the mean of at least three individual determinations. The standard error on time, $t$, in each kinetic run was better than ±0.05 s. The first-order analysis (Chapter 2, Section 2.3) was modified to give the error on time, $t$, as well as on absorbance, $P$, in order to compare the effectiveness of each scheme in describing the kinetics of reaction for a given system. In one calculation the standard error on $P$ assuming true times was obtained, whereas in another analysis, the standard error on time was calculated, assuming true absorbances.

The kinetic pattern outlined in Scheme IV (i.e. a significant zero-order contribution to the overall kinetics) is favoured near the start of a reaction and by a low concentration of acid. Therefore, many of the aquation reactions at a given mole fraction of organic cosolvent were monitored at both high and low acid concentration.

In '2BE + water' mixtures where $x_{BE} = 0.002$ the reactions followed first-order kinetics in [complex] at high and low acid concentration, 0.985 and $9.85 \times 10^{-3}$ mol dm$^{-3}$ respectively. The rate constant, $k_{obs}$, was linearly dependent on acid concentration. $k_{obs}$ increased regularly as the acid concentration increased (Fig. 8.6). Rate constants for
FIGURE 8.6
Dependence of first-order rate constants on [sulphuric acid] for aquation reaction of Fe(hxsbH)²⁺ in '2-butoxyethanol + water' where x₂BE = 0.002 at 298 K.

aquation where x_BE = 0.002 and in pure water (Chapter 7, Section 7.4.4, Table 7.5) were almost identical. In mixtures where x_BE = 0.006 and [sulphuric acid] = 9.58 × 10⁻² mol dm⁻³ the reaction followed first-order kinetics in [complex].

In the range 0.01 ≤ x_BE ≤ 0.1 the kinetic pattern was different. When x_BE = 0.01 and [sulphuric acid] = 9.31 × 10⁻² mol dm⁻³, kinetics of reaction conformed to Scheme IV. Similarly, when x_BE = 0.016 and 0.025 and [sulphuric acid] = 8.94 × 10⁻² and 8.42 × 10⁻² mol dm⁻³ respectively, the kinetics of reaction followed Scheme IV (Fig. 8.7).
FIGURE 8.7
(i) Dependence of absorbance on time at $\lambda_{\text{max}} = 612 \text{ nm}$ and (ii) dependence of $\gamma$ on $(P-P_{\infty})$ (equation 7.40), for aquation reactions of Fe(hxshb)$^2$ in '2-butoxyethanol + water' at 298 K where $x_{\text{BE}} = 0.016$ and [sulphuric acid] $= 8.94 \times 10^{-2}$ mol dm$^{-3}$. The full line represents the calculated curve using equation 7.28. (-----) represents the zero-order contribution in the event that $\beta_1=0$ and $\beta_2 \neq 0$ and (----) represents the first-order contribution in the event that $\beta_1 \neq 0$ and $\beta_2 = 0$. 
In mixtures where \( x_{BE} = 0.05 \) and [sulphuric acid] = \( 7.2 \times 10^{-3} \) and \( 7.2 \times 10^{-2} \) mol dm\(^{-3} \) the zero-order contribution in Scheme IV was significant [Figs. 8.8(a) and 8.8(b)]. The lower the acid concentration the more marked was the zero-order contribution. The fraction of sites, \( \gamma \), at the interphase occupied by the substrate at the start of the reaction \( (P_0) \) (Chapter 7, Section 7.3(iv), equation 7.40) was informative in displaying the contribution of the zero-order term described by Scheme IV. This contribution increased as \( \gamma \) increased. In mixtures where \( x_{BE} = 0.05 \) and [sulphuric acid] = \( 7.2 \times 10^{-2} \) mol dm\(^{-3} \), \( \gamma \) at \( P_0 \) = 0.46; when [sulphuric acid] = \( 7.2 \times 10^{-3} \) mol dm\(^{-3} \), \( \gamma \) at \( P_0 \) = 0.74. However, in systems where \( x_{BE} = 0.05 \) and [sulphuric acid] = 0.72 mol dm\(^{-3} \), no zero-order contribution in the kinetics of aquation was detected and kinetics were first-order in [complex] (Fig. 8.8g).

A similar pattern emerged in the kinetics of reaction in mixtures where \( x_{BE} = 0.075 \). When the acid concentration was low, \( 6.29 \times 10^{-2} \) and \( 6.29 \times 10^{-3} \) mol dm\(^{-3} \), the kinetics of reaction conformed to Scheme IV, but at high acid concentration, 0.629 mol dm\(^{-3} \), the kinetics of reaction were first-order in [complex]. \( \gamma \) at \( P_0 \) was 0.52 and 0.79 when [sulphuric acid] = \( 6.29 \times 10^{-2} \) and \( 6.29 \times 10^{-3} \) mol dm\(^{-3} \) respectively.

In mixtures where \( x_{BE} = 0.01 \), the kinetics of aquation conformed to Scheme IV, when [sulphuric acid] = 0.553 and \( 5.53 \times 10^{-2} \) mol dm\(^{-3} \). The kinetic pattern was consistent with the trends identified above.

In contrast the kinetics of aquation were first-order in [complex] in 'EtOH + water' and 't-BuOH + water' mixtures where \( x_2 = 0.1 \) and 0.05 and 8.54 \( \times 10^{-3} \) \( \lesssim \) [sulphuric acid] \( \lesssim 8.54 \times 10^{-2} \) mol dm\(^{-3} \).

According to Scheme IV, the zero-order contribution is dependent on acid concentration. When kinetics of a reaction follow a first-order dependence, it is impossible to differentiate between the kinetics.
FIGURE 8.8

(i) Dependence of absorbance on time at \( \lambda_{\text{max}} = 612 \text{ nm} \) and (ii) dependence of \( \gamma \) on \((P-P_\infty)\) (equation 7.40) for aquation reactions of Fe(hoxsbH)\(^2+\) in '2-butoxyethanol + water' mixtures containing different concentrations of sulphuric acid at 298 K where \( x_{\text{BE}} = 0.05 \).

(a) [sulphuric acid] = 7.2 \times 10^{-3} \text{ mol dm}^{-3}; (b) [sulphuric acid] = 7.2 \times 10^{-2} \text{ mol dm}^{-3}. In (a) and (b) the full line represents the calculated curve using equation 7.28. (...) represents the zero-order contribution in the event that \( \beta_1=0 \) and \( \beta_2=0 \) and (---) represents the first-order contribution in the event that \( \beta_1=0 \) and \( \beta_2=0 \).
FIGURE 8.8(c)

[Sulphuric acid] = 0.72 mol dm$^{-3}$. The data points follow a pattern required by first order dependence.
following Scheme I, [Chapter 7, Section 7.3(i)], a simple one-stage reaction with no adsorption phenomena or Scheme IV, in which there is negligible zero-order contribution. However, once the kinetics of a reaction have been identified in terms of Scheme IV at a particular acid concentration and a particular mole fraction of 2BE, it can be confidently concluded that the aqueous mixture is microheterogeneous.

For systems where the kinetics of reaction change from conforming to Scheme IV at low acid concentration to following a first-order dependence at high acid concentration, it seems unlikely that the kinetic scheme has changed from Scheme IV to Scheme I. In other words, when a system has been shown to be microheterogeneous by the kinetics of reaction at low acid concentration, all reactions follow Scheme IV even though at high acid concentration the dependence of absorbance on time may be first-order in [complex]. When [sulphuric acid] $> 0.629$ mol dm$^{-3}$ the zero-order contribution in Scheme IV was negligible and kinetics of reaction were first-order. When [sulphuric acid] $< 0.553$ mol dm$^{-3}$, the zero-order contribution was often significant and kinetics of reaction were satisfactorily analysed in terms of Scheme IV. If a reaction followed first-order kinetics when [sulphuric acid] $< 0.553$ mol dm$^{-3}$, Scheme I was in operation. Therefore, using the kinetic data for aquation reactions of Fe(hxsbH)$^{2+}$ as a probe, the criteria which emerged, for identifying microheterogeneity in 'organic cosolvent + water' mixtures, was that the kinetics of reaction followed Scheme IV when [sulphuric acid] $< 0.553$ mol dm$^{-3}$.

Three further aquation reactions were studied in water-rich '2BE + water' mixtures. When $x_{BE} = 0.025$ and $8.42 \times 10^{-3} < [\text{sulphuric acid}] < 8.42 \times 10^{-2}$ mol dm$^{-3}$, the kinetics of aquation were monitored at 308 K and 316 K. In both systems the kinetic data conformed to Scheme IV.
At 308 K and [sulphuric acid] = 8.42 × 10^{-2} mol dm^{-3}, γ at P₀ was 0.37.
At 316 K and [sulphuric acid] = 8.42 × 10^{-3} mol dm^{-3}, γ at P₀ was 0.74.

In mixtures where x_{BE} = 0.05 and [sulphuric acid] = 7.2 × 10^{-2} mol dm^{-3}, kinetics of aquation were monitored at 316 K. The kinetic data were fitted satisfactorily to Scheme IV in this latter system (Fig. 8.9), with γ at P₀ = 0.42. The total reaction time decreased when the temperature was raised.

8.3.2 Reactions of Fe(phen)₃²⁺

The kinetics of aquation of Fe(phen)₃²⁺ and reactions with hydroxide and cyanide ions were monitored in 2BE-rich '2BE + water' mixtures where x_{BE} = 0.8 and 0.9. In all systems where kinetic data were collected the reactions were first-order in [complex]. Kinetic data are reported in Table 8.2. Each rate constant is the mean of at least three individual determinations, the reproducibility being at worst (i.e. for the fastest reactions) within 5%.

The first-order rate constant for aquation in the mixture where x_{BE} = 0.8 and [sulphuric acid] = 1.66 × 10^{-2} mol dm^{-3}, was 2.39 × 10^{-6} s^{-1}, reflecting an increase of a factor of approximately 3 over the corresponding rate constant in water (i.e. 7.33 × 10^{-5} s^{-1}).

The first-order rate constants, k_{obs}, for reaction with hydroxide ions in mixtures where x_{BE} = 0.8 and 0.9 show a dramatic increase, a factor of 10³, relative to the corresponding rate constants in water. For reaction in a mixture where x_{BE} = 0.8 and [sodium hydroxide] = 3.3 × 10^{-2} mol dm^{-3}, k_{obs} = 3.27 × 10^{-1} s^{-1}, cf. in water at [sodium hydroxide] = 3.3 × 10^{-2} mol dm^{-3}, the predicted k_{obs} = 3.56 × 10^{-4} s^{-1}.

Reactions of Fe(phen)₃²⁺ with cyanide ions in mixtures where x_{BE} = 0.8 and 0.9 and [potassium cyanide] = 3.3 × 10^{-3} mol dm^{-3}, were too fast to be able to monitor kinetic data. The red colour of the complex di-
FIGURE 8.9
(i) Dependence of absorbance on time at $\lambda_{\text{max}} = 612 \text{nm}$ and (ii) dependence of $\gamma$ on $(P-P_\infty)$ (equation 7.40, for aquation reactions of Fe(hxsBH)$_2^+$ in '2-butoxyethanol + water' where $x_{2B} = 0.05$ and [sulphuric acid] = $7.2 \times 10^{-2}$ mol dm$^{-3}$ at 316 K. The full line represents the calculated curve using equation 7.28.
appeared almost immediately on mixing the reagents. From these qualitative observations it was concluded that the rates of reaction of Fe(phen)$_3^{2+}$ with cyanide ions in the two systems were accelerated by a factor of $>10^3$ relative to the corresponding rate$^{17}$ of reaction in water.

The increase in rate constants relative to the corresponding rate constants in water for reactions of Fe(phen)$_3^{2+}$ in these systems is analogous to that observed in microemulsions A and B (Chapter 7).

8.4 CONCLUSION

The kinetics of aquation reactions of Fe(hxsbH)$_2^{2+}$ were used as a probe in water-rich '2BE + water', to identify regions which are microheterogeneous, i.e. regions in which water-rich and 2BE-rich microphases co-exist. In Chapter 7, kinetics of various reactions in microemulsions were studied. It was observed (Section 7.5) that zero-order kinetics pointed to complexities, where some new factor controlled the reaction rate. A large proportion of the total concentration of Fe(hxsbH)$_2^{2+}$ was regarded as being adsorbed in the interfacial region between water-rich and hydrocarbon-rich domains within the microemulsions. Scheme IV was developed to account for the trends in kinetic data observed for the various reactions. In terms of Scheme IV, adsorption and desorption of the substrate occurred in the interfacial region. If Scheme IV is accepted as representing kinetics of reaction in a microheterogeneous environment, systems, where kinetics of reaction conform to Scheme IV, are probably microheterogeneous.

Under conditions where, in water-rich '2BE + water' mixtures, kinetics of aquation of Fe(hxsbH)$_2^{2+}$ conformed to Scheme IV, these mixtures were regarded as microheterogeneous. A proportion of the total concentration
of Fe(hxsbaH)\(^{2+}\) is adsorbed at the interface between water-rich and 
2BE-rich microphases.

In mixtures where \(x_{2BE} = 0.002\) and \(0.006\), no microheterogeneity was 
detected from the kinetic data for aquation of Fe(hxsbaH)\(^{2+}\). It was 
concluded that these mixtures are 'typically aqueous' (Chapter 1, 
Section 1.3).

Over the range \(x_{2BE} = 0.01\) to \(0.1\), kinetic evidence pointed to the 
presence of microheterogeneities formed by regions of water-rich and 
2BE-rich microphases. Holtermann and Engberts\(^{12}\) postulated that 
significant amounts of microphase exist over the range \(0.012 < x_{2BE} <
0.014\). The kinetic evidence described above points to significant 
amounts of microphase at \(x_{2BE} = 0.01\). Nevertheless, in broad terms, the 
conclusions reached here and by Holtermann and Engberts are in agreement.

When the temperature is raised the extent of microheterogeneity in 
water-rich '2BE + water' mixtures increases.\(^{12}\) Therefore, the kinetics 
of aquation of Fe(hxsbaH)\(^{2+}\) were investigated at higher temperatures. 
However, quantitative treatment of the data is complicated. The 
kinetics of reaction according to Scheme IV are: [Chapter 7, Section 
7.3(iv)].

\[
\begin{align*}
M + C & \xrightarrow{k_7} MC & \text{(IV(a))} \\
MC + X & \xrightarrow{k_9} C + \text{products} & \text{(IV(b))}
\end{align*}
\]

\(M\) is the reacting solute, \(C\) is the concentration of sites for adsorption 
in the interfacial region and \(X\) is the attacking reagent. A substantial 
zero-order contribution requires that \(k_7[M] > (k_8 + k_9[X])\). \(k_7[M]\) 
represents adsorption of \(M\) at the interfacial site and \(k_9[X]\) represents 
reaction to produce products. When the temperature is raised, even 
though the extent of microheterogeneity increases producing more sites

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for adsorption, both $k_7$ and $k_8$ are likely to increase. $k_9$ will also increase with temperature. Therefore, overall, no dramatic change occurs in the zero-order contribution as the temperature is increased.

In contrast, kinetics of aquation of Fe(hxsh)$_2^+$ in water-rich 'EtOH + water' and 't-BuOH + water' mixtures at $x_2=0.05$ and 0.1 revealed no complexity and no evidence for microheterogeneity.

In '2BE + water' mixtures where $x_{BE}=0.8$ and 0.9, there is little likelihood of microheterogeneity. The dramatic increase in rate constants for reaction of Fe(phen)$_3^{2+}$ with hydroxide and cyanide ions, although comparable to the trend in rate constants for reactions in microemulsions, are accounted for in terms of a large destabilisation of hydroxide and cyanide ions relative to water, or a large positive transfer chemical potential from water to '2BE + water' where $x_{BE}=0.8$ and 0.9 [cf. $\Delta([x_2=0]+x_2)^{\mu^\#}$ for hydroxide and cyanide ions in 'MeOH + water' mixtures (Chapter 3), and '2-PrOH + water' mixtures (Chapter 4)].
REFERENCES TO CHAPTER 8


CHAPTER
9

Reactions of iron(II) 4,7-dimethyl, 1,10-phenanthroline and iron(II) 3,4,7,8-tetramethyl, 1,10-phenanthroline with hydroxide ions in two, neutral, water-in-oil microemulsions
9.1 INTRODUCTION

Kinetic data are reported for reactions of iron(II), 4,7-dimethyl-1,10-phenanthroline [Fe(4,7-Me₂phen)₃²⁺] and iron(II), 3,4,7,8-tetramethyl-1,10-phenanthroline [Fe(3,4,7,8-Me₄phen)₃²⁺], with hydroxide ions in two neutral water-in-oil microemulsions. A comparison is drawn between kinetic data for reactions of these complexes with hydroxide ions and the corresponding data for reactions of iron(II), 5-nitro-1,10-phenanthroline [Fe(5-NO₂phen)₃²⁺] and iron(II), 1,10-phenanthroline [Fe(phen)₃²⁺] in two neutral water-in-oil microemulsions. Kinetic data for the latter two complexes are reported in Chapter 7.

The four complexes, Fe(5-NO₂phen)₃²⁺, Fe(phen)₃²⁺, Fe(4,7-Me₂phen)₃²⁺ and Fe(3,4,7,8-Me₄phen)₃²⁺ make an interesting series in that the hydrophobic nature and size of the ligands increases. Another interesting feature is that, relative to Fe(phen)₃²⁺, Fe(5-NO₂phen)₃²⁺ contains an electron withdrawing nitro-substituent, whereas the methyl substituents in the other complexes are electron donating.

(4,7-Me₂phen) and (3,4,7,8-Me₄phen) ligands are depicted in I and II respectively:

(I) 4,7-Me₂phen ligand

(II) 3,4,7,8-Me₄phen ligand

The mechanism of reaction of Fe(phen)₃²⁺ with hydroxide ions in aqueous solution is discussed in Chapter 1, Section 1.6.1. Effects of substituents on rates of hydroxide attack at Fe(X-phen)₃²⁺ in aqueous solution (X = substituent) are reviewed below because of their importance in analysing kinetic data for reactions involving Fe(X-phen)₃²⁺ complexes.
in the microemulsions.

There are at least five distinct processes by which a substituent can affect a distant reaction centre;¹

(a) The electric dipole field of the polar substituent-substrate bond influences the reaction centre across space (field effect);

(b) The primary inductive effect is transmitted to the reaction centre by successive polarisation of intervening σ-bonds;

(c) The electrostatic charge set up at a conjugated atom adjacent to the substituent polarises the corresponding π-electron system. The resulting charges set up in the π-electron system influences the reaction centre by a field effect or by secondary polarisation of intervening σ-bonds;

(d) The π-electron system is polarised by resonance interactions with the substituent;

(e) Mutual conjugation occurs between the substituent and reaction centre through an intervening conjugated system.

For Fe(X-phen)₃²⁺, where X is the substituent, there are three effects² which a substituent may have on the activation energies and hence rates of reaction with hydroxide ions in aqueous solution;

(i) changes in the σ-bonding between iron and nitrogen, (ii) changes in the π-bonding between iron and nitrogen and (iii) changes in the electron density around the iron atom. These latter three effects depend on the electron-withdrawing or -donating properties of the substituent, X.

π-Bonding is especially significant in 1,10-phenanthroline complexes (Chapter 1, Section 1.6). A substituent which is electron-withdrawing weakens the iron-nitrogen σ-bond, but strengthens the π-bonding. The converse applies for an electron donor.³ The relative magnitudes of

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these two opposing effects depends on whether the substituent affects primarily σ- or π-bonds.

With the exception of the 5-nitro complex, a similar dependence of the first-order rate constant on hydroxide-ion concentration in aqueous solution is observed for the substituted complexes and for the parent Fe(phen)$_3^{2+}$ complex ion (Chapter 1, Section 1.6.1). The rate constant, $k_{\text{obs}}$, is related to the hydroxide-ion concentration by:

$$k_{\text{obs}} = k_1 + k_2[\text{OH}^-]$$

The $k_1$-term is assigned to rate-determining dissociation of the complex; the $k_2$-term to associative reaction with hydroxide ions.

The dependence of kinetics of reaction of Fe(5-NO$_2$phen)$_3^{2+}$ on sodium hydroxide concentration is consistent with the formation of an intermediate (Chapter 7, Section 7.1).

Substituents affect the two reaction pathways in different ways. For the dissociative process the activation energies of the 5-nitro substituted and unsubstituted complexes are significantly different, and can be satisfactorily explained in terms of substituent effects on the iron-nitrogen σ-bond. Electron withdrawal by the nitro-group leads to a weaker σ-bond and lower activation energy.

The 4,7-dimethyl complex has an activation energy for dissociation significantly lower than that for the unsubstituted complex. Both π-inductive and hyperconjugative effects are important, the latter especially so as the 4- and the 7- position are para to the nitrogen atoms. Both effects decrease π-bonding but increase σ-bonding. As both effects are primarily of a π-nature, the decrease in π-bonding is dominant, consistent with the low activation energy.

Kinetic data in aqueous solution for aquation reactions and reaction with hydroxide ions of the 3,4,7,8-tetramethyl complex are reported.
Substituent effects on the dissociation process and the hydroxide dependent path are discussed in the appropriate section (Section 9.4.1).

Effects of substituents on the associative reaction with hydroxide ions are different to the effects described above for dissociation. Greater electron-withdrawal by a substituent, leaving the iron more positive, should facilitate attack by negatively charged hydroxide ions. Thus the activation energy for hydroxide attack on the 5-nitro complex is significantly lower than that for Fe(phen)$_3^{2+}$. The lowering in activation energy coupled with the evidence for formation of an intermediate (Chapter 7, Section 7.1), is consistent with the electron-withdrawing properties of the nitro-group, encouraging nucleophilic hydroxide attack at the iron atom.

For methyl-substituted complexes the activation energy for hydroxide attack is, in all cases, higher than for Fe(phen)$_3^{2+}$, the activation energy increasing with increasing methyl substitution. The magnitude of methyl substituent effects depends on the position of substitution. The effect on basicity can be explained by electron release from the methyl groups. Such electron release, in the case of alkali fission, increases the electron density in the neighbourhood of the iron atom and makes hydroxide attack more difficult. Maximum effect is observed for methyl substitution at the 4- and 7- position, which are para to the nitrogen atoms.

All Fe(X-phen)$_3^{2+}$ substituents are well removed from the reaction centre and should therefore not interfere sterically. Models with adjacent methyl groups on the 1,10-phenanthroline ligand show that steric effects due to adjacent methyl groups are not significant. However, kinetically significant "buttressing" effects have been ascribed to methyl groups adjacent to one another in the benzene nucleus. There-
fore, if any distortions are relieved in the transition state, a lowering of activation energy is possible.

Kinetic data for reactions of Fe(3,4,7,8-Me₄phen)₃²⁺ with hydroxide ions in two neutral water-in-oil microemulsions with added surfactant, SDS and CTAB, are also reported.

9.2 EXPERIMENTAL

Concentrated aqueous solutions of Fe(4,7-Me₂phen)₃²⁺ and Fe(3,4,7,8-Me₄phen)₃²⁺ were prepared as the sulphate salts (Chapter 7, Section 7.2).

Kinetics of reaction of the two complexes were monitored in two neutral water-in-oil microemulsions, MEA⁴ and MEB⁵ (Chapter 7, Section 7.2).

Reactions in MEA and MEB were monitored at 298 K. In all systems [complex] ≪ 10⁻⁶ mol dm⁻³ and [sodium hydroxide] ≫ [complex]. Reactions were monitored at several different concentrations of sodium hydroxide. In MEB the sodium hydroxide concentration had to be kept between the limits 3 × 10⁻⁶ < [sodium hydroxide] < 3 × 10⁻³ mol dm⁻³ (Chapter 7, Section 7.2).

Aqueous solutions of both complexes are bright red with λ_max = 512 nm. No shift in λ_max was observed when the complexes were dissolved in the microemulsions. Repeat scans of the dependence of absorbance on wavelength (Unicam SP800 spectrophotometer - Chapter 2, Section 2.4.1), revealed that the dependence of absorbance on time, for certain reactions, was not first-order. The absorbance decreased rapidly initially on addition of sodium hydroxide and then followed a much slower decay [Figs. 9.1(i) and (ii)]. The dependence of absorbance on time corresponded to a very fast initial process followed by a much slower step. Various
FIGURE 9.1(a)
Dependence of absorbance on wavenumber at time intervals of 100s for reaction of Fe(4,7-Me$_2$phen)$_3^{2+}$ with hydroxide ions in ME.A. where [sodium hydroxide] = 2.97 x 10$^{-3}$ mol dm$^{-3}$ at 298 K.
FIGURE 9.1(b)

Dependence of absorbance on wavenumber at time intervals of 100s for reaction of Fe(3,4,7,8-phen)₃⁺ with hydroxide ions in MgB, where [sodium hydroxide] = 2.11 x 10⁻⁵ mol dm⁻³ at 296 K.
kinetic schemes were examined in light of this discovery and new programs developed for the HP9825A computer. Kinetics of reaction were monitored at 512 nm (Unicam SP1800 spectrophotometer - Chapter 2, Section 2.4.1). Logging procedures of absorbance as a function of time were designed to record a pre-set number of data points at specified time intervals. The first thirty data points were recorded at very short time intervals to fully characterise the rapid initial process and the subsequent data points were recorded with longer time intervals between readings. After data-time logging was completed, several options were available for analysing the data. One of the options was a first-order analysis. Comparison between actual absorbance readings, $P_{obs}$, and calculated absorbances, $P_{calc}$, was aided by presenting the output on the HP7245A plotter. The success or failure of the chosen method was decided on the basis of these latter plots and from comparison of statistical parameters, e.g. standard errors, emerging from Least Squares fitting procedures to the kinetic equations.

The dependence of absorbance on time for reactions of Fe(4,7-Me$_2$phen)$_3^{2+}$ in MEA followed a pattern consistent with first-order kinetics. Kinetic data for the latter reactions were monitored at 512 nm and logging procedures were controlled by the computer (Chapter 2, Section 2.4.1). The absorbance data were fitted to a first-order kinetic expression (Chapter 2, Section 2.3).

Kinetic data were monitored for reactions of Fe(3,4,7,8-Me$_4$phen)$_3^{2+}$ with hydroxide ions in MEA and MEB with added surfactant, SDS and CTAB. In some reactions, absorbance data were fitted satisfactorily to a first-order dependence. In other reactions the dependence of absorbance on time corresponded to a fast initial process followed by a much slower reaction. Kinetic data were collected in analogous fashion to the
Dependence of absorbance on time for aquation reactions and reactions with hydroxide ions of Fe(3,4,7,8-Me4phen)$_3^{2+}$ in aqueous solution were consistent with first-order kinetics. Kinetic data were collected using the procedure described above for reactions where kinetic rates follow a first-order dependence.

9.3 ANALYSIS

Presentation of results and discussion of their significance are facilitated if, at this stage, the kinetic scheme described below is considered. Attention is concentrated on accounting for the dependence on time of the absorbance at fixed wavelength characteristic of the metal complex.

**Scheme V**

Scheme V is an extension of Scheme II [Chapter 7, Section 7.3(ii)].

Reaction between metal complex, M, and say, X, in solution, may proceed in two stages as;

\[
M + X \xrightarrow{k_1'} \frac{k_1}{k_2} \xrightarrow{k_3} \text{products, C} \quad \ldots \quad (\text{IIa})
\]

where I is the intermediate. In the limit that $[X] \gg [M]$, with $k_1 = k_1'[X]$, the Scheme can be simplified;

\[
M \xrightarrow{k_1}{\atop k_2} I \xrightarrow{k_3}{\atop k_2} C \quad \ldots \quad (\text{IIb})
\]

Then from equation (IIb);

\[
\frac{dM}{dt} = -k_1[M] + k_2[I] \quad \ldots \quad (9.1)
\]

\[
\frac{dI}{dt} = k_1[M] - (k_2 + k_3)[I] \quad \ldots \quad (9.2)
\]

\[
\frac{dC}{dt} = k_3[I] \quad \ldots \quad (9.3)
\]
at time, t = 0, \( [M] = [M_0], \) \( [I] = [C] = 0. \)

From equation 9.2 using the method of Laplace Transforms;

\[
s. [I] = k_1 [M] - [I]. (k_2 + k_3)
\]  \( \ldots \) (9.4)

Where \( s = \frac{d}{dt} \)

Then \( [I] = \frac{k_1 [M]}{s + k_2 + k_3} \) \( \ldots \) (9.5)

From equation 9.1,

\[
s. [M] - s. [M_0] = -k_1 [M] + k_2 [I]
\]  \( \ldots \) (9.6)

Combining equations 9.5 and 9.6 yields;

\[
s. [M] - s. [M_0] = -k_1 [M] + \frac{(k_2 - k_1) [M]}{s + k_2 + k_3}
\]  \( s + k_2 + k_3 \) \( \ldots \) (9.7)

Equation 9.7 is rearranged to yield;

\[
s. [M_0]. (s + k_2 + k_3) = [M]. \left\{ s^2 + s (k_1 + k_2 + k_3) + k_1 k_3 \right\}
\]  \( \ldots \) (9.8)

Let;

\[
s^2 + s(k_1 + k_2 + k_3) + k_1 k_3 = (s + \gamma_1) (s + \gamma_2)
\]  \( \ldots \) (9.9)

Using \( \gamma = \left\{ \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \right\} \) for equation 9.9, where \( a = 1, b = (k_1 + k_2 + k_3), \) \( c = k_1 k_3, \) then;

\[
\gamma = \frac{1}{2} \left\{ -(k_1 + k_2 + k_3) \pm \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} \right\}
\]  \( \ldots \) (9.10)

Therefore, from equation 9.10;

\[
\gamma_1 = \frac{1}{2} \left\{ -(k_1 + k_2 + k_3) + \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} \right\}
\]  \( \ldots \) (9.11)

and \( \gamma_2 = \frac{1}{2} \left\{ -(k_1 + k_2 + k_3) - \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} \right\}
\) \( \ldots \) (9.12)

Combination of equations 9.11 and 9.12 yields;

\[
\gamma_1 + \gamma_2 = -(k_1 + k_2 + k_3)
\]  \( \ldots \) (9.13)

and \( \gamma_1 \gamma_2 = k_1 k_3 \) \( \ldots \) (9.14)

Combination of equations 9.8 and 9.9 yields;

\[
\frac{[M]}{[M_0]} = \frac{s(s + k_2 + k_3)}{(s + \gamma_1)(s + \gamma_2)}
\]  \( \ldots \) (9.15)

If equation 9.15 is the transform, then (from tables) the original is;
\[
\frac{[M]}{[M_0]} = \frac{(k_2 + k_3 - \gamma_1) \exp(-\gamma_1 t) + (k_2 + k_3 - \gamma_2) \exp(-\gamma_2 t)}{(\gamma_2 - \gamma_1) (\gamma_1 - \gamma_2)} \quad \cdots \ (9.16)
\]

Combining equations 9.5, 9.8 and 9.9 yields;

\[
\frac{[I]}{[M_0]} = \frac{s \cdot k_1}{(s + \gamma_1)(s + \gamma_2)} \quad \cdots \ (9.17)
\]

If equation 9.17 is the transform, the original is;

\[
\frac{[I]}{[M_0]} = \frac{k_1}{(\gamma_2 - \gamma_1)} \exp(-\gamma_1 t) + \frac{k_1}{(\gamma_1 - \gamma_2)} \exp(-\gamma_2 t) \quad \cdots \ (9.18)
\]

Combining equations 9.3 and 9.17 yields;

\[
\frac{[C]}{[M_0]} = \frac{s \cdot k_1 \cdot k_3}{(s + \gamma_1)(s + \gamma_2)} \quad \cdots \ (9.19)
\]

If equation 9.19 is the transform, the original is;

\[
\frac{[C]}{[M_0]} = k_1 \cdot k_3 \left[ \frac{1}{\gamma_1 \gamma_2} \exp(-\gamma_1 t) - \frac{1}{\gamma_1 (\gamma_2 - \gamma_1) \gamma_2 (\gamma_1 - \gamma_2)} \exp(-\gamma_2 t) \right] \quad \cdots \ (9.20)
\]

But combining equations 9.20 and 9.14 yields;

\[
\frac{[C]}{[M_0]} = 1 - \frac{\gamma_2}{(\gamma_2 - \gamma_1)} \exp(-\gamma_1 t) - \frac{\gamma_1}{(\gamma_1 - \gamma_2)} \exp(-\gamma_2 t) \quad \cdots \ (9.21)
\]

In the experiments reported in this Chapter, the course of the reaction was monitored by measuring the rate of disappearance of metal complex, M. Therefore, in this Section, attention is centred on equation 9.16. However, in Chapter 10 (and Appendix 1) the course of the reaction is monitored by measuring the rate of appearance of products, C, and equation 9.21 is relevant. Equations 9.18 and 9.21 have been included in this section for the sake of fully characterising the kinetics of reaction described by Scheme V.

Therefore, consider Scheme (IIb), in which kinetics of reaction are monitored by measuring the rate of disappearance of M. If \( k_1 \gg k_2 \), the dependence of \([M]\) on time, \( t \), is first order;

\[
[M] = [M_0^0] \exp(-k_1 t)
\]
and hence dependence of absorbance of M on time is first-order (Chapter 2, Section 2.3).

If $k_1 \gg k_2$ and either $k_1 \gg k_3$ or $k_3 \gg k_1$, the absorbance of M follows a first-order dependence on time.

For the case where disappearance of M follows equation 9.16 (i.e. $k_2 = k_1$), equation 9.16 can be simplified:

$$\frac{[M]}{[M_0]} = a_1 \exp(-\gamma_1 t) + a_2 \exp(-\gamma_2 t) \quad \ldots \quad (9.22)$$

where $a_1 = \frac{(k_2 + k_3 - \gamma_1)}{(\gamma_2 - \gamma_1)}$ and $a_2 = \frac{(k_2 + k_3 - \gamma_2)}{(\gamma_1 - \gamma_2)}$.

Both $\gamma_1$ and $\gamma_2$ are dynamic constants, having units of $s^{-1}$, and they are functions of the individual rate constants, $k_1$, $k_2$ and $k_3$. Equation 9.22 cannot be solved to yield the rate constants $k_1$, $k_2$ and $k_3$.

Combining equation 9.22 and Beer's Law equation (i.e. $P = [M].\varepsilon.\ell$) yields:

$$\frac{(P - P_\infty)}{(P_0 - P_\infty)} = a_1 \exp(-\gamma_1 t) + a_2 \exp(-\gamma_2 t)$$

or

$$P = P_\infty + (P_0 - P_\infty) \left(a_1 \exp(-\gamma_1 t) + a_2 \exp(-\gamma_2 t)\right)$$

or

$$P = a_3 + a_1 \exp(-\gamma_1 t) + a_2 \exp(-\gamma_2 t) \quad \ldots \quad (9.23)$$

where $a_3 = P_\infty; \quad a_1 = (P_0 - P_\infty).a_1; \quad a_2 = (P_0 - P_\infty).a_2$.

Hence at a given time, $t$, the absorbance, $P$, is defined by five variables:

$$P = P[a_3, a_1, a_2, \gamma_1, \gamma_2] \quad \ldots \quad (9.24)$$

The general differential of equation 9.24 is given by:

$$dP = \left(\frac{\partial P}{\partial a_3}\right) \cdot da_3 + \left(\frac{\partial P}{\partial a_2}\right) \cdot da_2 + \left(\frac{\partial P}{\partial a_1}\right) \cdot da_1 + \left(\frac{\partial P}{\partial \gamma_1}\right) \cdot d\gamma_1 + \left(\frac{\partial P}{\partial \gamma_2}\right) \cdot d\gamma_2$$

$$\ldots \quad (9.25)$$
From equation 9.23;

\[ \frac{\delta P}{\delta a_3} = 1 \]

\[ \frac{\delta P}{\delta a_1} = \exp(-\gamma_1 t) \]

\[ \frac{\delta P}{\delta a_2} = \exp(-\gamma_2 t) \]

\[ \frac{\delta P}{\delta \gamma_1} = -a_1 t \exp(-\gamma_1 t) \]

\[ \frac{\delta P}{\delta \gamma_2} = -a_2 t \exp(-\gamma_2 t) \]

The analysis followed the Wentworth method. Starting from estimated values of \( a_1, a_2, a_3, \gamma_1 \) and \( \gamma_2 \) the five derivatives were calculated at each absorbance, \( P \). A Linear Least-Squares procedure (Chapter 2, Section 2.3) calculated the correctors \( da_1, da_2, da_3, dy_1 \) and \( dy_2 \) and an iterative calculation refined the values of \( a_1, a_2, a_3, \gamma_1, \gamma_2 \).

It was important to measure the absorbances over times where first \( \gamma_1 \) and then \( \gamma_2 \) dominate the time dependence of \( P \), otherwise the Least-Squares Analysis allows one exponential term to dominate, assigning residual scatter to the other exponential term.

A fine balance is struck between \( \gamma_1 \) and \( \gamma_2 \) functions in equation 9.23, which produce a dependence of \( P \) on time that can be confidently assigned to equation 9.23. In the most favourable case, \( a_1 \) and \( a_2 \) should differ only slightly; \( \gamma_1 \) and \( \gamma_2 \) should differ by a factor of approximately ten. If \( a_1 \gg a_2 \), the dependence will be first-order. If \( \gamma_1 \) approaches \( \gamma_2 \) or if \( \gamma_1 \) is much smaller than \( \gamma_2 \), it is again difficult to identify the two contributions, if the data cover time intervals of the order of \( (1/\gamma_2) \). Another problem which arises is that, for many reactions, both \( a_1 \) and \( a_2 \) are functions of \( \gamma_1 \) and \( \gamma_2 \).
9.4 RESULTS AND DISCUSSION

Each rate constant reported in this Chapter is the mean of at least three individual determinations, the reproducibility of first-order rate constants being at worst within 5%.

9.4.1 Aquation reactions and reactions with hydroxide ions of Fe(3,4,7,8-Me₄phen)₃²⁺ in aqueous solution

In aqueous solution both kinetics of aquation reactions of Fe(3,4,7,8-Me₄phen)₃²⁺ and kinetics of reaction with hydroxide ions were first-order in [complex]. Kinetic data are reported in Table 9.1, together with the corresponding kinetic data for Fe(4,7-Me₂phen)₃²⁺, Fe(phen)₃²⁺ and Fe(5-NO₂phen)₃²⁺.

The temperature dependence of the rate constants for reactions of Fe(3,4,7,8-Me₄phen)₃²⁺ was not investigated. Therefore, no data for the activation energy for aquation or reaction with hydroxide ions of Fe(3,4,7,8-Me₄phen)₃²⁺ are available. Effects of adding two methyl groups in the 3,8-position are, therefore, discussed by a comparison of first-order rate constants at 298 K.

The first-order rate constant for aquation of Fe(3,4,7,8-Me₄phen)₃²⁺ is $2.26 \times 10^{-4}$ s⁻¹, reflecting an increase in rate constant by a factor of approximately 10.5 relative to the corresponding rate constant for Fe(4,7-Me₂phen)₃²⁺.

Methyl substituents decrease π-bonding and increase σ-bonding between iron and nitrogen. Further, the electron density around the nitrogen atoms is increased by inductive electron-release by methyl groups. In the 4,7-dimethyl complex, effects on π-bonding dominate because the methyl groups are para to the nitrogen. Methyl groups in the 3,8-position are less affected by hyperconjugative π-bond weakening.

Nevertheless, the significant increase in rate constant for acid fission
of the tetramethyl complex compared to the corresponding rate constant for the dimethyl complex suggests the methyl groups in the 3,8-position are promoting further weakening of the iron-nitrogen bond. Kinetically significant "buttressing" by the 3,8-methyl groups adjacent to the 4,7-position may contribute to the enhancement in the rate of reaction.

For reactions of Fe(3,4,7,8-Me₄phen)₃⁺⁺ with hydroxide ions in aqueous solution where [sodium hydroxide] = 0.243 mol dm⁻³ and ionic strength, I = 0.243 mol dm⁻³, the first-order rate constant is 4.19 × 10⁻⁷ s⁻¹. The corresponding rate constants for Fe(4,7-Me₂phen)₃⁺⁺ and Fe(phen)₃⁺⁺ are 1.74 × 10⁻⁷ s⁻¹ and 26.32 × 10⁻⁷ s⁻¹ respectively. The decrease in rate constant for Fe(4,7-Me₂phen)₃⁺⁺ compared to the unsubstituted complex is accounted for by the increase in electron density around the iron atom by the methyl groups, making nucleophilic attack by hydroxide ions more difficult. It would therefore be expected that addition of two extra methyl groups would further discourage attack by hydroxide ions. However, the rate constant for reaction of hydroxide ions with Fe(3,4,7,8-Me₄phen)₃⁺⁺ is increased by a factor of 2.4 relative to the corresponding rate constant for Fe(4,7-Me₂phen)₃⁺⁺. A further interesting feature is that the rate constant for aquation, which corresponds to dissociation of the 1,10-phenanthroline ligand from the iron atom, for Fe(3,4,7,8-Me₄phen)₃⁺⁺ is of a comparable magnitude to the rate constant for hydroxide attack, when [sodium hydroxide] = 0.243 mol dm⁻³ and I = 0.243 mol dm⁻³, 2.26 × 10⁻⁴ s⁻¹ and 4.19 × 10⁻⁴ s⁻¹ respectively. This may be contrasted with the data for Fe(phen)₃⁺⁺, where rate constant for dissociation is 0.733 × 10⁻⁴ s⁻¹ and rate constant for hydroxide attack is 26.32 × 10⁻⁴ s⁻¹. For the 4,7-dimethyl substituted complex the rate constant for dissociation is 0.216 × 10⁻⁴ s⁻¹ and the rate constant for reaction with hydroxide ions is 1.74 × 10⁻⁷ s⁻¹. The
observations discussed above are consistent with the increase in rate constant for reaction of Fe(3,4,7,8-Me₄phen)₃²⁺ with hydroxide ions relative to the corresponding rate constant for Fe(4,7-Me₂phen)₃²⁺. The extra two electron-releasing methyl groups in the 3,8-position change the balance of the rate-determining dissociative and associative reaction with hydroxide ions. Therefore, it can be concluded that the extra electron density around the iron atom due to electron-release by four methyl groups discourages direct hydroxide attack to such an extent that dissociation of the iron-nitrogen bond plays an important rôle in the rate-determining step for reaction of Fe(3,4,7,8-Me₄phen)₃²⁺ with hydroxide ions. The overall effect is an increase in the rate constant for reaction relative to the corresponding rate constant for Fe(4,7-Me₂phen)₃²⁺.

The formation of an intermediate in nucleophilic substitution reactions at low spin iron(II) di-imine complexes is discussed in Chapter 7, Section 7.1. Evidence for the formation of intermediates in this class of reactions is presented in Chapter 7, Section 7.4.5 for reactions of hydroxide ions with Fe(hxsbH)²⁺, an unactivated iron(II) complex. Evidence for intermediates in the literature is restricted almost entirely to complexes in which the ligands contain strongly electron-withdrawing substituents such as nitro- and sulphonato- groups. Controversy still surrounds the nature of the intermediates. Nevertheless, an intermediate of type (V) (Section 7.1) is a strong possibility. Assuming that (V) is the structure of any transient intermediates formed during reactions of Fe(X-phen)₃²⁺ with hydroxide ions and from the discussion presented above, it is highly unlikely that an intermediate of type (V) is formed in reactions of Fe(4,7-Me₂phen)₃²⁺ and Fe(3,4,7,8-Me₄phen)₃²⁺ with hydroxide ions under any conditions.
9.4.2 Reactions of Fe(4,7-Me₂phen)₃²⁺ with hydroxide ions in MEA and MEB

In MEB the rate constants for reaction were first-order in [complex]. Kinetic data are reported in Table 9.2. The second-order rate constant for reaction in aqueous solution is $7.16 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Therefore, when [sodium hydroxide] = $2.72 \times 10^{-3} \text{ mol dm}^{-3}$, the corresponding first-order rate constant is $1.9 \times 10^{-6} \text{ s}^{-1}$. The rate constant for reaction in MEB when [sodium hydroxide] = $2.72 \times 10^{-3} \text{ mol dm}^{-3}$ is $3.69 \times 10^{-2} \text{ s}^{-1}$, corresponding to an acceleration in rate of reaction of a factor of approximately $1.94 \times 10^9$ relative to the corresponding rate in aqueous solution. This dramatic acceleration in rate of reaction was a feature of nucleophilic attack at low spin iron(II) di-imine complexes in neutral water-in-oil microemulsions discussed in Chapter 7.

In the range $3 \times 10^{-6} \leq [\text{sodium hydroxide}] \leq 3 \times 10^{-3} \text{ mol dm}^{-3}$, the first-order rate constants for reaction were independent of the sodium hydroxide concentration in MEB (Fig. 9.2).

Kinetics of reaction in MEA were not first-order in [complex]. The kinetic data fitted Scheme V, equation 9.23 satisfactorily. Figure 9.3 shows the dependence of absorbance at 512 nm, on time for reaction in MEA, where [sodium hydroxide] = $2.97 \times 10^{-3} \text{ mol dm}^{-3}$. The full line shows the best fitting curve using equation 9.23. Table 9.3 reports $\gamma_1$, $\gamma_2$, $a_1$, $a_2$ and $a_3$ for reaction in MEA where $2.97 \times 10^{-3} \leq [\text{sodium hydroxide}] \leq 5.2 \times 10^{-2} \text{ mol dm}^{-3}$. Each parameter is the mean of at least
FIGURE 9.2
Dependence of first-order rate constants on [sodium hydroxide] for reactions of Fe(4,7-Me$_2$phen)$_3^{2+}$ with hydroxide ions in ME.B. at 298 K.

FIGURE 9.3
Dependence of absorbance, $P$, on time, $t$, for reaction of Fe(4,7-Me$_2$phen)$_3^{2+}$ with hydroxide ions in ME.A. where [sodium hydroxide] = $2.97 \times 10^{-3}$ mol dm$^{-3}$ at 298 K. Full line shows the best fitting curve using equation 9.23.
three individual determinations. The reproducibility of the rate parameters for fast reactions ("half life" < 50 s) was at worst ±10%.

The dependence of $\gamma_1$ and $\gamma_2$ on sodium hydroxide concentration is shown in Figure 9.4. $\gamma_1$ identified the kinetics of the fast initial reaction. $\gamma_2$ identified the kinetics of the second, slower step. The large experimental limits on some of the $\gamma_1$ terms compared to the corresponding limits on $\gamma_2$ illustrates the difficulties which arise in identifying the two rate parameters in a statistically meaningful way.

$\gamma_1$ increased slightly with increase in sodium hydroxide concentration but when [sodium hydroxide] ≥ $2 \times 10^{-2}$ mol dm$^{-3}$, $\gamma_1$ was independent of sodium hydroxide concentration. $\gamma_2$ showed a similar dependence on alkali concentration. $\gamma_2$ increased regularly with increase in sodium hydroxide concentration and when [sodium hydroxide] ≥ $4.26 \times 10^{-2}$ mol dm$^{-3}$, $\gamma_2$ was independent of alkali concentration. The dependence of $\gamma_1$ and $\gamma_2$ on sodium hydroxide concentration was analogous to the concentration dependence of first-order rate constants for nucleophilic attack at low spin iron(II) di-imine complexes in MEA and MEB (Chapter 7).

The sodium hydroxide dependence of the ratio $a_2/a_1$ (equation 9.23) is shown in Figure 9.5. Parameter $a_1$ was the contribution of the fast, initial kinetic parameter $\gamma_1$, and $a_2$ was the contribution of the subsequent slower kinetic parameter, $\gamma_2$, to the overall kinetics of reaction. Therefore, the ratio $a_2/a_1$ was a measure of the ratio of "slow' reaction/'fast' reaction". The ratio $a_2/a_1$ showed little dependence on sodium hydroxide concentration in the range $2.97 \times 10^{-3} \leq$ [sodium hydroxide] ≤ $5.2 \times 10^{-2}$ mol dm$^{-3}$ (Fig. 9.5). $a_2/a_1$ when [sodium hydroxide] = $2.97 \times 10^{-2}$ mol dm$^{-3}$ is larger than the corresponding values at the other nine concentrations of sodium hydroxide but this could be attributed to the difficulties which arose in trying to identify the two
FIGURE 9.4
Dependence of $\gamma_1$ and $\gamma_2$ on [sodium hydroxide] for reactions of Fe(4,7-Me$_2$phen)$_3^{2+}$ with hydroxide ions in MEA at 298 K.
FIGURE 9.5
Dependence of \( \frac{a_2}{a_1} \) on [sodium hydroxide] for reactions of \( \text{Fe}(4,7-\text{Me}_2\text{phen})_3^{2+} \) with hydroxide ions in MEA at 298 K.

rate parameters \( \gamma_1 \) and \( \gamma_2 \). The average of the ratios of '\( \frac{a_2}{a_1} \)' in the sodium hydroxide concentration range, in which the reactions were monitored was 2.62, corresponding to a 27.62% contribution of the 'fast' kinetic parameter and a 72.38% contribution of the 'slow' kinetic parameter to the overall kinetics of reaction.

When [sodium hydroxide] = \( 2.97 \times 10^{-3} \) mol dm\(^{-3} \), \( \gamma_2 \) was \( 8.06 \times 10^{-4} \) s\(^{-1} \). The corresponding first-order rate constant for reaction in aqueous solution is \( 5 \times 10^{-6} \) s\(^{-1} \). An acceleration in rate of reaction by a factor of approximately \( 1.61 \times 10^2 \) in MEA relative to the corresponding rate of reaction in aqueous solution was detected.

Comparison of the increase in rate parameters for reaction, when [sodium hydroxide] \( \approx 3 \times 10^{-3} \) mol dm\(^{-3} \) in MEA and MEB (a factor of \( 1.61 \times 10^2 \) and \( 1.94 \times 10^4 \) respectively) relative to the corresponding rate constants in aqueous solution, revealed that the rate parameter in
MEA is a factor of approximately $10^2$ less than in MEB. The two-stage process in MEA, where the first stage is reversible [i.e. $k_1 \approx k_2$ - Scheme II(b)], is expected to be a slower process than a one-step mechanism ($k_1 \gg k_2$), in MEB, which is consistent with the observations made above.

9.4.3 Reactions of Fe(3,4,7,8-Me₄phen)₃²⁺ with hydroxide ions in MEB

In MEB the kinetics of reaction were not first-order. Kinetic data were fitted satisfactorily to equation 9.23 (Fig. 9.6). The mean of at least three individual determinations of $\gamma_1$, $\gamma_2$, $a_1$, $a_2$ and $a_3$, where $9.05 \times 10^{-4} \leq [\text{sodium hydroxide}] \leq 2.72 \times 10^{-3} \text{ mol dm}^{-3}$, are reported in Table 9.4, together with the ratios, '$a_2/a_1$'. Both $\gamma_1$ and $\gamma_2$ were independent of sodium hydroxide concentration in the range where kinetic parameters were monitored. The scatter on these latter plots (Fig. 9.7) illustrates the experimental difficulties in trying to identify the two exponential terms in equation 9.23.

Difficulties arose primarily because the reactions were so fast. The fast $\gamma_1$ parameter was approximately 0.1 s⁻¹; the slower $\gamma_2$ was approximately 0.009 s⁻¹.

The ratios '$a_2/a_1$' were independent of alkali concentration. The mean '$a_2/a_1$' (≈ 0.22) corresponded to an 81.97% contribution of 'fast' $\gamma_1$, and only 18.03% contribution of 'slow' $\gamma_2$ to the overall kinetics of reaction. The separate contributions of $\gamma_1$ and $\gamma_2$ in this system were the reverse of the corresponding 'fast' $\gamma_1$ and 'slow' $\gamma_2$ (27.62% and 72.38% respectively) contributions to the overall kinetics of reaction of Fe(4,7-Me₂phen)₃²⁺ in MEA. The difference between $a_1$ and $a_2$ was greater for reactions of Fe(3,4,7,8-Me₄phen)₃²⁺ than for reactions of Fe(4,7-Me₂phen)₃²⁺. Therefore, it was more difficult to identify the smaller $\gamma$ contribution in the former system.
FIGURE 9.6
Dependence of absorbance on time at $\lambda_{\text{max}} = 512 \text{ nm}$ for reactions of Fe($3,4,7,8$-$\text{Me}_2$phen)$_3^{2+}$ with hydroxide ions in ME.B. at 298 K where [sodium hydroxide] = $2.11 \times 10^{-3}$ mol dm$^{-3}$. Full line shows best fitting curve using (a) first-order equation and (b) equation 9.23.
FIGURE 9.7
Dependence of $Y_1$ and $Y_2$ on [sodium hydroxide] for reactions of Fe(3,4,7,8-Me,phen)$_2^{12+}$
with hydroxide ions in ME.B. at 298 K.
The first-order rate constant for reaction of Fe(3,4,7,8-Metphen)$_3^{2+}$ with hydroxide ions in aqueous solution when [sodium hydroxide] = 0.243 mol dm$^{-3}$ is $4.19 \times 10^{-4}$ s$^{-1}$, corresponding to a second-order rate constant of $1.72 \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$. Therefore, when [sodium hydroxide] = $2.72 \times 10^{-3}$ mol dm$^{-3}$, the predicted first-order rate constant for reaction is $4.6 \times 10^{-6}$ s$^{-1}$. 'Fast' $\gamma_1$ for the corresponding reaction in MEB contributed 81.97\% to the overall reaction rate. Therefore, comparison of 'fast' $\gamma_1$ (1.01 $\times 10^{-1}$ s$^{-1}$) when [sodium hydroxide] = $2.72 \times 10^{-3}$ mol dm$^{-3}$, with the corresponding first-order rate constant in aqueous solution, revealed that the acceleration in rate of reaction in MEB relative to water, was a factor of approximately $2.2 \times 10^4$; (cf. acceleration in rate of reaction of Fe(4,7-Me$_2$phen)$_3^{2+}$ in MEB relative to rate of reaction in water was a factor of approximately $1.94 \times 10^4$).

9.4.4 Reactions of Fe(3,4,7,8-Metphen)$_3^{2+}$ with hydroxide ions in MEA

Kinetic data were fitted to equation 9.23. The mean of at least three individual determinations of $\gamma_1$, $\gamma_2$, $a_1$, $a_2$ and $a_3$, where $2.97 \times 10^{-3} \leq$ [sodium hydroxide] $\leq 5.2 \times 10^{-2}$ mol dm$^{-3}$ are reported in Table 9.5, together with the ratios 'a$_2$/a$_1$' and percentage contributions of the individual $\gamma_1$ (fast) and $\gamma_2$ (slow) kinetic parameters to the overall kinetics of reaction.

Dependences of $\gamma_1$ and $\gamma_2$ on sodium hydroxide concentration were complicated (Fig. 9.8). These complexities were attributed to the dependence of the ratio 'a$_2$/a$_1$' on sodium hydroxide concentration (Fig. 9.9). The ratio 'a$_2$/a$_1$' decreased rapidly with initial increase in sodium hydroxide concentration when $2.97 \times 10^{-3} \leq$ [sodium hydroxide] $\leq 1.0 \times 10^{-2}$. When $1.5 \times 10^{-2} \leq$ [sodium hydroxide] $\leq 5.2 \times 10^{-2}$ mol dm$^{-3}$, 'a$_2$/a$_1$' showed a much more gradual decrease.

The dependence of 'a$_2$/a$_1$' on alkali concentration corresponded to
FIGURE 9.8
Dependence of $\gamma_1$ and $\gamma_2$ on [sodium hydroxide] for reactions of $\text{Fe}(3,4,7,8-\text{Me}_4\text{phen})_3^{2+}$ with hydroxide ions in MEA at 298 K.
FIGURE 9.9
Dependence of \((a_2/a_1)\) on [sodium hydroxide] for reactions of \(\text{Fe}(3,4,7,8-\text{Me}_4\text{phen})_3^{2+}\) with hydroxide ions in MEA at 298 K.
different contributions of $\gamma_1$ (fast) and $\gamma_2$ (slow) to the overall kinetics of reaction as the sodium hydroxide concentration increased.

At low concentration, $[\text{sodium hydroxide}] = 2.97 \times 10^{-3}$ mol dm$^{-3}$, $\gamma_2$ (slow) dominated, accounting for 79.34% of the total kinetics of reaction. When $1 \times 10^{-2} \leq [\text{sodium hydroxide}] \leq 2.079 \times 10^{-2}$ mol dm$^{-3}$, contribution of $\gamma_2$ (slow) and $\gamma_1$ (fast) to the total reaction rate, was approximately equal (i.e. $\approx 50\%$ each). When $[\text{sodium hydroxide}] = 5.2 \times 10^{-2}$ mol dm$^{-3}$, $\gamma_1$ (fast) term dominated, accounting for 79.37% of the total kinetics of reaction. In other words, as the sodium hydroxide concentration was increased, $\gamma_1$ switched with $\gamma_2$ in determining the overall kinetics of reaction.

9.4.5 Reactions of Fe(3,4,7,8-Me$_4$phen)$_3^{2+}$ with hydroxide ions in MEA and MEB with added SDS and CTAB

In a final series of experiments, the effects on kinetic parameters were examined, of adding $2.3 \times 10^{-2}$ mol dm$^{-3}$ of surfactants, CTAB and SDS to MEA and MEB. Kinetic data are reported in Table 9.6. Each parameter is the mean of at least three individual determinations.

In MEA, where $[\text{sodium hydroxide}] = 2.5 \times 10^{-2}$ mol dm$^{-3}$, with either $2.3 \times 10^{-2}$ mol dm$^{-3}$ of SDS or CTAB, kinetics of reaction were fitted to equation 9.23.

In MEA, when $[\text{SDS}] = 2.3 \times 10^{-2}$ mol dm$^{-3}$ and $[\text{sodium hydroxide}] = 2.5 \times 10^{-2}$ mol dm$^{-3}$, $\gamma_1$ was $1.60 \times 10^{-2}$ s$^{-1}$. The corresponding $\gamma_1$ in MEA with no added SDS, was $4.99 \times 10^{-2}$ s$^{-1}$. Therefore, addition of $2.3 \times 10^{-2}$ mol dm$^{-3}$ of SDS decreased $\gamma_1$ by a factor of approximately 3. $\gamma_2$ in MEA with (a) $2.3 \times 10^{-2}$ mol dm$^{-3}$ of SDS and (b) no added SDS, was $1.98 \times 10^{-3}$ s$^{-1}$ and $1.23 \times 10^{-2}$ s$^{-1}$ respectively. Therefore, 0.023 mol dm$^{-3}$ SDS in MEA decreased $\gamma_1$ by a factor of approximately 10. Addition of SDS also changed the balance of $a_1$ and $a_2$ terms. In the absence of SDS, '$a_2/a_1'$
≈ 0.67, corresponding to 59.88% contribution from \( \gamma_1 \) (fast) and 40.12% contribution from \( \gamma_2 \) (slow) to the total reaction rate. With added SDS, \( 'a_2/a_1' = 6.57 \), corresponding to 86.80% contribution from \( \gamma_2 \) (slow), and 13.2% contribution from \( \gamma_1 \) (fast) to the total kinetics of reaction.

Analogous effects on \( \gamma_1, \gamma_2 \) and \( 'a_2/a_1' \) were observed when \( 2.3 \times 10^{-2} \) mol dm\(^{-3} \) CTAB was added to MEA. From \( 'a_2/a_1' \) it was clear that addition of \( 2.3 \times 10^{-2} \) mol dm\(^{-3} \) surfactant to MEA causes \( \gamma_2 \) (slow) to dominate the kinetics of reaction when [sodium hydroxide] = \( 2.5 \times 10^{-2} \) mol dm\(^{-3} \). The kinetic data are approaching a first-order dependence in [complex].

In MEB when [sodium hydroxide] = \( 2.72 \times 10^{-3} \) mol dm\(^{-3} \) and [SDS] = \( 2.3 \times 10^{-2} \) mol dm\(^{-3} \), kinetics of reaction were first-order in [complex]. The first-order rate constant in the latter system was \( 8.34 \times 10^{-4} \) s\(^{-1} \). Therefore addition of \( 2.3 \times 10^{-2} \) mol dm\(^{-3} \) SDS to MEB changed the kinetics of reaction from conforming to equation 9.23 to first-order. In MEB when [sodium hydroxide] = \( 2.72 \times 10^{-3} \) mol dm\(^{-3} \), in the absence of SDS, \( \gamma_2 \) (slow) was \( 9.63 \times 10^{-3} \) s\(^{-1} \), corresponding to an increase in rate parameter by a factor of approximately 10, relative to the corresponding first-order rate constant when [SDS] = \( 2.3 \times 10^{-2} \) mol dm\(^{-3} \).

In MEB when [sodium hydroxide] = \( 2.72 \times 10^{-3} \) mol dm\(^{-3} \) and [CTAB] = \( 2.3 \times 10^{-2} \) mol dm\(^{-3} \), kinetic data were fitted satisfactorily to both equation 9.23, and to a first-order dependence in [complex]. \( \gamma_1 \) and \( \gamma_2 \) in this latter system were \( 2.59 \times 10^{-3} \) s\(^{-1} \) and \( 1.35 \times 10^{-3} \) s\(^{-1} \) respectively, and \( 'a_2/a_1' \approx 1 \). Indeed it was surprising that \( \gamma_1 \) and \( \gamma_2 \) were identified separately in view of their similarity. It was concluded, therefore, that for the latter system, the kinetic data hovered on the borderline between following a first-order expression and conforming to equation 9.23.
9.4.6 Comparison of kinetic parameters for reaction between hydroxide ions and Fe(5-NO$_2$phen)$_3^{2+}$, Fe(phen)$_3^{2+}$, Fe(4,7-Me$_2$phen)$_3^{2+}$ and Fe(3,4,7,8-Me$_4$phen)$_3^{2+}$ in MEA and MEB

Kinetic data for reaction of the four iron(II) complexes with hydroxide ions in MEA and MEB, where [sodium hydroxide] $\approx 3 \times 10^{-3}$ mol dm$^{-3}$ are reported in Table 9.7, together with the corresponding data in aqueous solution.

Rate parameters for reaction of all four complexes in MEA and MEB had increased dramatically relative to the corresponding rate constants in aqueous solution.

The dependence of kinetic parameters ($k_1$, $\gamma_1$ or $\gamma_2$), on sodium hydroxide concentration showed a similar pattern in MEA and MEB. Two trends were identified;

(i) $\gamma_1$, $\gamma_2$ and $k_1$ increased initially with increase in sodium hydroxide concentration and at a characteristic alkali concentration for a particular system, the kinetic parameters were independent of sodium hydroxide concentration (i.e. a saturation effect).

(ii) $\gamma_1$, $\gamma_2$ and $k_1$ were independent of sodium hydroxide concentration.

The trends identified in patterns (i) and (ii) can be drawn together, where pattern (ii) is the upper limit of pattern (i).

The hydrophobic nature of the ligands increases along the series, Fe(5-NO$_2$phen)$_3^{2+}$, Fe(phen)$_3^{2+}$, Fe(4,7-Me$_2$phen)$_3^{2+}$ and Fe(3,4,7,8-Me$_4$phen)$_3^{2+}$. The kinetic data were fitted to a first-order expression for reactions of Fe(phen)$_3^{2+}$ in MEA and MEB and for reactions of Fe(4,7-Me$_2$phen)$_3^{2+}$ in MEA. Kinetic data for reactions of Fe(4,7-Me$_2$phen)$_3^{2+}$ in MEA and Fe(3,4,7,8-Me$_4$phen)$_3^{2+}$ in MEA and MEB were fitted to equation 9.23. Therefore, as the hydrophobic nature of the ligands increases a long-lived intermediate (equation 9.23) is detected during the course of reaction.

In aqueous solution rate constants for reaction with hydroxide ions
increase by a factor of ten along the series Fe(5-NO₂phen)₃²⁺, Fe(phen)₃²⁺ and Fe(4,7-Me₂phen)₃²⁺. Reactions of all four complexes are accelerated by a factor of >10³ in MEA and MEB relative to the corresponding reactions in water. Therefore, failure to identify the formation of an intermediate in reactions of Fe(phen)₃²⁺ and Fe(5-NO₂phen)₃²⁺ could stem from the overall reaction being too rapid to allow the initial fast process to be monitored. However, in aqueous solution the first-order rate constant for reaction of Fe(4,7-Me₂phen)₃²⁺ is a factor of 2.38 less than the corresponding first-order rate constant for Fe(3,4,7,8-Me₄phen)₃²⁺. Therefore, the magnitude of the rate constants for reaction in aqueous solution does not have a direct bearing on the possibility of identifying a long-lived intermediate in MEA or MEB.

Formation of intermediates of type V (Section 9.4.1) for methyl-substituted complexes is highly unlikely. Therefore, it is reasonable to conclude that identification of long-lived intermediates in reactions of Fe(X-phen)₃²⁺ with hydroxide ions in MEA and MEB depends, primarily, on the hydrophobic nature of the ligands.

9.5 CONCLUSION

Spiro⁸ identified three important features of chemical reactions in heterogeneous systems;

(i) Molecules with polar heads and hydrophobic tails congregate largely at the interface between water-rich and oil-rich phases. Thus, most of their chemical reactions occur there. Reaction, therefore, between species at the interface will be much faster than in the bulk solution, because of their close proximity.

(ii) Molecules and ions at the surface are spatially orientated, quite
unlike the random arrangement of solute species in the solution itself. Such orientation can profoundly affect the rate of chemical reaction.

(iii) A regular array of charged species along the interface produces a powerful electric field which strongly attracts reacting ions of opposite charge to the film.

Both MEA and MEB are microheterogeneous water-in-oil mixtures, i.e. water is dispersed as microscopic droplets in an oil-rich continuum, with a large proportion of the co-surfactant being concentrated in the interfacial region between oil and water phases (Chapter 6).

Structures of Fe(X-phen)$_2^{2+}$ have the characteristics of a surfactant (Chapter 7, Section 7.5). Therefore, a proportion of the total substrate concentration exists in the interface between oil and water phases.

The dramatic accelerations in rates of nucleophilic attack at Fe(X-phen)$_3$ in MEA and MEB relative to the corresponding rates of reaction in aqueous solution, and the dependence of rate constants on nucleophile concentration in MEA and MEB are discussed in Chapter 7, Section 7.5. Both effects are consistent with the features identified by Spiro for chemical reaction in microheterogeneous mixtures.

If kinetic data for reactions of Fe(X-phen)$_3$ with hydroxide ions in MEA and MEB fit equation 9.23, a long-lived intermediate must be involved in the reaction mechanism (Section 9.3). A mechanism where the first stage involves attack by hydroxide ions at the complex, followed by rapid ligand loss (equation 9.26) is highly unlikely for methyl-substituted complexes (Chapter 7, Section 7.1 and Chapter 9, Section 9.4.1);

\[
\text{Complex} + \text{OH}^- \xrightarrow{k_1} [\text{intermediate} \overset{k_2}{\underset{k_3}{\rightleftarrows}} \text{products}] \quad \text{.... (9.26)}
\]
In Section 9.4.6 a relationship was identified between the hydrophobic nature of the ligand and formation of a long-lived intermediate. The more hydrophobic the ligand the more likely is the formation of an intermediate during the course of reaction. It is highly probable that the nature of the intermediate is related to some process which involves interaction with the interface.

That the interface plays a crucial rôle is evident in the aquation reactions of Fe(hxsbH)²⁺ in MEA (Chapter 7, Section 7.4.4) and in water-rich '2BE + water' mixtures (Chapter 8). The latter two systems identify the extreme where the ligand is so large and hydrophobic that the kinetics of reaction are controlled by adsorption at the interface, which is accounted for in terms of Langmuir-based equations.

Thus complexity in kinetics of reaction of Fe(4,7-Me₂phen)³⁺ in MEA and Fe(3,4,7,8-Me₄phen)³⁺ in MEA and MEB can be understood in terms of an adsorption process represented by;

\[
\text{[complex]} \xrightarrow{k_1/k_2} \text{[complex]}_s \xrightarrow{k_3} \text{OH}^- \rightarrow \text{products} \quad \ldots\ldots\ldots (9.27)
\]

where [complex]ₚ represents adsorption of the complex at the interface. Such a reaction scheme is envisaged as occurring in all reactions of Fe(X-phen)₃²⁺ in MEA and MEB but as the hydrophobic nature of the ligand increases the adsorption process begins to play a crucial rôle in the rate-determining step of reaction.

Thus for reactions of Fe(5-NO₂phen)₃²⁺, Fe(phen)₃²⁺ in MEA and MEB and Fe(4,7-Me₂phen)₃²⁺ in MEB, the reaction follows equation 9.27 but \( k_1 \gg k_2 \) and \( k_3 \gg k_1 \). For reactions of Fe(4,7-Me₂phen)₃²⁺ in MEA and Fe(3,4,7,8-Me₄phen)₃²⁺ in MEA and MEB, the adsorption and desorption equilibrium affects the rate-determining step for reaction with hydroxide ions, i.e. \( k_1 \) and \( k_2 \) are of comparable size. In the limit
for very hydrophobic ligands such as (hxsrbH) (Chapter 7, Section 7.4.4), adsorption and desorption completely control the rates of reaction.

Effects on kinetic parameters by surfactants SDS and CTAB are consistent with the theory developed above. SDS and CTAB compete with the complex ions for sites at the interface, resulting in a fall in rate of reaction and a much smaller contribution of the adsorption-desorption equilibrium of the complex ion to the rate-determining step of reaction with hydroxide ions.

In this and the previous two chapters attention has been centred on reactions of low-spin iron(II) diimine complexes in neutral microheterogeneous systems. In Chapter 10 attention is turned to reactions of organic substrates in microemulsions.
REFERENCES TO CHAPTER 9

CHAPTER 10

Reactions involving three organic substrates in neutral water-in-oil microemulsions
10.1 INTRODUCTION

In Chapters 7 and 9, kinetic data are reported showing that for many reactions involving inorganic substrates, the rates of reactions in neutral water-in-oil microemulsions are considerably faster than in corresponding aqueous solution. In this Chapter results of investigations are reported into kinetics of reactions involving organic substrates in similar systems.

Kinetic data are reported for hydrolysis reactions and reaction with hydroxide and cyanide ions of crystal violet (C.V. – trisparadimethylaminophenyl–methyl chloride) and malachite green (M.G. – bisparadimethylaminophenyl–phenyl methyl chloride), in two neutral water-in-oil microemulsions. Kinetic data are also reported for reactions of 2,4-dinitrochlorobenzene (DNCB) with hydroxide ions in one neutral water-in-oil microemulsion.

Structures of DNCB, M.G. and C.V. are shown in (I), (II) and (III) respectively;
Nucleophilic substitution reactions involving C.V. and M.G. are generally discussed in terms of the Winstein scheme\(^1,2\) (equation 10.1);

\[
RX \rightleftharpoons [R^+X^-] \rightleftharpoons [R^+]X^- \rightleftharpoons R^+ + X^- \quad \ldots \quad (10.1)
\]

Equation 10.1 is a scheme for an \(S_N1\) solvolysis reaction. The reaction with a nucleophile, \(Y\) (where \(Y = \) water, hydroxide or cyanide ions) then proceeds via equation 10.2;

\[
N(CH_3)_2 \quad N(CH_3)_2
\]

\[
\begin{array}{c}
\text{N}(\text{CH}_3)_2 \quad \text{N}(\text{CH}_3)_2 \\
\text{Z-} \quad \text{C}+ \quad + \quad Y^- \quad \rightarrow \quad \text{Z-} \quad \text{C}^- \quad \text{Y} \\
\text{N}(\text{CH}_3)_2 \quad \text{N}(\text{CH}_3)_2
\end{array}
\quad \ldots \quad (10.2)
\]

where \(Z = \) hydrogen for M.G. and \(-N(CH_3)_2\) for C.V.

In equation 10.1 the solvent-separated ion pair (\([R^+]X^-\)) can be of two types; (i) one molecule of solvent separates the ion pair or (ii) two molecules of solvent separate the ion pair. It was postulated\(^1\) that the transition state for the rate-determining step is either between the intimate and solvent-separated ion pairs (equation 10.1) or between the one-solvent separated and two-solvent separated ion pairs [between (i) and (ii)]. In either case the structure of the transition state is similar to the one-solvent separated ion pair (\([R^+]X^-\)).

For reactions of M.G. with various nucleophiles, the transition states\(^3\) are reactant-like. Therefore, the rate-determining step in reactions of M.G. with nucleophiles does not involve direct nucleophilic attack. In these terms the rate-determining step is probably between the intimate and solvent-separated ion pair (equation 10.1).
For reactions of DNCB with hydroxide ions in aqueous solution, the mechanism is well established,\(^4\) (equation 10.3);

\[
\begin{align*}
\text{Cl} & \quad \text{NO}_2 \\
\text{NO}_2 & \quad + \text{OH}^- \quad \xrightarrow{k_1/k_2} \quad \text{Cl} \quad \text{OH} \\
\text{Cl} & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \xrightarrow{k_3} \quad \text{OH} \\
\text{NO}_2 & \quad + \text{Cl}^-
\end{align*}
\]

INTERMEDIATE

In this bimolecular reaction (equation 10.3), the rate-determining step involves slow attack of hydroxide ion at the carbon atom bearing the chlorine atom. The subsequent step involves rapid decomposition of the intermediate. Formation of the intermediate anion is facilitated by the electron-withdrawing nitro-groups, which disperse the negative charge.

A comparison is made (Section 10.6) between effects on kinetic data for reaction of DNCB with hydroxide ions in (i) a neutral water-in-oil microemulsion (data reported here); (ii) an aqueous solution with ionic and non-ionic micelles\(^5\) and (iii) alcohol-water mixtures at alcohol mole fraction, \(x_2^*\) (Chapter 8, Section 8.1.2) with added cationic and non-ionic micelles.\(^6\) Effects on reactions of DNCB in (ii) and (iii) are reviewed below.

10.2 REACTIONS OF DNCB WITH HYDROXIDE IONS IN AQUEOUS MICELLAR MIXTURES

Reaction of DNCB with hydroxide ions in aqueous solution is catalysed\(^5\) by cationic micelles of CTAB, and retarded by anionic micelles of SDS. The results were explained on the basis of adsorption of DNCB onto the micelles. When DNCB is adsorbed onto a cationic micelle, electrostatic attraction facilitates hydroxide attack and the opposite is true for
adsorption of DNCB onto an anionic micelle.

Incorporation of DNCB onto a non-ionic micelle showed no significant effects on reactions of DNCB with hydroxide ions. Non-ionic micelles were shown to be very effective in adsorbing DNCB onto their surface.

Reactions of DNCB in aqueous solvent are catalysed by addition of a monohydric alcohol. The increase in rate constant in 'alcohol + water' mixtures relative to the corresponding rate constants in aqueous solution, was accounted for, in part, by the destabilisation of hydroxide ions in the former solutions (Chapters 3 and 4).

Addition of a monohydric alcohol to an aqueous alkaline solution at a fixed concentration of CTAB caused the micellar catalysed rate of hydrolysis of DNCB to decrease. The decrease of the rate of hydrolysis approached the rate of the uncatalysed reaction at a characteristic mole-fraction, $x^*_2$, of the alcohol. At mole fractions, $x^*_2$, in the absence of CTAB, the organisation of solvent and cosolvent can be understood in terms of component clustering to form microscopic heterogeneity (Chapter 8, Section 8.1.2). It was concluded that micellar catalysis is dependent on the structure of water and can be affected when cosolvents modify the bulk water structure.

10.3 EXPERIMENTAL

Kinetics of reaction were monitored in two neutral water-in-oil microemulsions, MEA and MEB (Chapter 7, Section 7.2), at 298 K. In all systems $\text{[substrate]} < 10^{-4}$ mol dm$^{-3}$ and $\text{[nucleophile]} > [\text{complex}].$

10.3.1 C.V. and M.G.

Concentrated aqueous solutions of C.V. and M.G. were prepared. Aqueous solutions of C.V. are very deep blue with $\lambda_{\text{max}} = 579$ nm and
aqueous solutions of M.G. are dark green with $\lambda_{\text{max}} = 625\,\text{nm}$. No shift in $\lambda_{\text{max}}$ was observed when the complexes were dissolved in the micro-emulsions.

Kinetic data for hydrolysis reactions of M.G. with water were monitored in MEA and MEB and kinetic data for hydrolysis of C.V. with water were monitored in MEA. Repeat scans of the dependence of absorbance on wavelength (Unicam SP800 spectrophotometer – Chapter 2, Section 2.4.1) revealed that the dependence of absorbance on time was first-order. Kinetics of reaction were monitored by following the disappearance of reactant at 625 nm for M.G. and 579 nm for C.V. (Unicam SP1800 spectrophotometer – Chapter 2, Section 2.4.1). The computer was programmed to fit the absorbance data to a first-order kinetic expression (Chapter 2, Section 2.3).

Reactions of M.G. with hydroxide and cyanide ions and reactions of C.V. with cyanide ions in MEA and MEB where $[\text{nucleophile}] \approx 1.5 \times 10^{-3}$ mol dm$^{-3}$ were extremely rapid, being complete almost instantaneously on mixing the reagents. Therefore, kinetic data were not monitored for these latter reactions. Solutions of cyanide ions in MEB were cloudy but despite this complication addition of M.G. or C.V. to this latter system resulted in immediate disappearance of the colour of the substrate.

Kinetic data for hydrolysis reactions of C.V. with water in MEB were not measured, because hydrolysates of C.V. with water even in the micro-emulsions are extremely slow.

Reactions of C.V. with hydroxide ions in MEA were monitored when $3 \times 10^{-4} \leq [\text{sodium hydroxide}] \leq 5.5 \times 10^{-4}$ mol dm$^{-3}$. When $[\text{sodium hydroxide}] > 6.54 \times 10^{-4}$ mol dm$^{-3}$ the reaction was too fast to monitor and when $[\text{sodium hydroxide}] \leq 3 \times 10^{-4}$ mol dm$^{-3}$ there was no apparent
reaction.

Reactions of C.V. with hydroxide ions in MEB were monitored when $3 \times 10^{-4} \leq [\text{sodium hydroxide}] \leq 3 \times 10^{-3}$ mol dm$^{-3}$ (Chapter 7, Section 7.2) at several different concentrations of alkali. The latter two reactions were first-order and kinetic data were monitored as described above.

### 10.3.2 DNCB

Concentrated solutions of DNCB in 2BE were prepared. Solutions of DNCB are colourless. Reactions of DNCB with hydroxide ions were monitored by following the appearance of the corresponding phenol at $\lambda = 358$ nm.

Kinetics for reaction of DNCB with hydroxide ions were monitored in MEA at several different concentrations of alkali. When $9 \times 10^{-3} \leq [\text{sodium hydroxide}] \leq 3 \times 10^{-2}$ mol dm$^{-3}$, repeat scans of the dependence of absorbance on wavelength (Unicam SP800 spectrophotometer - Chapter 2, Section 2.4.1) revealed that the dependence of absorbance on time was first-order. Kinetics of reaction were monitored at $\lambda = 358$ nm (Unicam SP1800 - Chapter 2, Section 2.4.1). The computer was programmed to fit the absorbance data to a first-order kinetic expression (Chapter 2, Section 2.3).

When $3 \times 10^{-3} \leq [\text{sodium hydroxide}] \leq 7 \times 10^{-3}$ mol dm$^{-3}$, the kinetic data were not fitted satisfactorily to a first-order dependence of absorbance on time. The first-order plots of $\ln\left(\frac{(P_\infty - P_t)}{(P_\text{oo} - P_t)}\right)$ against time, $t$, were curved, and the standard errors emerging from Least Squares fitting procedures to the first-order kinetic equation were high.

Initially the absorbance increased rapidly for these latter systems, followed by a much slower production of the phenol. The program developed for the HP9825A computer, for reactions of Fe$(3,4,7,8$-Me$_4$phen)$_3^{2+}$
with hydroxide ions in MEA and MEB was used (Chapter 9, Sections 9.2 and 9.3) to monitor kinetic data for reactions of DNCB in MEA where $3 \times 10^{-3} \leq \text{sodium hydroxide} \leq 7 \times 10^{-3}$ mol dm$^{-3}$. Logging procedures of absorbance as a function of time recorded a pre-set number of data points at specified time intervals (Chapter 9, Section 9.2).

10.4 ANALYSIS

For most of the reactions in this Section the dependence of absorbance on time was first-order (Chapter 2, Section 2.3). For reactions of DNCB with hydroxide ions in MEA where $3 \times 10^{-3} \leq \text{sodium hydroxide} \leq 7 \times 10^{-3}$ mol dm$^{-3}$, two kinetic schemes were considered.

(1) **Scheme V**

Scheme V (Chapter 9, Section 9.3) describes kinetics for a two-stage reaction in which the first stage is reversible. Reactions of DNCB with hydroxide ions were monitored by measuring the rate of appearance of products, C. Therefore in this Section attention is centred on equation 9.21:

$$\frac{[C]}{[M_0]} = 1 - \left(\frac{\gamma_2}{(\gamma_2-\gamma_1)}\right) \exp(-\gamma_1 t) - \left(\frac{\gamma_1}{(\gamma_1-\gamma_2)}\right) \exp(-\gamma_2 t) \quad \ldots \quad (9.21)$$

$\gamma_1$ and $\gamma_2$ are dynamic constants (units s$^{-1}$) and are functions of the individual rate constants $k_1$, $k_2$ and $k_3$ (Chapter 9, Section 9.3).

Equation 9.21 can be simplified to yield;

$$\frac{[C]}{[M_0]} = 1 - \alpha_1 \exp(-\gamma_1 t) - \alpha_2 \exp(-\gamma_2 t) \quad \ldots \quad (10.4)$$

where $\alpha_1 = \left(\frac{\gamma_2}{(\gamma_2-\gamma_1)}\right)$ and $\alpha_2 = \left(\frac{\gamma_1}{(\gamma_1-\gamma_2)}\right)$.

Combining equation 10.4 and Beer's Law equation yields;

$$P = a_3 - a_1 \exp(-\gamma_1 t) - a_2 \exp(-\gamma_2 t) \quad \ldots \quad (10.5)$$

where $a_3 = [M_0].\Sigma.\ell$, $a_1 = [M_0].\Sigma.\ell.\alpha_1$ and $a_2 = [M_0].\Sigma.\ell.\alpha_2$. 

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Hence at a given time, \( t \), the absorbance \( P \) (of the products) is defined by five variables;

\[
P = P \{ a_3, a_2, a_1, \gamma_1, \gamma_2 \} \quad \ldots \quad (10.6)
\]

The analysis used the Wentworth method (Chapter 8, Section 8.3).

**Scheme VI**

Scheme VI is analogous to Scheme V, but the first stage of the reaction is not reversible (i.e. Scheme VI is the limit in Scheme V that \( k_1 \gg k_2 \)). Scheme VI describes kinetics for a two-stage consecutive reaction between reactant, \( A \), and say \( X \) in solution;

\[
A + X \xrightarrow{k_4'} I \xrightarrow{k_5} \text{products, } C \quad \ldots \quad (VIa)
\]

where \( I \) is the intermediate. In the limit that \([X]\gg[A]\), with \( k_4 = k_4'[X] \), (VIa) can be simplified;

\[
A \xrightarrow{k_4} I \xrightarrow{k_5} \text{products, } C \quad \ldots \quad (VIb)
\]

Then;

\[
\frac{-d[A]}{dt} = -k_4[A] \quad \ldots \quad (10.7)
\]

\[
\frac{d[I]}{dt} = k_4[A] - k_5[I] \quad \ldots \quad (10.8)
\]

\[
\frac{d[C]}{dt} = k_5[I] \quad \ldots \quad (10.9)
\]

at time, \( t = 0 \), \([A] = [A_0], [I] = [C] = 0\).

Integration of equation 10.7 yields;

\[
[A] = [A_0] \cdot \exp(-k_4 t) \quad \ldots \quad (10.10)
\]

From equation 10.8 using the method of Laplace Transforms;

\[
s[I] = k_4[A] - k_5[I] \quad \ldots \quad (10.11)
\]

where \( s = d/dt \) and from equation 10.7;

\[
s[A] - s[A_0] = -k_4[A] \quad \ldots \quad (10.12)
\]

Combining equations 10.11 and 10.12 yields;

\[
s[I] = \frac{k_4 \cdot s[A_0] + k_5[I]}{s + k_4}
\]
or \[ \frac{[I]}{s+k_5} = \frac{k_u.s[A_0]}{(s+k_u)} \]

Therefore; \[ [I] = \frac{k_u.s[A_0]}{(s+k_5)(s+k_u)} \] .... (10.13)

If equation 10.13 is the transform, then (from tables) the original is;

\[ [I] = k_u.[A_0] \frac{\exp(-k_u t) - \exp(-k_s t)}{(k_s-k_u)} \] .... (10.14)

From equation 10.9 using the method of Laplace Transforms;

\[ s[C] = k_s.[I] \] .... (10.15)

Combining equations 10.15 and 10.13 yields;

\[ s[C] = \frac{k_u.k_s.[A_0]}{(s+k_u)(s+k_5)} \] .... (10.16)

If equation 10.16 is the transform, the original is;

\[ \frac{[C]}{[A_0]} = k_u.k_s.\left\{ \frac{1 - \frac{\exp(-k_u t) - \exp(-k_s t)}{(k_u)(k_u-k_s)}}{(k_s-k_u)} \right\} \]

or \[ \frac{[C]}{[A_0]} = 1 - \left\{ \frac{k_u}{(k_u-k_s)} \right\} .\exp(-k_u t) - \left\{ \frac{k_u}{(k_u-k_5)} \right\} .\exp(-k_s t) \] .... (10.17)

Equation 10.17 is analogous to equation 9.21 in which \( \gamma_1 \) and \( \gamma_2 \) parameters in equation 9.21 are \( k_u \) and \( k_s \) parameters in equation 10.17.

Combining equations 10.17 and Beer’s Law equation yields;

\[ P = a_3 - a_1.\exp(-k_u t) - a_2.\exp(-k_s t) \] .... (10.18)

where \( a_3 = [A_0].\varepsilon.l \), \( a_1 = [A_0].\varepsilon.l . \frac{k_u}{(k_u-k_s)} \) and \( a_2 = [A_0].\varepsilon.l . \frac{k_u}{(k_u-k_5)} \)

Equation 10.18 is analogous to equation 10.5. The analysis is then continued as in Scheme V.

In practice when appearance of products is monitored as a function of time, as in reactions of DNBC with hydroxide ions, it is not possible to differentiate between kinetics of reaction conforming to Scheme V or conforming to Scheme VI.

In the limit that \( k_u \gg k_5 \) or \( k_5 \gg k_u \), the dependence of the concentra-
tion of products, \([C]\) on time, \(t\) follow equation 10.19;

\[
\frac{[C]}{[A_0]} = 1 - \exp(-kt) \quad \ldots \quad (10.19)
\]

Kinetics for reactions conforming to equation 10.19 are characterised by a first-order rate constant, \(k\).

One further calculation was performed in those systems where kinetics of reaction followed either Scheme V or Scheme VI.

For Scheme V, from equation 10.5;

\[
a_3 = [M_0].e.l, \quad a_1 = [M_0].e.l.a_1 \quad \text{and} \quad a_2 = [M_0].e.l.a_2.
\]

But from equation 10.4;

\[
a_1 = \frac{Y_2}{(Y_2-Y_1)} \quad \text{and} \quad a_2 = \frac{Y_1}{(Y_1-Y_2)}
\]

Then;

\[
\frac{a_1}{a_2} = \frac{[M_0].e.l.[Y_2/(Y_2-Y_1)]}{[M_0].e.l.[Y_1/(Y_1-Y_2)]}
\]

or

\[
\frac{a_1}{a_2} = \frac{Y_2}{Y_1} \quad \ldots \quad (10.20)
\]

Analogously in Scheme VI;

\[
\frac{a_1}{a_2} = \frac{k_5}{k_4} \quad \ldots \quad (10.21)
\]

Equations 10.20 and 10.21 describe the conditions which must be conformed to by kinetics of a reaction characterised by Scheme V or Scheme VI in which the course of the reaction is monitored by measuring the rate of appearance of products, \(C\).

10.5 RESULTS AND DISCUSSION

10.5.1 Reactions of M.G. and C.V. in MEA and MEB

Kinetic data for hydrolysis reactions of C.V. and M.G. with water, hydroxide and cyanide ions in MEA and MEB are reported in Table 10.1, together with the corresponding data for reactions in aqueous solution. Each rate constant is the mean of at least three individual determinations. The reproducibility of rate constants for fast reactions was, at
worst, ±10%. Reactions of C.V. and M.G. were first-order in [substrate].

First-order rate constants for hydrolysis reactions of M.G. and C.V. with water in aqueous solution are $2.09 \times 10^{-4}$ s$^{-1}$ and $1.1 \times 10^{-5}$ s$^{-1}$ respectively. Therefore, assuming [water] = 55 mol dm$^{-3}$, the corresponding second-order rate constants for reaction of M.G. and C.V. are $3.8 \times 10^{-6}$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $2.0 \times 10^{-7}$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively.

First-order rate constants for the corresponding reactions in MEA of M.G. and C.V. were $2.02 \times 10^{-3}$ s$^{-1}$ and $1.7 \times 10^{-6}$ s$^{-1}$ respectively. In 1 dm$^3$ of MEA there are 29.70 cm$^3$ of water. Therefore in MEA, [water] = 1.65 mol dm$^{-3}$. Hence the corresponding second-order rate constants for reaction in MEA of M.G. and C.V. were $1.22 \times 10^{-3}$ and $1.0 \times 10^{-6}$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively, corresponding to an increase in second-order rate constants for water hydrolysis reactions of M.G. and C.V. in MEA relative to the corresponding rate constants in water, of a factor of approximately $3.2 \times 10^2$ and 5 respectively.

Following a similar comparison of second-order rate constants for water hydrolysis of M.G. in MEB, and in aqueous solution the former is increased by a factor of $1.5 \times 10^2$ relative to the latter.

Reactions of M.G. with hydroxide and cyanide ions in MEA and MEB were too fast to be followed spectrophotometrically. Second-order rate constants for these reactions were estimated to be >200 dm$^3$ mol$^{-1}$ s$^{-1}$ (cf. 1.6 and $4.9 \times 10^{-1}$ dm$^3$ mol$^{-1}$ s$^{-1}$ for reaction with hydroxide and cyanide ions respectively in aqueous solution).

Similarly the second-order rate constants for reactions of C.V. with cyanide ions in MEA and MEB were estimated to be >200 dm$^3$ mol$^{-1}$ s$^{-1}$ (cf. $6 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ for corresponding reaction in aqueous solution).

For reactions of C.V. with hydroxide ions in MEA, when [sodium hydroxide] = $6.54 \times 10^{-4}$ mol dm$^{-3}$, the first-order rate constant was
estimated to be $>3 \times 10^{-1}$ s$^{-1}$, because reaction was too rapid to monitor kinetic data. When $5.5 \times 10^{-9} \leq [\text{sodium hydroxide}] \leq 5 \times 10^{-8}$ mol dm$^{-3}$, first-order rate constants for reaction were monitored. When $[\text{sodium hydroxide}] < 5 \times 10^{-9}$ mol dm$^{-3}$, conditions were on the limit of pseudo first-order. Even over such a narrow alkali concentration range, the rate constant increased substantially, with increase in alkali concentration. It was not possible to establish if the rate constant became independent of sodium hydroxide concentration at higher concentrations of alkali because reactions were too fast to be monitored. However, on the basis of similar reactions in MEA and MEB (Chapters 7 and 9), it was assumed that a saturation effect was present in this system.

When $[\text{sodium hydroxide}] = 5.5 \times 10^{-4}$ mol dm$^{-3}$, the first-order rate constant for reaction of C.V. with hydroxide ions in MEA was $2.53 \times 10^{-1}$ s$^{-1}$. The corresponding rate constant in aqueous solution is $1.1 \times 10^{-4}$ s$^{-1}$. Therefore, the increase in rate constant for reaction in MEA when $[\text{sodium hydroxide}] = 5.5 \times 10^{-4}$ mol dm$^{-3}$ relative to the corresponding rate constant in water is a factor of $2.3 \times 10^3$.

In MEB first-order rate constants for reactions of C.V. with hydroxide ions were monitored when $4.47 \times 10^{-4} \leq [\text{sodium hydroxide}] \leq 2.5 \times 10^{-3}$ mol dm$^{-3}$. The rate constant increased with increase in alkali concentration and when $[\text{sodium hydroxide}] > 2 \times 10^{-3}$ mol dm$^{-3}$, the rate constant was independent of alkali concentration (Fig. 10.1). The acceleration in rate of this latter reaction in MEB relative to the corresponding rate of reaction in water is a factor of $>10^3$. The saturation effect and enhancements in rates of reaction in MEA and MEB of a factor of $>10^3$ relative to the corresponding rates in water was a common feature of many reactions in the microemulsions (Chapters 7 and 9).
FIGURE 10.1
Dependence of first-order rate constants on [sodium hydroxide] for reactions of C.V. with hydroxide ions in ME.B. at 298 K.
10.5.2 Reactions of DNCB with hydroxide ions in MEA

When $9 \times 10^{-3} \leq \text{[sodium hydroxide]} \leq 3 \times 10^{-2} \text{ mol dm}^{-3}$, reactions were first-order in [DNCB]. When $3 \times 10^{-3} \leq \text{[sodium hydroxide]} \leq 7 \times 10^{-3}$, the dependence of absorbance on time fitted equation 10.5 (or 10.18) (Fig. 10.2). First-order rate constants, reported in Table 10.2, are the mean of at least three individual determinations, the reproducibility being at worst within 5%.

Table 10.3 reports kinetic parameters, $\gamma_1$, $\gamma_2$, $a_1$, $a_2$, $a_3$, $(a_1/a_2)$ and $(\gamma_2/\gamma_1)$ for reactions conforming to equation 10.5 (or 10.18), together with the percentage contributions of $\gamma_1$ (fast) and $\gamma_2$ (slow) to the overall kinetics of reaction. Each parameter is the mean of at least three individual determinations. $\gamma_2$ and $\gamma_1$ are used as symbols for the 'slow' and 'fast' kinetic parameters respectively (equation 10.5), but it would be just as correct to use $k_5$ and $k_i$ (equation 10.18) because it is not possible to ascertain from kinetic measurements which scheme is operating.

The dependence of first-order rate constants on sodium hydroxide concentration (Fig. 10.3) followed the usual pattern observed for many reactions in MEA, i.e. a saturation effect.

When [sodium hydroxide] = $3 \times 10^{-2} \text{ mol dm}^{-3}$, the first-order rate constant is $8.77 \times 10^{-3} \text{ s}^{-1}$. At the same alkali concentration but at 10 K higher (318 K), the corresponding rate constant$^6$ in aqueous solution is $3.9 \times 10^{-5} \text{ s}^{-1}$. Therefore, even at 10 K lower in MEA the increase in rate constant is a factor of approximately $2.25 \times 10^2$ relative to the corresponding rate constant in water.

For reactions following equation 10.5, the dependence of $\gamma_2$ (slow) on alkali concentration follows the curve describing the dependence of first-order rate constants on sodium hydroxide concentration (Fig. 10.3).
FIGURE 10.2
Dependence of absorbance, \( P \) on time, \( t \) at \( \lambda_{\text{max}} = 358 \text{nm} \) for reactions of DNCB with hydroxide ions in MEA., where \([\text{NaOH}] = 3 \times 10^{-3} \text{ mol dm}^{-3}\). The full line represents the calculated curve using (a) first-order dependence and (b) equation 10.5 (or 10.18).
FIGURE 10.3
Dependence of rate parameters on [sodium hydroxide] for reactions of DNBCB with hydroxide ions in ME.A. When $3 \times 10^{-3} \leq [\text{NaOH}] \leq 7 \times 10^{-3}$ mol dm$^{-3}$, (---) represents dependence of $\gamma_1$ and (-----) represents dependence of $\gamma_2$. When $[\text{NaOH}] \geq 9 \times 10^{-3}$ mol dm$^{-3}$, (----) represents dependence of first-order rate constants.
increased with increase in alkali concentration and when \([\text{sodium hydroxide}] = 9 \times 10^{-3} \text{ mol dm}^{-3}\), \(\gamma_2\) (slow) is described by a single first-order rate constant. Therefore \(\gamma_2\) (slow) is ascribed to that part of the reaction which, at higher alkali concentrations, is described by the first-order rate constant.

\(\gamma_1\) (fast) also increased with increase in alkali concentration (Fig. 10.3). The large limits on \(\gamma_1\) reflect the experimental difficulties in identifying this latter parameter. The difficulties in identifying \(\gamma_1\) (fast) were attributed to the small contribution (\(\approx 18\%\)) that \(\gamma_1\) made to the overall kinetics of reaction.

When \([\text{sodium hydroxide}] \geq 9 \times 10^{-3} \text{ mol dm}^{-3}\), \(\gamma_1\) (fast) could not be identified. However, this does not mean that \(\gamma_1\) (fast) no longer contributes to the overall kinetics of reaction. It is more probable that the part of the reaction described by \(\gamma_1\) (fast) has become too fast at higher concentrations of alkali, to allow the parameter to be monitored spectrophotometrically.

Kinetic data in MEA when \(3 \times 10^{-3} \leq [\text{sodium hydroxide}] \leq 7 \times 10^{-3} \text{ mol dm}^{-3}\), satisfied the criteria set by equation 10.20 (or 10.21). Over nine independent measurements \((\gamma_1/\gamma_2) = 0.24 \pm 0.08\) and \((a_1/a_2) = 0.23 \pm 0.06\) (Table 10.3). Therefore in MEA at this latter alkali concentration range, kinetics of reactions of DNCB can be confidently assigned to a description by Scheme V or VI.

10.6 CONCLUSION

MEA and MEB are microheterogeneous water-in-oil microemulsions (Chapter 6). Molecules which contain both hydrophobic and hydrophilic moieties are envisaged as residing largely in the interfacial region in the non-ionic inverted micelles (2BE in MEA and 2-PrOH in MEB), between
water-rich and oil-rich phases (Chapters 7 and 9). Therefore, a large proportion of the concentration of the substrates, C.V., M.G. and DNCB is in the interface.

The dramatic accelerations in rates of reaction of C.V., M.G. and DNCB with hydroxide and cyanide ions in MEA and MEB relative to the corresponding rates in water, and the dependences of the rate constants on nucleophile concentration in the microemulsions were consistent with previous observations (Chapters 7 and 9).

Rates of reaction of C.V. and M.G. were monitored by measuring the rate of disappearance of reactants. Although kinetics of reaction were first-order, it did not mean that the reaction was a simple one-step process. In Scheme VI, rates of disappearance of reactants follow first-order kinetics (equation 10.10). Nucleophilic reactions of C.V. and M.G. can be represented by equation 10.22 (Section 10.1):

\[
\begin{align*}
\text{intimate solvent} & \quad \text{ion-pair} \quad \text{separated ion-pair} \\
-C^+ + X^- & \quad \frac{k_1}{k_2} \quad \left[ -C^+ \right] \left[ X^- \right] \quad \frac{X^-}{k_3} \quad -C^- Y + X^- \\
& \quad \text{..... (10.22)}
\end{align*}
\]

The rate-determining step was assigned to the formation of the solvent separated ion-pair. If \( k_1 \gg k_2 \) in equation 10.22 the reaction scheme is identical to Scheme VI and the rate of disappearance of reactants are first-order. Therefore, it is highly probable that kinetics of reaction of C.V. and M.G. in MEA and MEB conform to Scheme VI.

Reactions of DNCB with hydroxide ions in MEA at low alkali concentration were kinetically described in terms of Scheme V or VI. Kinetics of reaction with hydroxide ions of \( \text{Fe}(4,7-\text{Me}_2\text{phen})_3^{2+} \) in MEA and \( \text{Fe}(3,4,7,8-\text{Me}_4\text{phen})_3^{2+} \) in MEA and MEB conformed to Scheme V (Chapter 9). Kinetics of these latter reactions were understood in terms of the rôle played by adsorption of the metal complexes at the interface. The hydrophobic
nature of the ligands of the iron(II) di-imine complexes was crucial to the kinetic identification of the adsorption process.

DNCB is a much smaller molecule than the iron complexes and the mechanism for reaction of DNCB with hydroxide ions is well established (equation 10.3, Section 10.1). In contrast to reactions of the dimethyl- and tetramethyl-phenanthroline iron(II) complexes, γ₁ (fast) and γ₂ (slow) for reactions of DNCB could only be identified at low concentrations of alkali. It is therefore unlikely that the same equilibrium process is occurring in reactions of DNCB as in reactions of the two iron complexes. It is more probable that the kinetics of reaction of DNCB in MEA can be understood in terms of production of the intermediate [DNCB.OH]⁻ (equation 10.3) at the interface (cf. reactions of Fe(hxsbH)²⁺ with hydroxide ions in MEA and MEB - Chapter 7). If this assignment is correct, kinetics of reaction in microemulsions may have an important rôle to play in mechanistic studies.

Reactions of DNCB with hydroxide ions in aqueous micellar mixtures are reviewed in Section 10.2. Effects on rate constants for DNCB in MEA were similar but more dramatic than the corresponding effects in aqueous solutions containing cationic micelles. Catalysis by cationic micelles was explained in terms of electrostatic attractions, whereas in MEA the catalysis was explained in terms of a high local concentration and destabilisation of anions. The latter effect was identified in 'alcohol + water' mixtures in the absence of cationic micelles.

In 'alcohol + water' mixtures at alcohol mole-fractions, x₂*, with added cationic micelles, rate constants for reaction of DNCB decreased relative to the corresponding rate constants in the absence of alcohol. The size of the CTAB micelle is decreased when alcohol is added to the aqueous mixture. At x₂* of added alcohol CTAB is present partly as
reduced micelles in the water-rich phases and partly as molecular monomeric dispersions in the alcohol clusters. Therefore the ability of the CTAB micelles to incorporate DNCB is reduced and hence the catalysis of reactions with hydroxide ions is decreased. This is clearly not the case in MEA. In the latter system 2BE is analogous to inverted non-ionic micelles and a large proportion of 2BE exists between water-rich and oil-rich phases. Thus a large proportion of DNCB is present in the inverted non-ionic micelles in MEA.

In this Chapter and Chapters 7 and 9, it has been shown that neutral water-in-oil microemulsions are a powerful catalytic tool for numerous reactions. Further, these systems may have an important rôle to play in mechanistic studies in which lifetimes of short-lived intermediates might be extended and hence allow identification of these latter species, and a greater understanding of mechanisms of reactions.
REFERENCES TO CHAPTER 10

CHAPTER 11

Analysis of kinetic data for reactions of iron(II) 4-methyl, 1,10-phenanthroline with cyanide ions in aqueous solution in terms of Isothermal, Isobaric and related Isochoric activation parameters
11.1 INTRODUCTION

The dependence of rate constants for reactions of iron(II) 4-methyl, 1,10-phenanthroline [Fe(4-Me-phen)$_3^{2+}$, (I)] with cyanide ions on temperature, T, at ambient pressure, p ($\approx$ p$^\circ$), in aqueous solution is reported. Rate constants for aquation rates of Fe(4-Me-phen)$_3^{2+}$ at three different temperatures are also reported. The data are analysed to yield isobaric activation parameters.

![Image](image_url)

Previously reported data$^1$ for the dependence on pressure of rate constants for reactions of Fe(4-Me-phen)$_3^{2+}$ with cyanide ions at constant temperature are analysed to yield isothermal activation parameters.

The isothermal and isobaric activation parameters are used to calculate the corresponding isochoric activation parameters.

Definitions and relationships between isobaric, isothermal and isochoric parameters are examined below in some detail.

11.1.1 Thermodynamic Energy and Chemical Change

Consider a simple reaction in a closed single phase system, in which a single substance, B, reacts to form products, C (equation 11.1);

\[ B \rightarrow^{k} C \quad \cdots \quad (11.1) \]

The chemical substances B and C are, by definition, solutes in a chemically inert solvent, I, i.e. the solvent does not take part in the chemical reaction described by equation 11.1. In the reaction (equation
11.1) an 'energy barrier' separates B and C. Each mole of B has to cross the energy barrier to form a mole of C. The nature of the energy barrier separating B and C can be investigated by examining the dependence of rates of reaction on composition, temperature and pressure.

Spontaneous chemical reaction, in thermodynamic terms, describes an irreversible process, in which the rate of reaction, \( v \), is described by equation 11.2;

\[
v = \frac{de}{dt} \quad \text{..... (11.2)}
\]

where \( e \) describes the change and \( t \) is the time. From the Second Law of Thermodynamics, for a spontaneous reaction;

\[
A.de > 0 \quad \text{..... (11.3)}
\]

where \( A \) is the affinity or the driving force for reaction.

Combining equations 11.2 and 11.3 yields;

\[
A.\frac{de}{dt} = A.v > 0 \text{ for a spontaneous reaction} \quad \text{..... (11.4)}
\]

At time, \( t \), the change in the total Gibbs function, \( G \), for the system is given by;

\[
dG = -S.dT + V.dp - A.de \quad \text{..... (11.5)}
\]

where \( S \) is the entropy and \( V \) is the volume of the system. All spontaneous processes at constant \( T \) and \( p \) lower \( G \). \( G \) is the thermodynamic potential function of a system at fixed \( T \) and \( p \). \( S, V \) and \( A \) are related directly to \( G \) through the partial derivatives;

\[
S = -\left( \frac{\partial G}{\partial T} \right)_{p,e} \quad V = \left( \frac{\partial G}{\partial p} \right)_{T,e} \quad A = -\left( \frac{\partial G}{\partial e} \right)_{T,p} \quad \text{..... (11.6)}
\]

Also \( G = H - T.S \) \quad \text{..... (11.7)}

and \( \left( \frac{\partial H}{\partial T} \right)_p = Cp \) \quad \text{..... (11.8)}

where \( H \) is the enthalpy and \( Cp \) the isobaric heat capacity of the system.
As the reaction proceeds (equation 11.1) so G, V, H, S and Cp change. Eventually the system reaches chemical equilibrium which corresponds to a minimum in G. The composition of the system at equilibrium, ε_{eq}, is characteristic of the system, the temperature, T and pressure, p. At equilibrium, A and (dc/dt) are both zero and thus:

$$\left[ \frac{\partial G}{\partial \varepsilon} \right]_{T,p} = 0$$

The macroscopic thermodynamic variables, G, H, S, V and Cp are related to the partial molar properties of chemical substances in the system. For solute, j, in solution where j = 1, 2, 3 ... i, by definition;

$$\left( \frac{\partial G}{\partial n_j} \right)_{T,p,n_{i\neq j}} = \mu_j$$

or at a given time, t, at constant T, p and n_{i\neq j},

$$G = \sum_{j=1}^{j=i} \mu_j n_j \quad \ldots \quad (11.9)$$

where n_j is the number of moles of substance, j, and μ_j is the chemical potential of j. Combining equations 11.9 and 11.5 yields;

$$-A \cdot dc = \sum_{j=1}^{j=i} \mu_j \cdot dn_j \quad \ldots \quad (11.10)$$

but

$$\frac{dn_j}{dc} = v_j \quad \ldots \quad (11.11)$$

where v_j is the stoichiometry of j, being positive for products and negative for reactants. Combining equations 11.10 and 11.11 yields;

$$A = - \sum_{j=1}^{j=i} \mu_j \cdot v_j = 0 \quad \text{at equilibrium} \quad \ldots \quad (11.12)$$

Similarly for X = H, S, V and Cp;

$$X = \sum_{j=1}^{j=i} n_j \cdot X_j \quad \ldots \quad (11.13)$$
where \( X_j \) is the partial molar property of solute, \( j \).

The chemical potential, \( \mu_j \), of \( j \) in solution is related to the molality, \( m_j = n_j/n_1 M_1 \), where \( n_1, M_1 \) are the number of moles and molar mass of solvent 1 respectively) at constant \( T, p \) and \( n_{izj} \) (Chapter 1, Section 1.3.1) by:

\[
\mu_j(\text{system};T;p) = \mu_j^\phi(\text{sln};T) + R.T.\ln \left( \frac{m_j \gamma_j}{m_j^\phi} \right) + \int_p^{\phi} V_j^\infty(\text{sln};T;p)dp
\]

(11.14)

where limit \( (m_j \to 0, m_i \to 0) \), \( \gamma_j = 1.0 \) at all \( T \) and \( p \). \( \mu_j^\phi \) is the standard chemical potential of \( j \) in solution where \( m_j = 1, \gamma_j = 1 \) at temperature, \( T \), and standard pressure, \( p^\phi \), i.e. an isobaric-isothermal standard state. \( V_j^\infty(\text{sln};T;p^\phi) \) is the partial molar volume of \( j \) at infinite dilution at temperature \( T \) and pressure \( p^\phi \).

For \( X_j = V_j, H_j \) and \( C_p \) (Chapter 1, Section 1.3.1) at \( p = p^\phi \);

Limit \( (m_j \to 0, m_i \to 0) \); \( X_j(\text{system};T;p^\phi) = X_j^\infty(\text{sln};T;p^\phi) = X_j^\phi(\text{sln};T) \).

In this section it has been shown how the macroscopic thermodynamic variables of a system are related to the partial molar properties of chemical substances in the system.

11.1.2 Chemical Kinetics

The rate constant, \( k \), for reaction (equation 11.1) is an intensive dependent variable defined by the independent variables \( T \) and \( p \);

\[
\ln k = \ln k [T,p]
\]

(11.15)

The general differential of equation 11.15 is given by;

\[
d(\ln k) = \left( \frac{\partial \ln k}{\partial T} \right)_p dT + \left( \frac{\partial \ln k}{\partial p} \right)_T dp
\]

(11.16)

The quantitative relationship between \( k, T \) and \( p \) is unknown. The dependence of \( k \) on \( T \) and \( p \) is probed by measuring the rate constant for reaction over a range of fixed \( T \) and \( p \). Various equations can then be
tested with the aim of describing the observed dependence. For
reactions at constant $p$, the dependence of $\ln k$ on $T$, can be expressed
about a reference temperature $\theta$, such that in the limit $T \to \theta$,
$\ln k \to \ln k(\theta)$. Such a dependence can be expressed by equation 11.17;

$$\ln k = \ln k(\theta) + a_2 \left[ \frac{1}{T} - \frac{1}{\theta} \right] + a_3 \ln \left( \frac{T}{\theta} \right) \quad \ldots \quad (11.17)$$

and

$$\left( \frac{\partial \ln k}{\partial T} \right)_p = \frac{a_2}{K T^2} + \frac{a_3 K}{T} \quad \ldots \quad (11.18)$$

Similarly for reaction at fixed $T$, the dependence of $k$ on $p$ may be
fitted about $k(\pi)$ at reference pressure, $\pi$, using equation 11.19;

$$\ln k = \ln k(\pi) + \left( \frac{b_2}{\text{Pa}} \right) (p-\pi) + \left( \frac{b_3}{\text{Pa}^2} \right) (p-\pi)^2 \quad \ldots \quad (11.19)$$

and

$$\left( \frac{\partial \ln k}{\partial p} \right)_T = \left( \frac{b_2}{\text{Pa}} \right) + 2 \left( \frac{b_3}{\text{Pa}^2} \right) (p-\pi) \quad \ldots \quad (11.20)$$

Statistical analysis using Least Squares procedures yields estimates
of $\ln k(\theta)$ and $\ln k(\pi)$, together with the dimensionless constants $a_i$ and
$b_i$ for $i = 2$ to 3. Choosing $\theta$ and $\pi$ near the middle of the experimental
$T$ and $p$ range yields the best independent estimates for $a_i$ and $b_i$.

Alternatively equation 11.19 can be modified by replacing $p$ and $\pi$ by $T$ and
$\theta$ respectively and used to fit the dependence of $k$ on $T$ at fixed $p$.

Numerous other equations\(^2\) have been formulated for the dependence of
$k$ on $T$ and $p$, the validity of the equations being dependent on the type
of chemical reaction under study, and the type of model adopted to
describe the chemical system. There is, as yet, no universally accepted
method for analysing the dependence of $k$ on $T$ and $p$.

The two partial derivatives in equation 11.16 are orthogonal, i.e.
no direct relationship exists between the isobaric and isothermal
quantities.
11.1.3 Properties of Solvents

Consider liquid, 1, at temperature, T and pressure, p in a closed system. The volume, V, of this system is an extensive property. The molar volume, \( V_1^{*} (=V/n_1) \) is an intensive property defined by the intensive independent variables T and p;

\[
V_1^{*} = V_1^{*}[T,p] \quad .... \text{(11.21)}
\]

The general differential of equation 11.21 is;

\[
dV_1 = \left( \frac{\partial V_1^{*}}{\partial T} \right)_p \, dT + \left( \frac{\partial V_1^{*}}{\partial p} \right)_T \, dp \quad .... \text{(11.22)}
\]

For reversible changes, i.e. equilibrium conditions the (isobaric) thermal expansivity, \( \alpha_1^{*} \), is given by;

\[
\alpha_1^{*} = \left( \frac{1}{V_1^{*}} \right) \left( \frac{\partial V_1^{*}}{\partial T} \right)_p \quad .... \text{(11.23)}
\]

and the (isothermal) compressibility \( \kappa_1^{*} \) is given by;

\[
\kappa_1^{*} = - \left( \frac{1}{V_1^{*}} \right) \left( \frac{\partial V_1^{*}}{\partial p} \right)_T \quad .... \text{(11.24)}
\]

From equation 11.21, at \( T=\theta \) and \( p=\pi \), the molar volume of liquid, 1, is defined by \( V_1^{*}[\theta,\pi] \). If the temperature is changed from \( \theta \) to \( \theta + \delta \theta \), the molar volume of liquid, 1, is defined by \( V_1^{*}[\theta + \delta \theta,\pi] \).

For \( V_1^{*} \) to be the same at \( T=\theta \) and \( \theta + \delta \theta \), the pressure has to change from \( \pi \) to \( \pi + \delta \pi_1 \). This isochoric condition can be expressed by;

\[
V_1^{*}[\theta;\pi] = V_1^{*}[\theta + \delta \theta;\pi + \delta \pi_1] \quad .... \text{(11.25)}
\]

\( \delta \pi_1 \) is characteristic of the liquid, \( \theta \) and \( \pi \).

11.1.4 Kinetic Parameters

The Arrhenius equation\(^3\) links the rate constant with the activation energy, \( E_A \), for reaction;

\[
k = A \, \exp (-E_A/R.T)
\]

or

\[
\ln k = \ln A - \frac{E_A}{(R.T)} \quad .... \text{(11.26)}
\]
where $A$ is the "frequency" factor and $R$ the gas constant. Differentiating equation 11.26 with respect to temperature at constant pressure yields:

$$\left( \frac{\partial \ln k}{\partial T} \right)_p = \frac{E_A}{(R.T^2)} \quad \ldots \quad (11.27)$$

For a given reaction, $E_A$ is dependent on $T$, $p$ and solvent.

The dependence of rate constant on $p$ at constant $T$, defines an activation volume, $\Delta V$;

$$\left( \frac{\partial \ln k}{\partial p} \right)_T = -\frac{\Delta V}{(R.T)} \quad \ldots \quad (11.28)$$

The isobaric and isothermal dependences of $\ln k$ are characterised by $E_A$ and $\Delta V$ respectively.

In another analysis the dependence of $(\ln k)$ on $T$ is considered where the pressure changes to keep the molar volume, $V_{1^*}$, of solvent, 1, constant (equation 11.25), i.e. an isochoric condition with respect to the molar volume, $V_{1^*}$, of solvent, 1. The required partial derivative is:

$$\left( \frac{\partial \ln k}{\partial T} \right)_{V_{1^*}} \quad \ldots \quad (11.29)$$

Similarly the dependence of $(\ln k)$ on $p$, where $T$ changes to keep $V_{1^*}$ constant yields the partial derivative;

$$\left( \frac{\partial \ln k}{\partial p} \right)_{V_{1^*}} \quad \ldots \quad (11.30)$$

It is helpful, at this stage, to recall certain operations in differential calculus. Consider a variable, $u$, which is a function of $x$ and $y$;

$$u = u[x,y]$$

Then

$$du = \left( \frac{\partial u}{\partial x} \right)_y \cdot dx + \left( \frac{\partial u}{\partial y} \right)_x \cdot dy \quad \ldots \quad (11.31)$$

At constant $u$, $du = 0$, and equation 11.31 becomes;
\[
0 = \left( \frac{\partial u}{\partial x} \right)_y \left( \frac{\partial x}{\partial y} \right)_u + \left( \frac{\partial u}{\partial y} \right)_x
\]

or
\[
\left( \frac{\partial u}{\partial x} \right)_y \left( \frac{\partial x}{\partial y} \right)_u \cdot \left( \frac{\partial y}{\partial u} \right)_x = -1 \quad \cdots \ (11.32)
\]

Consider another variable, \( z \), which is also a function of \( x \) and \( y \);

\[ z = z[x,y] \]

Then;
\[ \frac{dz}{dy} = \left( \frac{\partial z}{\partial x} \right)_y \cdot dx + \left( \frac{\partial z}{\partial y} \right)_x \cdot dy \quad \cdots \ (11.33) \]

At constant, \( u \);
\[
\left( \frac{\partial z}{\partial x} \right)_u = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \cdot \left( \frac{\partial y}{\partial x} \right)_u \quad \cdots \ (11.34)
\]

Combining equations 11.32 and 11.34 yields;
\[
\left( \frac{\partial z}{\partial x} \right)_u = \left( \frac{\partial z}{\partial x} \right)_y - \left( \frac{\partial z}{\partial y} \right)_x \cdot \left( \frac{\partial y}{\partial x} \right)_y \cdot \left( \frac{\partial u}{\partial x} \right)_x \quad \cdots \ (11.35)
\]

Equation 11.35 changes a partial derivative at constant \( y \), to the corresponding partial derivative at constant \( u \).

Therefore from equation 11.35, the isochoric (with respect to \( V_1^* \)) partial derivatives 11.29 and 11.30 are related to the isobaric and isothermal derivatives by;
\[
\left( \frac{\partial \ln k}{\partial T} \right)_{V_1^*} = \left( \frac{\partial \ln k}{\partial T} \right)_p - \left( \frac{\partial \ln k}{\partial p} \right)_T \cdot \left( \frac{\partial V_1^*}{\partial T} \right)_p \quad \cdots \ (11.36)
\]

\[
\left( \frac{\partial \ln k}{\partial p} \right)_{V_1^*} = \left( \frac{\partial \ln k}{\partial p} \right)_T - \left( \frac{\partial \ln k}{\partial T} \right)_p \cdot \left( \frac{\partial V_1^*}{\partial p} \right)_T \cdot \left( \frac{\partial T}{\partial V_1^*} \right)_p \quad \cdots \ (11.37)
\]

The two partial derivatives calculated by equations 11.36 and 11.37 are not orthogonal. Combining equations 11.36 and 11.37 yields;
\[
\left( \frac{\partial \ln k}{\partial T} \right)_{V_1^*} = - \left( \frac{\partial \ln k}{\partial p} \right)_{V_1^*} \cdot \left( \frac{\partial p}{\partial V_1^*} \right)_T \cdot \left( \frac{\partial V_1^*}{\partial T} \right)_p \quad \cdots \ (11.38)
\]

Equation 11.38 shows how the two partial derivatives, \( (\partial \ln k/\partial T)_{V_1^*} \) and \( (\partial \ln k/\partial p)_{V_1^*} \) are related through the properties of the solvent.

By definition;
\[
\left( \frac{\partial \ln k}{\partial T} \right)_{V_1^*} = \frac{E_A(V_1^*)}{(R.T^2)} \quad \cdots \ (11.39)
\]
where $E_A(V_i^*)$ is an isochoric ($V_i^*$) energy of activation.

11.1.5 Transition State Theory

Transition State Theory (Chapter 3, Section 3.1.4) provides a route for analysis of kinetic data in terms of the thermodynamic properties of a system. In these terms reaction (equation 11.1) is described using equation 11.40, where $V_i^*$ represents the transition state;

\[ B \rightarrow^{V_i^*} \rightarrow C \quad \text{.... (11.40)} \]

If the transmission coefficient is unity at all $T$ and $p$, then,

\[ k = \left( \frac{k_B T}{h} \right)^* K^\phi \left( \text{sln;} T \right) \exp \left[ \int_p^{p^*} \frac{\Delta^* V^\infty \left( \text{sln;} T, p \right)}{R T} \, dp \right] \quad \text{.... (11.41)} \]

where

\[ \Delta^* G^\phi \left( \text{sln;} T \right) = -R T \ln^* K^\phi \left( \text{sln;} T \right) = \mu^* \phi \left( \text{sln;} T \right) - \mu_B^\phi \left( \text{sln;} T \right) \quad \text{.... (11.42)} \]

$K^\phi$ is the standard equilibrium constant for activation, $\Delta^* V^\infty$ is the molar volume of activation. The rate constant, $k$, is determined by $\Delta^* V^\infty$ and the difference between the standard chemical potentials of reactant and transition state. $K^\phi$ depends on temperature but not on pressure. By analogy with the Van't Hoff equation for the dependence of $K^\phi$ on $T$;

\[ \frac{\partial \ln (k/T)}{\partial T} = \frac{\Delta^* H^\infty \left( \text{sln;} T, p \right)}{R T^2} \quad \text{.... (11.43)} \]

where

\[ \Delta^* H^\infty \left( \text{sln;} T, p \right) = H^\infty_s \left( \text{sln;} T, p \right) - H^\infty_B \left( \text{sln;} T, p \right). \]

But at $p = p^*$ in the limit ($m^* \rightarrow 0; m_B \rightarrow 0$);

\[ \Delta^* H^\phi \left( \text{sln;} T \right) = H^\phi_s \left( \text{sln;} T \right) - H^\phi_B \left( \text{sln;} T \right) \]

$\Delta^* H^\infty$ is dependent on both $T$ and $p$, but $\Delta^* H^\phi$ is only dependent on $T$.

The molar volume of activation is given by (cf. equation 11.28);

\[ \left( \frac{\partial \ln k}{\partial p} \right)_T = -\frac{\Delta^* V^\infty \left( \text{sln;} T, p \right)}{R T} \quad \text{.... (11.44)} \]
\[ \Delta^* V^\infty (sln; T; p) = V^\infty_A(sln; T; p) - V^\infty_B(sln; T; p) \]

\( \Delta^* V^\infty \) is dependent on both \( T \) and \( p \).

The molar isobaric heat capacity of activation, \( \Delta^* C_p^\infty \), is given by:

\[ \Delta^* C_p^\infty = \left( \frac{\partial (\Delta^* H^\infty)}{\partial T} \right)_p \quad \text{.... (11.45)} \]

Also using a Maxwell's equation:

\[ \left( \frac{\partial (\Delta^* H^\infty)}{\partial p} \right)_T = \Delta^* V^\infty - T \left( \frac{\partial (\Delta^* V^\infty)}{\partial T} \right)_p \quad \text{.... (11.46)} \]

Activation parameters, \( \Delta^* V^\infty \) and \( \Delta^* H^\infty \) refer to the differences between the partial molar properties of reactants and transition states in ideal solutions under isothermal-isobaric conditions.

11.1.6 Isochoric Activation Parameters

\( \Delta^* H^\infty (sln; T; p) \) describes the dependence of rate constants for a given reaction on \( T \) under isobaric conditions (equation 11.43). The dependence of \( \ln(k/T) \) on \( T \), when the pressure changes, so that the molar volume \( (V_1^*) \) of the solvent is kept constant, is expressed using equation 11.35 by:

\[ \left( \frac{\partial \ln(k/T)}{\partial T} \right)_{V_1^*} = \left( \frac{\partial \ln(k/T)}{\partial T} \right)_p - \left( \frac{\partial \ln(k/T)}{\partial p} \right)_T \cdot \left( \frac{\partial V_1^*}{\partial T} \right)_p \cdot \left( \frac{\partial p}{\partial V_1^*} \right)_T \quad \text{.... (11.47)} \]

Combining equations 11.47, 11.23 and 11.24 yields:

\[ \left( \frac{\partial \ln(k/T)}{\partial T} \right)_{V_1^*} = \left( \frac{\partial \ln(k/T)}{\partial T} \right)_p + \left( \frac{\alpha_1^*}{K_1^*} \right) \cdot \left( \frac{\partial \ln(k/T)}{\partial p} \right)_T \quad \text{.... (11.48)} \]

But \( T \) is not dependent on pressure; thus equation 11.48 can be re-written:

\[ \left( \frac{\partial \ln(k/T)}{\partial T} \right)_{V_1^*} = \left( \frac{\partial \ln(k/T)}{\partial T} \right)_p + \left( \frac{\alpha_1^*}{K_1^*} \right) \cdot \left( \frac{\partial \ln k}{\partial p} \right)_T \quad \text{.... (11.49)} \]

A quantity '\( \psi \)' is defined^5a,^5b by equation 11.50:

\[ \left( \frac{\partial \ln(k/T)}{\partial T} \right)_{V_1^*} = \frac{\Delta^* \psi(V_1^*)}{(R.T^2)} \quad \text{.... (11.50)} \]
\[ \Delta^*\psi(V_i^*) \] is the isochoric \((V_i^*)\) equivalent of the isobaric parameter \(\Delta^+H^\infty\) (cf. equation 11.43) and is expressed in \(\text{J mol}^{-1}\). \(\Delta^*\psi(V_i^*)\) is a pseudo isochoric activation parameter, where the isochoric condition refers to the molar volume of the pure solvent. The isochoric condition in equation 11.49 is extrinsic (i.e. not directly related) to the reacting system.

Similarly, the dependence of \(k\) on \(p\) at constant \(V_i^*\) is described by equation 11.51;

\[
\left( \frac{\partial \ln (k/T)}{\partial p} \right)_{V_i^*} = \left( \frac{\partial \ln k}{\partial p} \right)_T + \left( \frac{\partial \ln (k/T)}{\partial T} \right)_P 
\]

where by definition;

\[
\left( \frac{\partial \ln (k/T)}{\partial p} \right)_{V_i^*} = -\frac{\Delta^*\phi(V_i^*)}{(R.T)} 
\]

\(\Delta^*\phi(V_i^*)\) is expressed in \(\text{m}^3 \text{ mol}^{-1}\) (cf. equation 11.44) and is an extrinsic isochoric activation parameter. Equations 11.49 and 11.51 can be rewritten in terms of the molar isobaric and isothermal activation parameters, i.e. combining equations 11.49, 11.50, 11.43 and 11.44 yields;

\[
\Delta^*\psi(V_i^*) = \Delta^+H^\infty(sln;T;p) - T.\Delta^+V^\infty(sln;T;p).\frac{\Delta l_s^*}{(\kappa_1^*)} 
\]

and combining equations 11.51, 11.52, 11.43 and 11.44 yields;

\[
\Delta^*\phi(V_i^*) = \Delta^+V^\infty(sln;T;p) - \left( \frac{\Delta^+H^\infty(sln;T;p)}{T} \right).\frac{\Delta l_s^*}{(\kappa_1^*)} 
\]

The isochoric condition applies therefore to the pure solvent and not to either the system under examination or some ideal solution containing unit molalities of the solutes.

\(\Delta^*\psi(V_i^*)\) and \(\Delta^*\phi(V_i^*)\) are dependent on both temperature and pressure. For a reaction in a binary aqueous mixture, \(V_m\) (i.e. the molar volume of a liquid having a particular mole fraction, \(x_2\), composition) depend
on $T$ and $p$. Thus $\Delta^* \psi (V_m)$ and $\Delta^* \phi (V_m)$ also depend on $T$ and $p$. If kinetic data in aqueous solution are the reference, then the transfer parameters $\Delta [(x_2=0) \rightarrow x_2] \Delta^* \psi (V_m)$ and $\Delta [(x_2=0) \rightarrow x_2] \Delta^* \phi (V_m)$ are given by;

$$
\Delta [(x_2=0) \rightarrow x_2] \Delta^* \psi (V_m) = \Delta^* \psi [V_m (x_2)] - \Delta^* \psi [V_m (x_2=0)] \quad ... \quad (11.55)
$$

$$
\Delta [(x_2=0) \rightarrow x_2] \Delta^* \phi (V_m) = \Delta^* \phi [V_m (x_2)] - \Delta^* \phi [V_m (x_2=0)] \quad ... \quad (11.56)
$$

The parameters on the right-hand side of equations 11.55 and 11.56 are isochoric ($V_m$) parameters for (i) a mixture and for (ii) water, i.e. local to each solvent system. The two transfer parameters, $\Delta [(x_2=0) \rightarrow x_2] \Delta^* \psi (V_m)$ and $\Delta [(x_2=0) \rightarrow x_2] \Delta^* \phi (V_m)$ therefore, only measure the differences between these local quantities. They do not measure differences under an overall isochoric condition.

Similarly (cf. equations 11.49 and 11.51) equations can be written for derived isochoric ($V_1^*$) activation parameters, e.g. $\Delta^* V^\infty$;

$$
\left( \frac{\partial \Delta^* V^\infty}{\partial T} \right)_{V_1^*} = \left( \frac{\partial \Delta^* V^\infty}{\partial T} \right)_p + \left( \frac{\alpha_1^*}{K_1^*} \right) \left( \frac{\partial \Delta^* V^\infty}{\partial p} \right)_T \quad ... \quad (11.57)
$$

A similar equation can be written for the isochoric ($V_1^*$) dependence of $\Delta^* V^\infty$ on pressure, and the isochoric ($V_1^*$) dependences of $\Delta^* H^\infty$ on $T$ and $p$.

In the analysis presented in this section, the term 'isochoric' can be understood in terms of variations in $T$ and $p$ which preserve constant molar volume ($V_1^*$) of pure solvent, 1. The isochoric conditions are extrinsic to a reaction characterised by a rate constant, $k$, i.e. they refer to another system, the solvent, rather than the solution. The term 'isochoric' is not used in the above analysis with respect to a thermodynamic change at constant volume, where the Helmholtz function, $F$, is the isochoric-isothermal thermodynamic potential function. Under the latter conditions the isochoric parameters are intrinsic to the chemical process under consideration. The distinction is important.
because the chemical equilibrium under isochoric ($V_i^*$) conditions (equation 11.40) between initial and transition state describes a system at a minimum in $G$ and the reference states for the solutes are isobaric-isothermal.

11.2 EXPERIMENTAL

Concentrated aqueous solutions of Fe$(4$-Me-phen$)_3^{2+}$ as the sulphate salt were prepared. Kinetics of reaction of Fe$(4$-Me-phen$)_3^{2+}$ with cyanide ions were monitored in aqueous solution where [potassium cyanide] = 0.5 mol dm$^{-3}$, at seven different temperatures between 298 K and 318 K. In all systems [complex] $< 10^{-4}$ mol dm$^{-3}$ and [potassium cyanide] $> [\text{complex}]$.

Aqueous solutions of Fe$(4$-Me-phen$)_3^{2+}$ are bright red, $\lambda_{\text{max}} = 513$ nm. Repeat scans of the dependence of absorbance on wavelength (Unicam SP800 spectrophotometer - Chapter 2, Section 2.4.1) revealed that the dependence of absorbance on time was first-order. Kinetics of reaction were monitored at $\lambda_{\text{max}} = 513$ nm (Unicam SP800 spectrophotometer - Chapter 2, Section 2.4.1). The computer was programmed to fit the absorbance data to a first-order kinetic expression (Chapter 2, Section 2.3). The thermostat was adjusted to yield the appropriate temperatures at which kinetic data were monitored.

Kinetic data for aquation reactions of Fe$(4$-Me-phen$)_3^{2+}$ in aqueous solution where [sulphuric acid] = 0.5 mol dm$^{-3}$, were monitored at 298 K, 308 K and 315 K by analogous methods.

The kinetic data and previously reported$^1$ kinetic data for reactions of Fe$(4$-Me-phen$)_3^{2+}$ with cyanide ions at different pressures were analysed to obtain isobaric and isothermal activation parameters. These latter parameters were used to obtain the corresponding isochoric ($V_i^*$)
activation parameters.

11.3 LINEAR LEAST SQUARES ANALYSIS

It is helpful at this stage to examine some important aspects of the analytical technique, which are used to describe the dependence of \( (k/T) \) on temperature.

The input to the analysis is a set of dependent variables, \( Y \) [e.g. \( \ln(k/T) \)] and independent variables, \( X \) (e.g. \( T \)). For example, consider the equation;

\[
\ln(k/T) = a_1 + a_2 \cdot [T] + a_3 \cdot [T]^2 \tag{11.58}
\]

\( a_1, a_2 \) and \( a_3 \) are the unknown linear variables. Equation 11.58 can be rewritten as a matrix for \( n \) data points;

\[
\begin{array}{cccc}
1 & x_1 & x_1^2 & a_1 \\
1 & x_2 & x_2^2 & a_2 \\
1 & x_3 & x_3^2 & a_3 \\
\vdots & \vdots & \vdots & \vdots \\
1 & x_n & x_n^2 & a_n \\
\end{array}
\begin{array}{c}
= \\
Y_1 \\
Y_2 \\
Y_3 \\
\vdots \\
Y_n \\
\end{array}
\tag{11.59}
\]

In practice the variables \( a_1, a_2 \) and \( a_3 \) (\( \equiv \beta \)) are given by;

\[
Y = X\beta + \epsilon \tag{11.60}
\]

\( Y \) is the column vector of the dependent variables \( [\ln(k/T)] \); \( X \) is a matrix comprising functions of the known independent variables \( (T) \); \( \beta \) is a column vector of the unknown parameters \( (a_1, a_2 \) and \( a_3 \)) and \( \epsilon \) is a column vector of the unknown errors associated with the measured dependent variables. The Linear Least Squares analysis is based on equation 11.61, where \( X^T \) denotes the transpose of \( X \);

\[
\hat{\beta} = (X^T X^{-1}) X^T Y \tag{11.61}
\]

Estimates, \( \hat{\beta} \), minimise the sum of the squares of differences between
\[ \hat{Y}_{\text{calc}} \text{ and } Y_{\text{obs}}, \text{i.e. } \sum_{i=1}^{n} [Y_{\text{obs}} - \hat{Y}_{\text{calc}}]^2 \text{ is a minimum (e.g. between measured } \ln(k/T) \text{ and estimated } \ln(k/T) \text{ over } n \text{ values}). \text{ Thus from estimates, } \hat{\beta}, \text{ the calculated } Y-\text{values are obtained using equation 11.62; (e.g. } \ln(k/T) \text{ from estimates } a_1, a_2 \text{ and } a_3).\]

\[ Y_{\text{calc}} = X.\hat{\beta} \quad \text{.... (11.62)} \]

Parameters \( \hat{\beta} \) are the most precise unbiased estimates of \( \beta \). If the experiment were repeated 'q' times (q sets of 'n' values for \( \ln(k/T) \) and T), the individual estimates of each \( \beta_j \) parameter would be distributed about the true value of \( \beta_j \), with minimum variance, \( S_j \), e.g. equation 11.63 for \( \beta_1 \);

\[ S_j^2 = \sum_{j=1}^{q} [\hat{\beta}_j(j) - \beta_1]/(q-1) \quad \text{.... (11.63)} \]

The Least Squares estimate \( \hat{\beta} \) can be used to estimate the variance, \( \hat{\sigma}^2 \), associated with the errors;

\[ \hat{\sigma}^2 = (Y - X.\hat{\beta})^T(Y - X.\hat{\beta})/(n-m) \quad \text{.... (11.64)} \]

where \( n \) is the number of independent measurements and \( m \) is the number of unknowns to be estimated.

The quantity \( n-m \) is the number of degrees of freedom. If the experiment is repeated q times, analysis will provide q values of \( \hat{\sigma}^2 \). Each estimate \( \hat{\sigma}^2 \) is an unbiased estimate of the variance \( S^2 \) and q values of \( \hat{\sigma}^2 \) will be distributed about \( S^2 \).

For a single set of data the estimate \( \hat{\sigma}^2 \) is a guide to the success of the equation in accounting for the dependence of \( \ln(k/T) \) on T. The square root, \( \hat{\sigma} \), of \( \hat{\sigma}^2 \) is the standard deviation on the fitted quantity \( \ln(k/T) \). It is helpful to plot \( \Delta(= \hat{Y} - Y) \) against the independent variable X [e.g. \( \{ \hat{\ln}(k/T) - \ln(k/T) \} \) vs T]. A satisfactory description of the dependence of \( \ln(k/T) \) on T results in a scatter of \( \Delta \) greater than and less than zero.
The symmetric variance-covariance matrix (equation 11.65) provides further detail concerning the estimates \( \hat{\beta} \).

\[
\hat{\beta} = \hat{\sigma}^2 V \tag{11.65}
\]

where the dispersion matrix, \( V \), is given by equation 11.66;

\[
V = (X^TX)^{-1} \tag{11.66}
\]

For three linear coefficients (cf. equation 11.58), \( \hat{\beta} \) is a 3 x 3 matrix; (equation 11.67)

\[
\begin{array}{ccc}
a_1 & a_2 & a_3 \\
a_1 & \hat{\beta}_{11} & \hat{\beta}_{12} & \hat{\beta}_{13} \\
a_2 & \hat{\beta}_{21} & \hat{\beta}_{22} & \hat{\beta}_{23} \\
a_3 & \hat{\beta}_{31} & \hat{\beta}_{32} & \hat{\beta}_{33} \\
\end{array} \tag{11.67}
\]

The diagonal elements \( \hat{\beta}_{11}, \hat{\beta}_{22} \) and \( \hat{\beta}_{33} \) in equation 11.67 are estimates of the variance of \( a_1, a_2 \) and \( a_3 \). The smaller the value of \( \hat{\beta}_{kk} \) (where \( k = 1, 2, 3 \)) then the closer \( \hat{\beta}_k \) is to the true value of \( \beta_k \). \( \hat{\beta}_{kk} \) is always positive. The square root of \( \hat{\beta}_{kk} \) is the standard error associated with \( \hat{\beta}_k \).

The normalized variance-covariance matrix \( C \), is given by;

\[
C_{ij} = \theta_{ij}/(\theta_{ii} \theta_{jj})^{1/2} \tag{11.68}
\]

For equation 11.58 the analysis gives three values of \( \hat{\beta} \) (\( \hat{a}_1, \hat{a}_2 \) and \( \hat{a}_3 \)), so \( C \) is a 3 x 3 matrix where the diagonal elements are unity (e.g. \( C_{11} = \theta_{11}/(\theta_{11} \theta_{11})^{1/2} = 1.0 \)). The off-diagonal elements are between -1 and +1. The magnitude of \( C_{ij} \) measures the extent of the dependence of \( \hat{\beta}_i \) on \( \hat{\beta}_j \) (e.g. \( C_{12} \) measures the extent \( \hat{a}_1 \) depends on \( \hat{a}_2 \)). If \( C_{ij} \) is approximately ±1, the interdependence is significant. The smaller the value of \( |C_{ij}| \), the smaller the dependence of the estimates, \( \hat{a}_1, \hat{a}_2 \) and \( \hat{a}_3 \) on each other. The values of \( C_{ij} \) are not estimates and therefore provide a sound basis for assessing the validity of the equation used to describe the dependence of \( Y [\ln(k/T)] \) on \( X(T) \).

Equation 11.58 is a polynomial in \( T \) and can be extended to include
terms in higher powers of $T$. It is necessary to test which terms in $T$
are statistically significant and hence decide on the most appropriate
equation which describes the dependence of $\ln(k/T)$ on $T$ for a particular
system. The F-test is one method which can be used to test the
statistical significance of the individual terms in $T$. Consider
equation 11.58 and 11.69;

$$\ln(k/T) = a_1 + a_2[T] \quad \text{.... (11.69)}$$

Let $\hat{\sigma}_2^2$ be the variance associated with the errors for the dependence
of $\ln(k/T)$ on $T$ given by equation 11.69 and $\hat{\sigma}_3^2$ be the variance
associated with the errors for the dependence given by equation 11.58.
For $n$ data points, $(n-2)$ and $(n-3)$ degrees of freedom are associated
with $\hat{\sigma}_2^2$ and $\hat{\sigma}_3^2$ respectively. It is necessary to determine whether or
not $\hat{\sigma}_2^2 > \hat{\sigma}_3^2$. The F-test follows the general procedure for significance
tests by adopting a null hypothesis, i.e. the assumption that the
samples were drawn from populations with the same variance; (equation
11.70)

$$H_0 \equiv \hat{\sigma}_2^2 = \hat{\sigma}_3^2 \quad \text{.... (11.70)}$$

If $\hat{\sigma}_2^2 < \hat{\sigma}_3^2$ there is no need for a statistical test because it is
clear that the third term in $[T]^2$ (equation 11.58) is not significant.
If $\hat{\sigma}_2^2 > \hat{\sigma}_3^2$ then $F[(n-2),(n-3)]$ is given by;

$$F[(n-2),(n-3)] = \frac{\hat{\sigma}_2^2}{\hat{\sigma}_3^2} \quad \text{.... (11.71)}$$

The degrees of freedom associated with an F-value should always be
quoted. The calculated $F[(n-2),(n-3)]$ (equation 11.71) is compared with
the tabulated value. These latter values are tabulated to give $p\%$
(where $p = 90, 95$ and $99\%$) confidence limits, i.e. the limits within
which there is a $p\%$ confidence that the true value exists. For example,
if $p = 95\%$ there is a $5\%$ chance that the true value exists outside these
limits. If tabulated $F_{95\%}[(n-2),(n-3)] >$ calculated $F[(n-2),(n-3)]$, the
third term in $[T]^2$ (equation 11.58) is not statistically significant at
a 95% confidence limit and thus equation 11.69 is a better description
of the dependence of $\ln(k/T)$ on $T$, than equation 11.58.

11.4 RESULTS AND DISCUSSION

In aqueous solution both kinetics of aquation reactions of Fe(4-Me-
phen)$_3^{2+}$ and kinetics of reaction with cyanide ions were first order in
[complex]. Kinetic data are reported in Table 11.1. Each rate constant
is the mean of at least three individual determinations, the reproducibil-
ity being, at worst, within 5%.

Rate constants for aquation at 301 K, 305 K, 312 K and 318 K were inter-
polated from a graph of $\ln k$ vs. $1/T$ (Fig. 11.1).

Reaction between Fe(4-Me-phen)$_3^{2+}$ and cyanide ions to give Fe(4-Me-
phen)$_2$CN$_2$ and free ligand follows the rate expression; (Chapter 1,
Section 1.6.1).

$$- \frac{d \text{[complex]}}{dt} = (k_1 + k_2 \cdot [\text{CN}^-]) \cdot \text{[complex]}$$

Then $k_{obs} = k_1 + k_2 \cdot [\text{CN}^-]$.

The $k_2$-term was obtained from $(k_{obs} - k_1)/[\text{CN}^-]$ and is reported in Table
11.2.

The Arrhenius activation energy, $E_A$, for the aquation reaction, was
estimated from the slope of the straight line plot of $\ln k_1$ vs. $1/T$ (Fig.
11.1) (i.e. slope = $-E_A/R$) and was found to be 125.6 (±1.28) kJ mol$^{-1}$.

The dependence of $(k/T)$ on temperature and pressure was fitted to the
equation;

$$\ln(k/T) = \ln(k[\theta;\pi]/\theta) + a_1(T-\theta) + a_2(p-\pi) + a_3(T-\theta)^2$$
$$+ a_4(p-\pi)^2 + a_5(p-\pi)(T-\theta) + a_6(T-\theta)^2(p-\pi)$$

about a reference temperature $\theta$ (298.2 K) and reference pressure $\pi$ (68 bars)
FIGURE 11.11 Dependence of $\ln(k)$ on $(1/T)$ for aquation reactions of Fe(4-Me-Phen)$_2^{2+}$ in aqueous solution.
The calculated second-order rate constant, $k_2$, for reaction of the iron complex with cyanide ions is expressed in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (i.e. on the concentration scale). Standard activation parameters are expressed on the molal scale. Therefore, the rate constant $k_2(c)$ was corrected to $k_2(m)$ (equation 11.73) using the density ($\rho_1^*$) of the pure solvent:

$$\rho_1^* k_2(c\text{-scale}) = k_2(m\text{-scale}) .... \hspace{1cm} (11.73)$$

Equation 11.72 was chosen to account for the dependence of $\ln(k/T)$ on $T$ and $p$ because the results obtained using the same analysis, to account for the dependence of first-order rate constants on $T$ and $p$, for solvolysis of benzyl chloride were consistent with previously reported data.

Eleven data points were used in equation 11.72 - seven data points reported here and four from reference 1. Only the first three terms were statistically significant in the fitting of kinetic data for this reaction to equation 11.72 (Section 11.3).

Parameter $a_1$ corresponds to the partial differential $[\partial \ln(k/T)/\partial T]_p$ and $a_2$ corresponds to the partial differential $[\partial \ln(k/T)/\partial p]_T$. Using these latter parameters the isothermal-isobaric standard activation parameters $\Delta^*H^\circ$ and $\Delta^*V^\circ$ were calculated using equations 11.43 and 11.44.

Using equations 11.49, 11.51 and published data for $a_1^*$ and $k_1^*$, the isochoric ($V_1^*$) partial differentials $[\partial \ln(k/T)/\partial T]_{V_1^*}$ and $[\partial \ln(k/T)/\partial p]_{V_1^*}$ were calculated. From these latter differentials and using equations 11.50 and 11.52, the isochoric ($V_1^*$) activation parameters $\Delta^*\psi(V_1^*)$ and $\Delta^*\phi(V_1^*)$ were obtained. The isobaric, isothermal and isochoric partial differentials and corresponding activation parameters are reported in Table 11.4.
Isochoric $(V_i^*)$ activation parameters for reaction of the iron complex with cyanide ions were calculated because there are many claims in the literature that isochoric activation parameters are less complicated than the corresponding isothermal-isobaric derivatives. This view is supported by Whalley and co-workers in their analysis of the dependence of activation parameters on solvent composition for reactions in binary aqueous mixtures.\textsuperscript{11-13} Gay and Whalley concluded\textsuperscript{13} that constant-volume activation parameters were more appropriate for fundamental discussion. Holtermann and Engberts,\textsuperscript{14} however, found no compelling evidence for this view, following a study of the water-catalyzed hydrolysis of p-methoxyphenyl 2,2-dichloropropionate in typically aqueous solution.

This Chapter, therefore, has attempted to examine which volume is held constant and which reference (or standard) states for reactants and transition state are referred to in derived parameters such as the isochoric thermodynamic energy and isochoric heat capacity of activation.

The term 'isochoric' is not used in the thermodynamic sense, where the rate constant for a given reaction characterises the approach of a system to a minimum in $F$ (Helmholtz Function), under isothermal-isochoric conditions.

As far as can be discerned from published papers,\textsuperscript{10-13} the rate constant for a given chemical reaction under so-called 'isochoric' conditions always characterises the approach of a system to a minimum in $G$ under isothermal-isobaric conditions. Reported isochoric functions are calculated using, for example, equation 11.53, in which the properties of the pure solvent are used. In other words, 'isochoric' means at constant molar volume of pure solvent, $V_i^*$.\textsuperscript{11} Therefore, the
term 'isochoric ($V_i^*$)' has been used in this Chapter.

Other isochoric functions have been mentioned. For example, Whalley\textsuperscript{15} claims that the volume kept constant is 'the volume of an equilibrium mixture of initial and transition state'. Caldin\textsuperscript{16} suggested that a set of isochoric ($\Delta^* V^\infty$) parameters could be calculated. The analysis in Section 11.1.6 can be repeated where $\Delta^* V^\infty$ replaces $V_i^*$ in equations 11.21 and 11.25, and the partial differentials of $\ln(k/T)$ with respect to $T$ and $p$ would have the form:

$$\left(\frac{\partial \ln(k/T)}{\partial T}\right)_{\Delta^* V^\infty} \text{ and } \left(\frac{\partial \ln(k/T)}{\partial p}\right)_{\Delta^* V^\infty}$$

In general, therefore, the constant volumes are extrinsic to the system undergoing reaction. The problem is raised as to the significance to be attached to $\Delta^* \psi(V_i^*)$ and $\Delta^* \phi(V_i^*)$ (equations 11.50 and 11.52). $\Delta^* \psi(V_i^*)$ as defined by equation 11.50 is not the thermodynamic energy of activation and $\Delta^* \phi(V_i^*)$ as defined by equation 11.52 is not an activation volume. Further, the temperature derivative of $\Delta^* \psi(V_i^*)$ is not the molar isochoric heat capacity of activation.

Consider a plot of $\ln(k/T)$ vs. $T$ at constant pressure. As the temperature is increased, so the molar volume of the pure solvent, $V_i^*$, changes at fixed pressure. For a corresponding plot of $\ln(k/T)$ vs. $T$ at constant $V_i^*$, each point on the plot is calculated for a local isochoric condition corresponding to a characteristic change in pressure, $\delta \Pi_1$ (equation 11.25). For reaction in a binary aqueous mixture, the molar volume of a solvent mixture when mole fraction of added cosolvent, $x_2 = 0.1$ is not the same as when $x_2 = 0.3$. Hence, in a comparison of the variation of $\ln(k/T)$ with $T$ at constant molar volume of solvent, neither the volume of the solvent nor the local pressure increments are constant across the plot.

Isobaric activation parameters, however, do not create the ambiguity.
associated with isochoric parameters.

The aim of this Chapter has been to clarify and explore the definitions implied by isochoric activation parameters. At this stage, relatively little data are available so no patterns have been identified.
REFERENCES TO CHAPTER 11


Appendix 1

Effects of Alcohols and Microemulsions on Kinetics of Substitution at cis-bis-pyridinetetracarbonylmolybdenum(0)
Effects of alcohols and microemulsions on kinetics of substitution at cis-bis-pyridinetetracarbonylmolybdenum(0)

Kinetic data for substitution reactions of cis-bis-pyridinetetracarbonylmolybdenum(0) (Mo(CO)$_4$py$_2$) with bidentate diimine ligands LL, where LL = 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen) are reported at 298 K in ME.B., ME.C., 'toluene + n-butanol' mixtures and 'hexane + isopropanol' mixtures. ME.B. and ME.C. comprised of: 45 mol % isopropanol + 40 mol % hexane + 15 mol % water, and 'SDS + 30 mass % n-butanol + 5 mass % toluene + 65 mass % water' (SDS : n-butanol was 1 : 2) respectively (Chapter 6, Sections 6.6.2 and 6.6.3).

Kinetics of reaction were monitored by measuring the rate of appearance of products, Mo(CO)$_4$phen and Mo(CO)$_4$bipy. Both these latter complexes are solvatochromic $\lambda_{max}$ of the complexes in the various solvent mixtures are reported in Table A.1.

Kinetic results presented in this Appendix were part of a joint project with H. Elias, H.-T. Macholdt, K. Wannowius and co-workers at Darmstadt University, West Germany. Kinetic data for reaction in many of the mixed solvent systems were fitted to a two exponential expression (Scheme (V), Scheme (VI) - Chapter 10, Section 10.4, equations 10.5 and 10.18). In other systems kinetics of reaction conformed to first-order (Chapter 2, Section 2.3). In view of the complexities in the kinetics of reaction in many of the solvent systems, investigations are being continued in Darmstadt.

Each rate parameter is the mean of at least three individual determinations, the reproducibility being at worst within 10%.
### TABLE A.1.

Solvent effects on frequencies of maximum absorption ($\nu_{\text{max}}$) of Mo(CO)$_4$(LL) in the visible region

<table>
<thead>
<tr>
<th>Solvent medium$^a$</th>
<th>$\nu_{\text{max}}$/cm$^{-1}$</th>
<th>$\text{Mo(CO)}_4\text{bipy}$</th>
<th>$\text{Mo(CO)}_4\text{(phen)}$</th>
<th>$\text{Mo(CO)}_4\text{(dab)}$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>'toluene + n-butanol'</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>20200</td>
<td>20300</td>
<td>18180</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>20490</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>21100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>67</td>
<td>21200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>83</td>
<td>21300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>100$^c$</td>
<td>20920</td>
<td>21300</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>100$^c$</td>
<td>21230</td>
<td>21510</td>
<td></td>
</tr>
<tr>
<td>'n-hexane + i-propanol'</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>20880</td>
<td>21190</td>
<td>17920</td>
</tr>
<tr>
<td>33</td>
<td>67</td>
<td>21190</td>
<td></td>
<td>18320</td>
</tr>
<tr>
<td>-</td>
<td>100</td>
<td>20880</td>
<td>21190</td>
<td>18320</td>
</tr>
<tr>
<td>Microemulsions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ME.B</td>
<td>20880</td>
<td>21190</td>
<td></td>
<td>18320</td>
</tr>
<tr>
<td>ME.C</td>
<td>21230</td>
<td>21510</td>
<td></td>
<td>18320</td>
</tr>
</tbody>
</table>

$^a$ Compositions in ideal volume %.

$^b$ (dab) - Schiff base;

$^c$ 100% n-butanol containing a trace of water.
TABLE A.2.

Kinetic data for reaction of Mo(CO)$_2$py$_2$ with phen and bipy in ME.B and ME.C at 298 K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$10^2$ [LL]/mol dm$^{-3}$</th>
<th>$10^2 \gamma_1$ (fast)/s$^{-1}$</th>
<th>$10^4 \gamma_2$ (slow)/s$^{-1}$</th>
<th>$a_1/a_2$ (fast/slow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME.C</td>
<td>0.69 ≤ [phen] ≤ 6.9</td>
<td>1.32</td>
<td>3.66</td>
<td>0.10</td>
</tr>
<tr>
<td>ME.C</td>
<td>0.69 ≤ [bipy] ≤ 6.9</td>
<td>1.78</td>
<td>3.71</td>
<td>0.21</td>
</tr>
<tr>
<td>ME.B</td>
<td>2.9 ≤ [bipy] ≤ 5.9</td>
<td>1.78</td>
<td>4.31</td>
<td>0.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$10^4 k_1$/s$^{-1}$</th>
</tr>
</thead>
</table>
| ME.B    | 0.77 ≤ [phen] ≤ 7.7 | 4.03 |-
<table>
<thead>
<tr>
<th>Ideal vol. % 2-PrOH</th>
<th>10^2 [LL]/mol cm^-3</th>
<th>10^2 γ_1 (fast)/s^-1</th>
<th>10^8 γ_2 (slow)/s^-1</th>
<th>a_1/a_2 (fast/slow)</th>
<th>10^4 k_1/s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>6.5 ≤ [bipy] ≤ 13</td>
<td>1.46</td>
<td>4.33</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>[bipy] = 13</td>
<td>2.49</td>
<td>4.31</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>[bipy] = 16</td>
<td>0.92</td>
<td>4.11</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>[bipy] = 14</td>
<td>-</td>
<td>4.04</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>[bipy] = 3.3</td>
<td>-</td>
<td>4.04</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>[bipy] = 6.7</td>
<td>-</td>
<td>3.98</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>[bipy] = 7.3</td>
<td>-</td>
<td>3.76</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>[bipy] = 13</td>
<td>-</td>
<td>3.48</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>[bipy] = 6.7</td>
<td>-</td>
<td>3.17</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>[bipy] = 13</td>
<td>-</td>
<td>1.91</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>2.3 ≤ [phen] ≤ 6.7</td>
<td>-</td>
<td>4.60</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>1.7 ≤ [phen] ≤ 17</td>
<td>-</td>
<td>4.37</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>1.3 ≤ [phen] ≤ 13</td>
<td>-</td>
<td>4.11</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.79 ≤ [phen] ≤ 7.9</td>
<td>-</td>
<td>3.8</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.7 ≤ [phen] ≤ 2.0</td>
<td>-</td>
<td>3.48</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>[phen] = 0.35</td>
<td>-</td>
<td>3.16</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>[phen] = 0.20</td>
<td>-</td>
<td>2.02</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE A.4.

Kinetic data for reaction of $\text{Mo(CO)}_4\text{py}_2$ with phen in 'toluene + n-butanol' mixtures at 298 K

<table>
<thead>
<tr>
<th>Ideal vol. % n-BuOH</th>
<th>10[phen]/mol dm$^{-3}$</th>
<th>$10^2 \gamma_1$ (fast)/s$^{-1}$</th>
<th>$10^4 \gamma_2$ (slow)/s$^{-1}$</th>
<th>$a_1/a_2$ (fast/slow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.3</td>
<td>1.06</td>
<td>6.78</td>
<td>0.11</td>
</tr>
<tr>
<td>90</td>
<td>1.3</td>
<td>1.07</td>
<td>5.89</td>
<td>0.10</td>
</tr>
<tr>
<td>80</td>
<td>1.6</td>
<td>1.24</td>
<td>5.31</td>
<td>0.25</td>
</tr>
<tr>
<td>70</td>
<td>1.4</td>
<td>1.19</td>
<td>4.83</td>
<td>0.28</td>
</tr>
<tr>
<td>40</td>
<td>0.8</td>
<td>1.12</td>
<td>3.65</td>
<td>0.18</td>
</tr>
<tr>
<td>10</td>
<td>0.2</td>
<td>0.94</td>
<td>2.46</td>
<td>0.29</td>
</tr>
</tbody>
</table>

$10^3 k_1$/s$^{-1}$

| 0$^a$ | 2.2 |

$^a$ data from Darmstadt, West Germany.
Appendix 2

Chapter 3 Data Tables
## TABLE 3.1

Conversions of transfer chemical potentials for single ions between m-, c- and x-scales

<table>
<thead>
<tr>
<th>Wt. % MeOH</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu(x) \rightarrow \mu(m) )</td>
<td>0.11</td>
<td>0.23</td>
<td>0.35</td>
<td>0.48</td>
<td>0.61</td>
<td>0.76</td>
<td>0.91</td>
<td>1.07</td>
<td>1.24</td>
</tr>
<tr>
<td>( \mu(c) \rightarrow \mu(m) )</td>
<td>-0.05</td>
<td>-0.093</td>
<td>-0.13</td>
<td>-0.18</td>
<td>-0.23</td>
<td>-0.29</td>
<td>-0.35</td>
<td>-0.43</td>
<td>-0.51</td>
</tr>
<tr>
<td>( \mu(x) \rightarrow \mu(c) )</td>
<td>0.16</td>
<td>0.32</td>
<td>0.48</td>
<td>0.66</td>
<td>0.85</td>
<td>1.04</td>
<td>1.26</td>
<td>1.49</td>
<td>1.75</td>
</tr>
<tr>
<td>x(MeOH)</td>
<td>0.059</td>
<td>0.123</td>
<td>0.194</td>
<td>0.272</td>
<td>0.36</td>
<td>0.458</td>
<td>0.57</td>
<td>0.692</td>
<td>0.835</td>
</tr>
<tr>
<td>id. vol. % MeOH</td>
<td>12.10</td>
<td>24.10</td>
<td>36.00</td>
<td>46.90</td>
<td>57.10</td>
<td>67.1</td>
<td>76.8</td>
<td>85.20</td>
<td>92.90</td>
</tr>
</tbody>
</table>
### TABLE 3.2

First-order rate constants for reaction between Fe(gmi)$_3^{2+}$ and hydroxide ions in water and 'methanol + water' mixtures at constant ionic strength $I = 0.33$ mol dm$^{-3}$ at 298 K

<table>
<thead>
<tr>
<th>Vol. % (id) MeOH</th>
<th>wt. % MeOH</th>
<th>0.005</th>
<th>$[\text{NaOH}]$/mol dm$^{-3}$</th>
<th>$10^6$ k/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0075</td>
<td>0.01</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.263</td>
<td>0.465</td>
<td>0.551</td>
</tr>
<tr>
<td>20</td>
<td>16.6</td>
<td>0.998</td>
<td>1.83</td>
<td>2.07</td>
</tr>
<tr>
<td>40</td>
<td>34.6</td>
<td>4.17</td>
<td>6.26</td>
<td>8.18</td>
</tr>
<tr>
<td>60</td>
<td>54.4</td>
<td>13.5</td>
<td>20.3</td>
<td>26.6</td>
</tr>
<tr>
<td>80</td>
<td>76.1</td>
<td>39.7</td>
<td>60.3</td>
<td>74.6</td>
</tr>
</tbody>
</table>
TABLE 3.3
Second-order rate constants for reaction between Fe(gmi)$_2^{2+}$ + OH$^-$ in water and 'methanol + water' mixtures at 298 K and I = 0.33 mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Wt. % MeOH</th>
<th>Vol. % (id) MeOH</th>
<th>$10^2$ k/dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.574 (±0.023)</td>
</tr>
<tr>
<td>16.6</td>
<td>20</td>
<td>2.43 (±0.13)</td>
</tr>
<tr>
<td>34.6</td>
<td>40</td>
<td>8.66 (±0.17)</td>
</tr>
<tr>
<td>54.4</td>
<td>60</td>
<td>29.5 (±0.60)</td>
</tr>
<tr>
<td>76.1</td>
<td>80</td>
<td>76.6 (±2.3)</td>
</tr>
</tbody>
</table>
### Table 3.4

Solubility\(^a\) data and $\Delta[(x_2=0) \rightarrow x_2] \mu^\text{(c)}(\text{Fe(gmi)}_3(\text{ClO}_4)_2)$ ($\lambda_{\text{max}} = 554 \text{ nm}$, $\Sigma_{554} = 860 \text{ m}^2 \text{ mol}^{-1}$) from water to 'water + methanol' mixtures at 298 K

<table>
<thead>
<tr>
<th>Vol. % (id) MeOH</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility/mol dm(^{-3})</td>
<td>0.04465</td>
<td>0.0485</td>
<td>0.0485</td>
<td>0.0516</td>
<td>0.0541</td>
<td>0.0440</td>
<td>0.0160</td>
<td>0.0056</td>
</tr>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2] \mu^\text{(c)}$/kJ mol(^{-1})</td>
<td>0</td>
<td>-0.61</td>
<td>-0.61</td>
<td>-1.08</td>
<td>-1.43</td>
<td>+0.11</td>
<td>7.63</td>
<td>15.44</td>
</tr>
</tbody>
</table>

\(^a\) data from Ref. 36 (Chapter 3)
### TABLE 3.5

Transfer parameters, for reaction of Fe(gmi)₃²⁺ with hydroxide ions, from water to 'water + methanol' mixtures at 298 K on the c-scale using single ion transfer parameters reported by Abraham.

[Units of transfer parameters in kJ mol⁻¹.]

<table>
<thead>
<tr>
<th>Vol. % (id) (MeOH)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. % (MeOH)</td>
<td>0</td>
<td>8.03</td>
<td>16.6</td>
<td>24.80</td>
<td>34.6</td>
<td>54.4</td>
<td>76.1</td>
</tr>
<tr>
<td>10² k₂/ dm³ mol⁻¹ s⁻¹</td>
<td>0.574</td>
<td>-</td>
<td>2.43</td>
<td>-</td>
<td>8.66</td>
<td>29.5</td>
<td>76.6</td>
</tr>
<tr>
<td>Δ[(x₂=0) → x₂]μ⁺(c)</td>
<td>0</td>
<td>-</td>
<td>-3.58</td>
<td>-</td>
<td>-6.73</td>
<td>-9.77</td>
<td>-12.13</td>
</tr>
<tr>
<td>Δ[(x₂=0) → x₂]μ⁺(c) [Fe(gmi)₃(CIO₄)₂]</td>
<td>0</td>
<td>-0.61</td>
<td>-0.61</td>
<td>-1.08</td>
<td>-1.43</td>
<td>+0.11</td>
<td>7.63</td>
</tr>
<tr>
<td>Δ[(x₂=0) → x₂]μ⁺(c) (2CIO₄⁻)</td>
<td>0</td>
<td>-0.08</td>
<td>+0.06</td>
<td>+0.15</td>
<td>-0.16</td>
<td>+0.34</td>
<td>+3.16</td>
</tr>
<tr>
<td>Δ[(x₂=0) → x₂]μ⁺(c) [Fe(gmi)₃₂⁺]</td>
<td>0</td>
<td>-0.53</td>
<td>-0.67</td>
<td>-1.23</td>
<td>-1.27</td>
<td>-0.23</td>
<td>4.47</td>
</tr>
<tr>
<td>Δ[(x₂=0) → x₂]μ⁺(c) (OH⁻)</td>
<td>0</td>
<td>-0.06</td>
<td>-0.12</td>
<td>-0.13</td>
<td>-0.02</td>
<td>1.44</td>
<td>5.78</td>
</tr>
<tr>
<td>Δ[(x₂=0) → x₂]μ⁺(c) [Fe(gmi)₃₂⁺ + OH⁻] reactants (I.S.)</td>
<td>0</td>
<td>-0.59</td>
<td>-0.79</td>
<td>-1.36</td>
<td>-1.29</td>
<td>1.21</td>
<td>10.25</td>
</tr>
<tr>
<td>Δ[(x₂=0) → x₂]μ⁺(c) (T.S.)</td>
<td>0</td>
<td>-</td>
<td>-4.37</td>
<td>-</td>
<td>-8.02</td>
<td>-8.56</td>
<td>-1.88</td>
</tr>
<tr>
<td>Δ[(x₂=0) → x₂]μ⁺(c) [Fe(gmi)₃(OH)₂]</td>
<td>0</td>
<td>-0.65</td>
<td>-0.91</td>
<td>-1.49</td>
<td>-1.31</td>
<td>2.65</td>
<td>16.03</td>
</tr>
</tbody>
</table>

* data from Ref. 10 (Chapter 3)
TABLE 3.6
Transfer parameters for reaction of Fe(gmi)$_3^{2+}$ with OH$^-$ ions, from water to 'water + methanol' mixtures at 298 K on the c-scale using single ion transfer parameters reported by Wells$^a$ [Units of transfer parameters in kJ mol$^{-1}$]

<table>
<thead>
<tr>
<th>Vol. % (id) MeOH</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. % MeOH</td>
<td>0</td>
<td>8.03</td>
<td>16.6</td>
<td>34.6</td>
<td>54.4</td>
</tr>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2] G^#(c)$</td>
<td>0</td>
<td>-3.58</td>
<td>-6.73</td>
<td>-9.77</td>
<td></td>
</tr>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2] u^*(c) [Fe(gmi)$_3$(ClO$_4$)$_2$]$</td>
<td>0</td>
<td>-0.61</td>
<td>-0.61</td>
<td>-1.43</td>
<td>+0.11</td>
</tr>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2] u^*(c) (2ClO$_4$)$</td>
<td>0</td>
<td>1.20</td>
<td>1.95</td>
<td>5.16</td>
<td>11.38</td>
</tr>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2] u^*(c) [Fe(gmi)$_3^{2+}$]$</td>
<td>0</td>
<td>-1.81</td>
<td>-2.56</td>
<td>-6.59</td>
<td>-11.27</td>
</tr>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2] u^*(c) (OH^-)$</td>
<td>0</td>
<td>0.98</td>
<td>1.76</td>
<td>3.78</td>
<td>7.29</td>
</tr>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2] u^*(c) [Fe(gmi)$_3^{2+}$ + OH$^-$]$</td>
<td>0</td>
<td>-0.83</td>
<td>-0.80</td>
<td>-2.81</td>
<td>-3.98</td>
</tr>
<tr>
<td>I.S.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2] u^*(c) (T.S.)$</td>
<td>0</td>
<td>-4.38</td>
<td>-9.54</td>
<td>-13.75</td>
<td></td>
</tr>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2] u^*(c) [Fe(gmi)$_3$(OH)$_2$]$</td>
<td>0</td>
<td>0.15</td>
<td>0.96</td>
<td>+0.97</td>
<td>-3.31</td>
</tr>
</tbody>
</table>

$^a$ Data from Ref. 9 (Chapter 3)
Appendix

3

Chapter 4 Data Tables
<table>
<thead>
<tr>
<th>Salt</th>
<th>10^3 solubilities/mole dm^-3</th>
<th>Ideal vol. % acetone</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb_2Cr_2O_7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ph_3As)_2PtBr_6</td>
<td>166.6</td>
<td>85.35</td>
<td>36.89</td>
<td>6.617</td>
<td>1.180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K_2PtBr_6)</td>
<td>0.684</td>
<td>2.725</td>
<td>9.372</td>
<td>24.05</td>
<td>30.7</td>
<td>14.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K_2PtBr_6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>46.96</td>
<td>35.79</td>
<td>29.00</td>
<td>14.90</td>
<td>5.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ph_3As)_2Cr_2O_7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ph_3As)_2PtBr_6</td>
<td>0.019</td>
<td>0.022</td>
<td>0.206</td>
<td>0.298</td>
<td>0.405</td>
<td>0.870</td>
<td></td>
</tr>
<tr>
<td>(K_2PtBr_6)</td>
<td>0.012</td>
<td>0.042</td>
<td>0.089</td>
<td>0.177</td>
<td>0.396</td>
<td>0.936</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ph_3As)_2PtBr_6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0538^b</td>
<td>0.314^b</td>
<td>2.66b</td>
<td>14.7b</td>
<td>36.3b</td>
<td>42.6b</td>
<td></td>
</tr>
</tbody>
</table>

^b solubility data from Ref. 8

---

**Table 4.1**

Solubility data and Δ[(x_0^2) + x_1^2]_[w](c)/KJ mol^-1 of Rb_2Cr_2O_7, (Ph_3As)_2Cr_2O_7, (Ph_3As)_2PtBr_6, and K_2PtBr_6 in acetone + water mixtures at 298 K.
TABLE 4.2

Solubility data and $\Delta[(x_2=0) + x_2]u^\#(c)$ from water to 'water + acetone' mixtures at 298 K for perchlorate$^a$ and silver$^b$ salts and potassium chloride$^c$

<table>
<thead>
<tr>
<th>Salt</th>
<th>$10^3$ solubilities/mol dm$^{-3}$</th>
<th>$\Delta[(x_2=0) + x_2]u^#(c)$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ideal volume % acetone</td>
<td>ideal volume % acetone</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>KClO$_4$</td>
<td>147.1</td>
<td>166</td>
</tr>
<tr>
<td>RbClO$_4$</td>
<td>71.4</td>
<td>77.0</td>
</tr>
<tr>
<td>CsClO$_4$</td>
<td>83.1</td>
<td>97.0</td>
</tr>
<tr>
<td>Me$_4$NClO$_4$</td>
<td>75.0</td>
<td>101</td>
</tr>
<tr>
<td>nPr$_2$NClO$_4$</td>
<td>19.6</td>
<td>41.0</td>
</tr>
<tr>
<td>nBu$_4$NClO$_4$</td>
<td>10.32</td>
<td>31.0</td>
</tr>
<tr>
<td>AgCl</td>
<td>0.0156</td>
<td>0.00768</td>
</tr>
<tr>
<td>AgBr</td>
<td>0.000877</td>
<td>0.000484</td>
</tr>
<tr>
<td>AgI</td>
<td>0.0000124</td>
<td>0.00000967</td>
</tr>
<tr>
<td>AgSCN</td>
<td>0.00139</td>
<td>0.00122</td>
</tr>
<tr>
<td>KCl</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ solubility data from Ref. 2;
$^b$ solubility data from Ref. 4;
$^c$ $\Delta[(x_2=0) + x_2]u^\#(c)$ after conversion from the molal scale from Ref. 3.
\( \Delta \left( (x_2=0) \rightarrow x_3 \right) \mu^+(c) / \text{kJ mol}^{-1} \) from water to 'water + acetone' mixtures at 298 K using Ph4As+/Ph4B− assumption

<table>
<thead>
<tr>
<th>Vol. % (id) acetone</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>-1.49</td>
<td>-3.56</td>
<td>-4.53</td>
<td>-3.56</td>
<td>-2.37</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>-1.26</td>
<td>-3.57</td>
<td>-4.49</td>
<td>-3.12</td>
<td>-1.68</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>-1.66</td>
<td>-4.11</td>
<td>-5.12</td>
<td>-3.7</td>
<td>-2.23</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>-0.98</td>
<td>-4.51</td>
<td>-5.79</td>
<td>-4.63</td>
<td>-</td>
</tr>
<tr>
<td>Me₄N⁺</td>
<td>-2.35</td>
<td>-5.34</td>
<td>-6.76</td>
<td>-5.82</td>
<td>-4.42</td>
</tr>
<tr>
<td>nPr₄N⁺</td>
<td>-4.54</td>
<td>-10.34</td>
<td>-15.64</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>nBu₄N⁺</td>
<td>-6.34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ph₄As⁺/Ph₄B⁻</td>
<td>-7.49</td>
<td>-15.77</td>
<td>-23.32</td>
<td>-29.24</td>
<td>-31.42</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>0.89</td>
<td>2.37</td>
<td>3.34</td>
<td>4.41</td>
<td>5.98</td>
</tr>
<tr>
<td>SCN⁻</td>
<td>1.64</td>
<td>4.85</td>
<td>7.23</td>
<td>12.13</td>
<td>-</td>
</tr>
<tr>
<td>I⁻</td>
<td>2.21</td>
<td>6.57</td>
<td>10.65</td>
<td>15.56</td>
<td>-</td>
</tr>
<tr>
<td>Br⁻</td>
<td>3.92</td>
<td>8.85</td>
<td>14.65</td>
<td>24.69</td>
<td>-</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>4.49</td>
<td>10.56</td>
<td>16.93</td>
<td>25.26</td>
<td>-</td>
</tr>
<tr>
<td>PtBr₆⁴⁻</td>
<td>5.00</td>
<td>10.70</td>
<td>17.6</td>
<td>22.95</td>
<td>-</td>
</tr>
<tr>
<td>Cr₂O₇²⁻</td>
<td>4.7</td>
<td>12.11</td>
<td>20.19</td>
<td>30.22</td>
<td>40.15</td>
</tr>
<tr>
<td>Wt % acetone</td>
<td>16.6</td>
<td>34.6</td>
<td>54.4</td>
<td>76.1</td>
<td>87.7</td>
</tr>
</tbody>
</table>
TABLE 4.4

Rate constants for reaction of Fe(phen)$_3^{2+}$ with OH$^-$ ions in water (a) and 'iso-propanol + water' mixtures at 298 K and constant ionic strength I = 0.0167 mol dm$^{-3}$ and rate constant for aquation of Fe(phen)$_3^{2+}$ in 20% volume (id) iso-propanol + water

<table>
<thead>
<tr>
<th>ideal vol. % iso-propanol</th>
<th>[NaOH]/mol dm$^{-3}$</th>
<th>$10^3$ k$_1$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0033</td>
<td>0.0067</td>
</tr>
<tr>
<td>0(a)</td>
<td>0.125</td>
<td>0.194</td>
</tr>
<tr>
<td>20</td>
<td>0.197</td>
<td>0.305</td>
</tr>
<tr>
<td>40</td>
<td>0.530</td>
<td>1.06</td>
</tr>
<tr>
<td>60</td>
<td>2.23</td>
<td>4.07</td>
</tr>
<tr>
<td>80</td>
<td>11.3</td>
<td>24.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ideal vol. % 2PrOH</th>
<th>$10^3$ k/s$^{-1}$ for aquation</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.07</td>
</tr>
</tbody>
</table>

(a) — Kinetic data from Ref. 11.
### TABLE 4.5

Second-order rate constants for reaction of Fe(phen)$_3^{2+}$ with hydroxide ions in aqueous [Ref. 11] solvent and 'isopropanol + water' mixtures at 298 K and constant ionic strength $I = 0.0167$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Ideal volume % isopropanol</th>
<th>0$^a$</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10 \text{ k}_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$</td>
<td>$0.232 \pm 0.005$</td>
<td>$0.436 \pm 0.027$</td>
<td>$1.68 \pm 0.07$</td>
<td>$6.29 \pm 0.41$</td>
<td>$53.2 \pm 4.1$</td>
</tr>
</tbody>
</table>

$^a$ Data from Ref. 11
TABLE 4.6

Solubility data and $\Delta [(x_2=0) \rightarrow x_2] \mu^c(c)/\text{kJ mol}^{-1}$ for (Ph$_4$As)$_2$Cr$_2$O$_7$, Rb$_2$Cr$_2$O$_7$, RbBPh$_4$, RbClO$_4$, Fe(phen)$_3$(ClO$_4$)$_2$, Co(en)$_3$I$_3$, Co(en)$_3$(ClO$_4$)$_3$, and HI at 298 K

<table>
<thead>
<tr>
<th>Salt</th>
<th>$10^3$ Solubilities/mol dm$^{-3}$</th>
<th>$\Delta [(x_2=0) \rightarrow x_2] \mu^c(c)/\text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ideal vol. % 2PrOH</td>
<td>ideal vol. % 2PrOH</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>(Ph$_4$As)$_2$Cr$_2$O$_7$</td>
<td>0.684</td>
<td>2.37</td>
</tr>
<tr>
<td>RbBPh$_4$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rb$_2$Cr$_2$O$_7$</td>
<td>166.6</td>
<td>78.94</td>
</tr>
<tr>
<td>RbClO$_4$</td>
<td>71.6</td>
<td>42.3</td>
</tr>
<tr>
<td>Fe(phen)$_3$(ClO$_4$)$_2$</td>
<td>0.80</td>
<td>2.12</td>
</tr>
<tr>
<td>Co(en)$_3$I$_3$</td>
<td>63</td>
<td>38</td>
</tr>
<tr>
<td>Co(en)$_3$(ClO$_4$)$_3$</td>
<td>372</td>
<td>298</td>
</tr>
<tr>
<td>HI</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(* interpolated)

<table>
<thead>
<tr>
<th>a</th>
<th>solubility data from S. Radulovic - private communication;</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>data from Ref. 12;</td>
</tr>
<tr>
<td>b</td>
<td>transfer parameters from solubility analysis by S. Radulovic - private communication.</td>
</tr>
</tbody>
</table>
TABLE 4.7

Conversion of single ion transfer parameters (kJ mol\(^{-1}\)) from water to 'isopropanol + water' mixtures from the x-scale to the c-scale

<table>
<thead>
<tr>
<th>wt. % 2-PrOH</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol. % &quot; &quot;</td>
<td>12.6</td>
<td>24.8</td>
<td>36.0</td>
<td>47.4</td>
<td>57.2</td>
<td>67.2</td>
</tr>
<tr>
<td>x 2-PrOH</td>
<td>0.032</td>
<td>0.07</td>
<td>0.114</td>
<td>0.167</td>
<td>0.231</td>
<td>0.310</td>
</tr>
<tr>
<td>(\Delta [x_2=0 \rightarrow x_2]\mu^#(x))</td>
<td>0.227</td>
<td>0.457</td>
<td>0.719</td>
<td>1.005</td>
<td>1.324</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 4.8

$pK_w$\(^a\) in water and 'water + isopropanol' mixtures and calculated $\Delta[(x_2=0) \rightarrow x_2]\mu^\#(c)$ of (H\(^+\).OH\(^-\)) at 298 K from water to 'water + isopropanol' mixtures

<table>
<thead>
<tr>
<th>Weight % isopropanol</th>
<th>Vol. % (ideal) isopropanol</th>
<th>$pK_w$(^a)</th>
<th>$\Delta[(x_2=0) \rightarrow x_2]\mu^#(c)$ (H(^+).OH(^-))/kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>14.00</td>
<td>0</td>
</tr>
<tr>
<td>3.77</td>
<td>4.7</td>
<td>14.11</td>
<td>0.628</td>
</tr>
<tr>
<td>7.26</td>
<td>9.00</td>
<td>14.19</td>
<td>1.085</td>
</tr>
<tr>
<td>10.50</td>
<td>13.20</td>
<td>14.29</td>
<td>1.656</td>
</tr>
<tr>
<td>13.50</td>
<td>16.90</td>
<td>14.36</td>
<td>2.055</td>
</tr>
<tr>
<td>16.40</td>
<td>20.3</td>
<td>14.44</td>
<td>2.512</td>
</tr>
<tr>
<td>21.50</td>
<td>26.2</td>
<td>14.56</td>
<td>3.197</td>
</tr>
<tr>
<td>26.10</td>
<td>31.5</td>
<td>14.64</td>
<td>3.654</td>
</tr>
<tr>
<td>30.10</td>
<td>36.1</td>
<td>14.73</td>
<td>4.167</td>
</tr>
<tr>
<td>33.7</td>
<td>40.2</td>
<td>14.81</td>
<td>4.624</td>
</tr>
<tr>
<td>37.0</td>
<td>44.0</td>
<td>14.91</td>
<td>5.195</td>
</tr>
<tr>
<td>40.0</td>
<td>47.4</td>
<td>14.98</td>
<td>5.595</td>
</tr>
<tr>
<td>42.7</td>
<td>50.1</td>
<td>15.04</td>
<td>5.937</td>
</tr>
<tr>
<td>45.1</td>
<td>52.3</td>
<td>15.10</td>
<td>6.230</td>
</tr>
<tr>
<td>47.4</td>
<td>54.7</td>
<td>15.15</td>
<td>6.565</td>
</tr>
<tr>
<td>49.5</td>
<td>57.1</td>
<td>15.17</td>
<td>6.680</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vol. % 2-PrOH</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta[(x_2=0) \rightarrow x_2]\mu^#(c)$ (H(^+).OH(^-))/kJ mol(^{-1})</td>
<td>2.48</td>
<td>4.60</td>
<td>6.85*</td>
</tr>
</tbody>
</table>

* - extrapolated

\(^a\) Data from Ref. 14
TABLE 4.9

Single ion $\Delta[(x_2=0) \rightarrow x_2] \mu^\circ(c)/kJ \text{mol}^{-1}$ from water to 'water + isopropanol' mixtures at 298 K

<table>
<thead>
<tr>
<th>Vol. % (id)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPh$_4^-$/Ph$_3$As$^+$</td>
<td>-5.04</td>
<td>-11.80</td>
<td>-13.80</td>
<td>-16.10</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>2.37</td>
<td>2.31</td>
<td>2.46</td>
<td>5.75</td>
</tr>
<tr>
<td>Cr$_2$O$_7^{2-}$</td>
<td>0.81</td>
<td>6.52</td>
<td>11.34</td>
<td>15.81</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>0.24</td>
<td>2.17</td>
<td>4.74</td>
<td>6.45</td>
</tr>
<tr>
<td>Fe(phen)$_3^{2+}$</td>
<td>-7.73</td>
<td>-17.51</td>
<td>-21.92</td>
<td>-17.11</td>
</tr>
<tr>
<td>H$^+$</td>
<td>-0.89</td>
<td>-2.62</td>
<td>-4.75</td>
<td>-</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>3.37</td>
<td>7.22</td>
<td>11.60</td>
<td>-</td>
</tr>
<tr>
<td>I$^-$</td>
<td>1.19</td>
<td>3.00</td>
<td>5.87</td>
<td>8.59</td>
</tr>
<tr>
<td>Co(en)$_3^{3+}$</td>
<td>1.48</td>
<td>-2.41</td>
<td>-7.4</td>
<td>-3.99</td>
</tr>
<tr>
<td>wt. % 2-PrOH</td>
<td>16.2</td>
<td>33.5</td>
<td>52.8</td>
<td>74.2</td>
</tr>
</tbody>
</table>
### TABLE 4.10

Transfer parameters in kJ mol\(^{-1}\) for reaction of Fe(phen)\(_3\)\(^{2+}\) with hydroxide ions from water to 'water + isopropanol' mixtures at 298 K on the c-scale using \(\Delta [(x_2=0) \rightarrow x_2] \mu^\#(c)\) for OH\(^-\) from \(pK_w\).

<table>
<thead>
<tr>
<th>Vol. % (id)(2PrOH)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 (k_2/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})</td>
<td>0.232(^b)</td>
<td>0.436</td>
<td>1.68</td>
<td>6.29</td>
<td>53.2</td>
</tr>
<tr>
<td>(\Delta [(x_2=0) \rightarrow x_2] \Delta^G^#(c)/\text{kJ mol}^{-1})</td>
<td>0</td>
<td>-1.56</td>
<td>-4.91</td>
<td>-8.18</td>
<td>-13.47</td>
</tr>
<tr>
<td>(\Delta [(x_2=0) \rightarrow x_2] \mu^#(c) [\text{Fe(phen)(_3)} ^{2+}])</td>
<td>0</td>
<td>-7.73</td>
<td>-17.51</td>
<td>-21.92</td>
<td>-17.11</td>
</tr>
<tr>
<td>(\Delta [(x_2=0) \rightarrow x_2] \mu^#(c) (\text{OH}^-))</td>
<td>0</td>
<td>3.37</td>
<td>7.22</td>
<td>11.60</td>
<td>-</td>
</tr>
<tr>
<td>(\Delta [(x_2=0) \rightarrow x_2] \mu^#(c) [(\text{Fe(phen)(_3)} ^{2+} + \text{OH}^-)^+]) I.S.</td>
<td>0</td>
<td>-4.36</td>
<td>-10.29</td>
<td>-10.32</td>
<td>-</td>
</tr>
<tr>
<td>(\Delta [(x_2=0) \rightarrow x_2] \mu^#(c) (\text{T.S.}))</td>
<td>0</td>
<td>-5.92</td>
<td>-15.20</td>
<td>-18.5</td>
<td>-</td>
</tr>
<tr>
<td>(\Delta [(x_2=0) \rightarrow x_2] \mu^#(c) [\text{Fe(phen)(_3)} (\text{OH})_2])</td>
<td>0</td>
<td>-0.99</td>
<td>-3.07</td>
<td>1.28</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) data from Ref. 14;
\(^b\) data from Ref. 11.
Appendix 4

Chapter 5 Data Tables
### TABLE 5.2a

Kinetic data for the neutral hydrolysis of PDCA in aqueous solutions and in solutions containing known concentrations of MX and R₄NX electrolytes at 298 K. [X = F⁻, Cl⁻, Br⁻; M = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺; R = Me, Et, Pr, n-Bu]

<table>
<thead>
<tr>
<th>M/R</th>
<th>10²k₁/s⁻¹</th>
<th>log₁₀ k₁/k₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>not soluble enough</td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.71</td>
<td>0.308</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.19</td>
<td>0.533</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>1.06</td>
<td>0.483</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>1.14</td>
<td>0.514</td>
</tr>
<tr>
<td>Me₄N⁺</td>
<td>1.49</td>
<td>0.630</td>
</tr>
<tr>
<td>Et₄N⁺</td>
<td>1.88</td>
<td>0.731</td>
</tr>
<tr>
<td>Pr₄N⁺</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-Bu₄N⁺</td>
<td>0.77 to 0.87</td>
<td>0.343 to 0.398</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M/R</th>
<th>10³k₁/s⁻¹</th>
<th>log₁₀ k₁/k₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>2.24</td>
<td>-0.193</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2.25</td>
<td>-0.191</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.40</td>
<td>-0.163</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>2.65</td>
<td>-0.120</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>2.68</td>
<td>-0.115</td>
</tr>
<tr>
<td>Me₄N⁺</td>
<td>2.23</td>
<td>-0.195</td>
</tr>
<tr>
<td>Et₄N⁺</td>
<td>1.63</td>
<td>-0.331</td>
</tr>
<tr>
<td>Pr₄N⁺</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-Bu₄N⁺</td>
<td>0.37</td>
<td>-0.978</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M/R</th>
<th>10³k₁/s⁻¹</th>
<th>log₁₀ k₁/k₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>2.42</td>
<td>-0.159</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2.61</td>
<td>-0.126</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.23</td>
<td>-0.198</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>3.09</td>
<td>-0.053</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>2.90</td>
<td>-0.080</td>
</tr>
<tr>
<td>Me₄N⁺</td>
<td>1.90</td>
<td>-0.264</td>
</tr>
<tr>
<td>Et₄N⁺</td>
<td>1.41</td>
<td>-0.394</td>
</tr>
<tr>
<td>Pr₄N⁺</td>
<td>0.76</td>
<td>-0.661</td>
</tr>
<tr>
<td>n-Bu₄N⁺</td>
<td>0.24</td>
<td>-1.163</td>
</tr>
</tbody>
</table>
TABLE 5.2b

Kinetic data for the neutral hydrolysis of PDCA in aqueous solutions and in solutions containing known concentrations of n-Bu4NBr and KBr at 298 K

<table>
<thead>
<tr>
<th>Salt</th>
<th>[salt]/mol dm⁻³</th>
<th>10[^3]k/s⁻¹</th>
<th>log₁₀ k₁/k₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>3.49</td>
<td>-</td>
</tr>
<tr>
<td>n-Bu₄NBr</td>
<td>0.1</td>
<td>2.90</td>
<td>-0.080</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>2.29</td>
<td>-0.183</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>1.87</td>
<td>-0.271</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.904</td>
<td>-0.587</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.240</td>
<td>-1.163</td>
</tr>
<tr>
<td>KBr</td>
<td>0.1</td>
<td>3.43</td>
<td>-0.008</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>3.22</td>
<td>-0.035</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>2.68</td>
<td>-0.115</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.09</td>
<td>-0.223</td>
</tr>
</tbody>
</table>
TABLE 5.3

Activity coefficients, $\gamma_+$, of MX and R$_n$NX electrolytes at [salt] = 0.9 mol dm$^{-3}$ in aqueous solvent at 298 K
(where X = F$^-$, Cl$^-$, Br$^-$; M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$; R = Me, Et, Pr, n-Bu)

<table>
<thead>
<tr>
<th>Salt</th>
<th>$\gamma_+$ at [salt] = 0.9 mol dm$^{-3}$</th>
<th>loge$\gamma_+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl$^-$</td>
<td>0.764</td>
<td>-0.117</td>
</tr>
<tr>
<td>NaCl$^-$</td>
<td>0.659</td>
<td>-0.181</td>
</tr>
<tr>
<td>KCl$^-$</td>
<td>0.610</td>
<td>-0.215</td>
</tr>
<tr>
<td>RbCl$^-$</td>
<td>0.590</td>
<td>-0.229</td>
</tr>
<tr>
<td>CsCl$^-$</td>
<td>0.553</td>
<td>-0.257</td>
</tr>
<tr>
<td>LiBr$^-$</td>
<td>0.789</td>
<td>-0.103</td>
</tr>
<tr>
<td>NaBr$^-$</td>
<td>0.687</td>
<td>-0.163</td>
</tr>
<tr>
<td>KBr$^-$</td>
<td>0.622</td>
<td>-0.206</td>
</tr>
<tr>
<td>RbBr$^-$</td>
<td>0.586</td>
<td>-0.232</td>
</tr>
<tr>
<td>CsBr$^-$</td>
<td>0.547</td>
<td>-0.262</td>
</tr>
<tr>
<td>NaF$^-$</td>
<td>0.582</td>
<td>-0.235</td>
</tr>
<tr>
<td>KF$^-$</td>
<td>0.646</td>
<td>-0.190</td>
</tr>
<tr>
<td>RbF$^-$</td>
<td>0.682</td>
<td>-0.166</td>
</tr>
<tr>
<td>CsF$^-$</td>
<td>0.710</td>
<td>-0.149</td>
</tr>
<tr>
<td>Me$_n$NCl$^-$</td>
<td>0.546</td>
<td>-0.263</td>
</tr>
<tr>
<td>Et$_n$NCl$^-$</td>
<td>0.557</td>
<td>-0.254</td>
</tr>
<tr>
<td>n-Bu$_n$NCl$^-$</td>
<td>0.625</td>
<td>-0.204</td>
</tr>
<tr>
<td>Me$_n$NBr$^-$</td>
<td>0.483</td>
<td>-0.316</td>
</tr>
<tr>
<td>Et$_n$NBr$^-$</td>
<td>0.427</td>
<td>-0.370</td>
</tr>
<tr>
<td>Pr$_n$NBr$^-$</td>
<td>0.411</td>
<td>-0.386</td>
</tr>
<tr>
<td>n-Bu$_n$NBr$^-$</td>
<td>0.397</td>
<td>-0.401</td>
</tr>
<tr>
<td>Me$_n$NF$^d$</td>
<td>0.902</td>
<td>-0.045</td>
</tr>
<tr>
<td>Et$_n$NF$^d$</td>
<td>1.192</td>
<td>+0.076</td>
</tr>
<tr>
<td>n-Bu$_n$NF$^d$</td>
<td>1.785</td>
<td>+0.252</td>
</tr>
</tbody>
</table>

- T. Tien, J. Phys. Chem., 67, 532 (1963);
- S. Lindenbaum and G. E. Boyd, J. Phys. Chem., 68, 911 (1964);
- extrapolated values.
**TABLE 7.1**

Rate constants for aquation reactions and reactions with CN⁻ ions of Fe(phen)₃²⁺ in w/o microemulsions at 298 K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Aquation (hydrolysis) $k_1$/s⁻¹</th>
<th>Cyanide $k_2$/dm³ mol⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous solution</td>
<td>$7.33 \times 10^{-5}$ ᵇ</td>
<td>$3.0 \times 10^{-2}$ ᵇ</td>
</tr>
<tr>
<td>Microemulsion (A)</td>
<td>$2.17 (\pm 0.19) \times 10^{-4}$</td>
<td>$&gt;300$</td>
</tr>
<tr>
<td>Microemulsion (B)</td>
<td>$2.33 (\pm 0.01) \times 10^{-4}$</td>
<td>$&gt;300$</td>
</tr>
</tbody>
</table>

ᵃ Ref. 22
ᵇ Ref. 4
Table 7.2
Rate constants for reaction of Fe(phen)$_3^{2+}$ with OH$^-$ ions in w/o microemulsions at 298 K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>0.0297</th>
<th>0.0214</th>
<th>0.0119</th>
<th>0.00594</th>
<th>0.00297</th>
<th>0.002</th>
<th>0.00086</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k/s$^{-1}$</td>
<td>k/s$^{-1}$</td>
<td>k/s$^{-1}$</td>
<td>k/s$^{-1}$</td>
<td>k/s$^{-1}$</td>
<td>k/s$^{-1}$</td>
<td>k/s$^{-1}$</td>
</tr>
<tr>
<td>Microemulsion A</td>
<td>2.20</td>
<td>2.02</td>
<td>1.75</td>
<td>1.28</td>
<td>1.27</td>
<td>0.899</td>
<td>0.361</td>
</tr>
<tr>
<td>Microemulsion B</td>
<td>2.84</td>
<td>2.64</td>
<td>2.20</td>
<td>2.10</td>
<td>1.17</td>
<td>2.12</td>
<td>1.3</td>
</tr>
<tr>
<td>Microemulsion:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 mol % 2B.E</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 mol % decane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 mol % water</td>
<td>1.43</td>
<td>0.182</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 7.3

Rate constants for reaction of Fe(phen)$_3^{2+}$ with OH$^-$ ions in ME.B. with added SDS and CTAB as surfactants at 298 K

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>0.0301</th>
<th>0.022</th>
<th>0.0181</th>
<th>0.0143</th>
<th>[NaOH] mol dm$^{-3}$</th>
<th>$10^2$ k/s$^{-1}$</th>
<th>0.0074</th>
<th>0.006</th>
<th>0.00301</th>
<th>0.0015</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.012 mol dm$^{-3}$ SDS</td>
<td>1.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.924</td>
<td>0.592</td>
</tr>
<tr>
<td>0.023 mol dm$^{-3}$ SDS</td>
<td>1.06</td>
<td>0.955</td>
<td>0.939</td>
<td>0.969</td>
<td>1.15</td>
<td>0.929</td>
<td>0.908</td>
<td>0.598</td>
<td>0.265</td>
<td></td>
</tr>
<tr>
<td>0.023 mol dm$^{-3}$ CTAB</td>
<td>6.76</td>
<td>5.70</td>
<td>4.30</td>
<td>3.93</td>
<td>3.95</td>
<td>3.3</td>
<td>1.83</td>
<td>0.903</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.046 mol dm$^{-3}$ CTAB</td>
<td>4.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.10</td>
<td></td>
<td>0.420</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 7.4
Rate constants for aquation reactions of Fe(5-NO$_2$phen)$_3^{2+}$ in 4 neutral w/o microemulsions at 298 K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Aquation (Hydrolysis) $10^3 k_1$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>microemulsion A</td>
<td>2.41±0.09</td>
</tr>
<tr>
<td>&quot; B</td>
<td>5.21±0.15</td>
</tr>
<tr>
<td>&quot; C</td>
<td>2.19±0.18</td>
</tr>
<tr>
<td>&quot; D</td>
<td>2.48±0.19</td>
</tr>
</tbody>
</table>

TABLE 7.5
Rate constants for aquation reactions of Fe(hxsibH)$_2^{2+}$ in aqueous solution at 298 K

<table>
<thead>
<tr>
<th>[H$_2$SO$_4$]/mol dm$^{-3}$</th>
<th>Aquation (Hydrolysis) $10^2 k$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.226</td>
</tr>
<tr>
<td>0.3</td>
<td>1.02</td>
</tr>
<tr>
<td>0.5</td>
<td>1.59</td>
</tr>
<tr>
<td>0.7</td>
<td>1.80</td>
</tr>
<tr>
<td>0.8</td>
<td>1.95</td>
</tr>
<tr>
<td>0.9</td>
<td>2.14</td>
</tr>
<tr>
<td>1</td>
<td>2.53</td>
</tr>
<tr>
<td>2</td>
<td>2.53</td>
</tr>
</tbody>
</table>
TABLE 7.6

Rate constants for aquation reactions of Fe(hxsblH)²⁺ in microemulsion (B) at 298 K

<table>
<thead>
<tr>
<th>Acid</th>
<th>[acid]/mol dm⁻³</th>
<th>Aquation (Hydrolysis) 10³ k/s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>0.003</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>3.44</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>4.52</td>
</tr>
<tr>
<td></td>
<td>0.0453</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>5.46</td>
</tr>
<tr>
<td>HCl</td>
<td>0.003</td>
<td>0.314</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>2.31</td>
</tr>
</tbody>
</table>
TABLE 7.7

$P_0$, $P_\infty$, $\beta_1$, $\beta_2$ and $\gamma$ values (Scheme IV) for the aquation of Fe(hxsbH)$_2^+$ in ME.A. at 298 K

<table>
<thead>
<tr>
<th>acid</th>
<th>[acid]/mol dm$^{-3}$</th>
<th>$10^2 \beta_1$/s</th>
<th>$10^2 \beta_2$/s</th>
<th>$P_0$</th>
<th>$P_\infty$</th>
<th>$\gamma$ at $P_0$</th>
<th>$\gamma$ at $P_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MePhSO$_3$H</td>
<td>0.0297</td>
<td>1.35</td>
<td>2.86</td>
<td>0.90</td>
<td>0.075</td>
<td>0.66</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>0.0149</td>
<td>1.47</td>
<td>4.11</td>
<td>1.10</td>
<td>0.07</td>
<td>0.75</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>0.00297</td>
<td>1.65</td>
<td>8.6</td>
<td>1.21</td>
<td>0.09</td>
<td>0.85</td>
<td>0.30</td>
</tr>
<tr>
<td>HCl</td>
<td>0.0297</td>
<td>1.66</td>
<td>1.10</td>
<td>1.09</td>
<td>0.07</td>
<td>0.38</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>0.0149</td>
<td>5.85</td>
<td>3.29</td>
<td>1.50</td>
<td>0.09</td>
<td>0.46</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>0.00297</td>
<td>2.91</td>
<td>9.90</td>
<td>1.50</td>
<td>0.12</td>
<td>0.84</td>
<td>0.31</td>
</tr>
</tbody>
</table>
TABLE 7.8

Rate constants for reactions of Fe(hxsbH)$^{2+}$ with CN$^-$ ions in ME.A. at 298 K

<table>
<thead>
<tr>
<th>[KCN]/mol dm$^{-3}$</th>
<th>$10^2$ k/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0297</td>
<td>5.85</td>
</tr>
<tr>
<td>0.0223</td>
<td>4.90</td>
</tr>
<tr>
<td>0.0149</td>
<td>4.74</td>
</tr>
<tr>
<td>0.0074</td>
<td>4.37</td>
</tr>
<tr>
<td>0.00297</td>
<td>2.51</td>
</tr>
</tbody>
</table>
Appendix 6

Chapter 8 Data Tables
**TABLE 8.1(a)**

Aquation of Fe(hxsph)\(^{2+}\) in 'B.E + water', 'EtOH + water' and 't-BuOH + water' mixtures at 298 K

**FIRST ORDER ANALYSIS**

<table>
<thead>
<tr>
<th>x (B.E)</th>
<th>(10^2[H_2SO_4]/\text{mol dm}^{-3})</th>
<th>(10^3 k_1/\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>98.5</td>
<td>22.25</td>
</tr>
<tr>
<td></td>
<td>9.85</td>
<td>2.243</td>
</tr>
<tr>
<td></td>
<td>0.985</td>
<td>0.238</td>
</tr>
<tr>
<td>0.006</td>
<td>9.58</td>
<td>2.28</td>
</tr>
<tr>
<td>0.05</td>
<td>72</td>
<td>19.4</td>
</tr>
<tr>
<td>0.075</td>
<td>62.9</td>
<td>14.6</td>
</tr>
<tr>
<td>x (EtOH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>8.54</td>
<td>1.52</td>
</tr>
<tr>
<td>0.05</td>
<td>0.854</td>
<td>0.163</td>
</tr>
<tr>
<td>0.1</td>
<td>7.35</td>
<td>1.11</td>
</tr>
<tr>
<td>x (t-BuOH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>7.84</td>
<td>1.34</td>
</tr>
<tr>
<td>0.1</td>
<td>6.32</td>
<td>1.24</td>
</tr>
</tbody>
</table>
TABLE 8.1(b)

Aquation of Fe(hxsBH)²⁺ in 'BE + water' mixtures when $0.01 \leq x_{BE} \leq 0.1$ at 298 K

**SCHEME IV**

<table>
<thead>
<tr>
<th>x (B.E)</th>
<th>$10^2[H_2SO_4]/mol dm^{-3}$</th>
<th>$10^{-2} \beta_1 (s)$</th>
<th>$10^{-2} \beta_2 (s)$</th>
<th>$\gamma$ at $P_o$</th>
<th>$\gamma$ at $P_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>9.31</td>
<td>3.57</td>
<td>1.91</td>
<td>0.28</td>
<td>0.04</td>
</tr>
<tr>
<td>0.016</td>
<td>8.94</td>
<td>3.29</td>
<td>2.86</td>
<td>0.38</td>
<td>0.04</td>
</tr>
<tr>
<td>0.025</td>
<td>8.42</td>
<td>3.36</td>
<td>2.38</td>
<td>0.38</td>
<td>0.06</td>
</tr>
<tr>
<td>0.025^a</td>
<td>8.42</td>
<td>1.30</td>
<td>1.06</td>
<td>0.37</td>
<td>0.07</td>
</tr>
<tr>
<td>0.025^b</td>
<td>0.842</td>
<td>1.48</td>
<td>5.48</td>
<td>0.74</td>
<td>0.02</td>
</tr>
<tr>
<td>0.05</td>
<td>7.2</td>
<td>3.04</td>
<td>3.07</td>
<td>0.46</td>
<td>0.07</td>
</tr>
<tr>
<td>0.05^b</td>
<td>0.72</td>
<td>5.83</td>
<td>27.1</td>
<td>0.80</td>
<td>0.32</td>
</tr>
<tr>
<td>0.05^b</td>
<td>7.2</td>
<td>0.627</td>
<td>0.586</td>
<td>0.42</td>
<td>0.12</td>
</tr>
<tr>
<td>0.075</td>
<td>6.29</td>
<td>2.92</td>
<td>3.69</td>
<td>0.52</td>
<td>0.08</td>
</tr>
<tr>
<td>0.075</td>
<td>0.629</td>
<td>5.45</td>
<td>24.8</td>
<td>0.79</td>
<td>0.26</td>
</tr>
<tr>
<td>0.1</td>
<td>55.3</td>
<td>0.564</td>
<td>0.216</td>
<td>0.23</td>
<td>0.04</td>
</tr>
<tr>
<td>0.1</td>
<td>5.53</td>
<td>2.63</td>
<td>3.77</td>
<td>0.56</td>
<td>0.09</td>
</tr>
</tbody>
</table>

^a $T = 308$ K; ^b $T = 316$ K.
TABLE 8.2

Kinetic data for reactions of Fe(phen)$_3^{2+}$ with acid, OH$^-$ and CN$^-$ ions in ZBE-rich "ZBE + H$_2$O" mixtures at x(BE) = 0.8 and 0.9 at 298 K

<table>
<thead>
<tr>
<th>x(BE)</th>
<th>$[\text{H}_2\text{SO}_4] = 1.66 \times 10^{-2}$ mol dm$^{-3}$</th>
<th>$10^2$[NaOH]/mol dm$^{-3}$</th>
<th>$10k$(obs)/s$^{-1}$</th>
<th>$[\text{KCN}] = 3.3 \times 10^{-3}$ mol dm$^{-3}$</th>
<th>$k$(obs)/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>2.39</td>
<td>3.30</td>
<td>3.27</td>
<td>&gt;1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.33</td>
<td>1.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>-</td>
<td>1.50</td>
<td>3.25</td>
<td>&gt;1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td>1.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix 7

Chapter 9 Data Tables
TABLE 9.1

Rate constants for aquation reactions of Fe(3,4,7,8-Me₄phen)₃²⁺ and reaction with hydroxide ions in aqueous solution at 298 K. Corresponding data for Fe(5-NO₂phen)₃²⁺, Fe(phen)₃²⁺ and Fe(4,7-Me₂phen)₃²⁺ are also shown for comparison.

<table>
<thead>
<tr>
<th>Fe(X-phen)₃²⁺</th>
<th>Aquration (hydrolysis) $10^4 k_1$/s⁻¹</th>
<th>[NaOH] = 0.243 mol dm⁻³ $10^4 k_1$/s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(3,4,7,8-Me₄phen)₃²⁺</td>
<td>2.26</td>
<td>4.19</td>
</tr>
<tr>
<td>Fe(4,7-Me₂phen)₃²⁺</td>
<td>0.216⁻ᵃ</td>
<td>1.74ᵇ</td>
</tr>
<tr>
<td>Fe(phen)₃²⁺</td>
<td>0.733ᵇ</td>
<td>26.3ᵇ</td>
</tr>
<tr>
<td>Fe(5-NO₂phen)₃²⁺</td>
<td>4.87ᵇ</td>
<td>226.7ᵇ</td>
</tr>
</tbody>
</table>

Ionic strength for hydroxide ion attack = 0.243 mol dm⁻³

ᵇ " " " " " " (1965), 4697.
TABLE 9.2
First-order rate constants for reactions of Fe(4,7-Me2phen)$_3^{2+}$ with OH$^-$ ions in ME(B) at 298 K

<table>
<thead>
<tr>
<th>[NaOH]/mol dm$^{-3}$</th>
<th>$10^2 k_1/s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00272</td>
<td>3.69</td>
</tr>
<tr>
<td>0.00211</td>
<td>3.81</td>
</tr>
<tr>
<td>0.00181</td>
<td>3.85</td>
</tr>
<tr>
<td>0.00151</td>
<td>3.71</td>
</tr>
<tr>
<td>0.000905</td>
<td>3.79</td>
</tr>
</tbody>
</table>
TABLE 9.3

Kinetic parameters for reaction of Fe(4,7-Me₂phen)$_2^{2+}$ with hydroxide ions in M.E.A. at 298 K [Scheme V]

<table>
<thead>
<tr>
<th>[NaOH]/mol dm$^{-3}$</th>
<th>$10^2Y_1$/s$^{-1}$</th>
<th>$10^3Y_2$/s$^{-1}$</th>
<th>$a_1(Y_1)$</th>
<th>$a_2(Y_2)$</th>
<th>$a_3$</th>
<th>$a_2/a_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00297</td>
<td>1.51</td>
<td>0.806</td>
<td>0.09</td>
<td>0.31</td>
<td>0.12</td>
<td>3.44</td>
</tr>
<tr>
<td>0.00594</td>
<td>2.04</td>
<td>2.26</td>
<td>0.14</td>
<td>0.38</td>
<td>0.11</td>
<td>2.71</td>
</tr>
<tr>
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TABLE 9.4
Kinetic parameters for reaction of Fe(3,4,7,8-Me₄phen)₃²⁺ with hydroxide ions in M.E.B. at 298 K [Scheme V]

<table>
<thead>
<tr>
<th>[NaOH]/mol dm⁻³</th>
<th>10^2γ₁/s⁻¹</th>
<th>10^3γ₂/s⁻¹</th>
<th>a₁(γ₁)</th>
<th>a₂(γ₂)</th>
<th>a₃</th>
<th>a₂/a₁</th>
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</thead>
<tbody>
<tr>
<td>0.000905</td>
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<tr>
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<tr>
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</table>
## Table 9.5

Kinetic parameters for reaction of Fe(3,4,7,8-Me₄phen)₃²⁺ with hydroxide ions in M.E.A. at 298 K [Scheme V]

<table>
<thead>
<tr>
<th>[NaOH]/mol dm⁻³</th>
<th>$10^2\gamma_1$/s⁻¹</th>
<th>$10^2\gamma_2$/s⁻¹</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_2/a_1$</th>
<th>% contribution $\gamma_1$(fast)</th>
<th>% contribution $\gamma_2$(slow)</th>
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<tbody>
<tr>
<td>0.00297</td>
<td>8.95</td>
<td>0.824</td>
<td>0.19</td>
<td>0.73</td>
<td>0.13</td>
<td>3.84</td>
<td>20.66</td>
<td>79.34</td>
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<td>0.00594</td>
<td>9.02</td>
<td>1.04</td>
<td>0.28</td>
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<td>0.10</td>
<td>1.86</td>
<td>34.96</td>
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<tr>
<td>0.01</td>
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<td>1.30</td>
<td>0.35</td>
<td>0.45</td>
<td>0.10</td>
<td>1.29</td>
<td>43.67</td>
<td>56.33</td>
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<td>1.46</td>
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<td>69.45</td>
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<td>0.20</td>
<td>0.08</td>
<td>0.26</td>
<td>79.37</td>
<td>20.63</td>
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</table>
### TABLE 9.6

[a] Kinetic parameters for reaction of Fe(3,4,7,8-Me₄phen)₃²⁺ with hydroxide ions in ME.A. with 0.023 mol dm⁻³ added SDS and CTAB at 298 K

<table>
<thead>
<tr>
<th>[NaOH]/mol dm⁻³</th>
<th>Surfactant/mol dm⁻³</th>
<th>10²Y₁/s⁻¹</th>
<th>10³Y₂/s⁻¹</th>
<th>a₁</th>
<th>a₂</th>
<th>a₃</th>
<th>a₂/a₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>0.023 SDS</td>
<td>1.60</td>
<td>1.98</td>
<td>0.14</td>
<td>0.92</td>
<td>0.10</td>
<td>6.57</td>
</tr>
<tr>
<td>0.025</td>
<td>0.023 CTAB</td>
<td>2.63</td>
<td>2.17</td>
<td>0.08</td>
<td>0.80</td>
<td>0.09</td>
<td>10</td>
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</table>

[b] Kinetic parameters for reaction of Fe(3,4,7,8-Me₄phen)₃²⁺ with hydroxide ions in ME.B. with 0.023 mol dm⁻³ added SDS and CTAB at 298 K

<table>
<thead>
<tr>
<th>[NaOH]/mol dm⁻³</th>
<th>Surfactant/mol dm⁻³</th>
<th>Data fitting (1st. order) 10³κ₁/s⁻¹</th>
<th>Data fitting equation 9.23</th>
<th>10³Y₁</th>
<th>10³Y₂</th>
<th>a₁</th>
<th>a₂</th>
<th>a₃</th>
<th>a₂/a₁</th>
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<tr>
<td>0.00272</td>
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<tr>
<td>0.00272</td>
<td>0.023 CTAB</td>
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<td></td>
<td></td>
<td>2.59</td>
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<td>0.35</td>
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<td>0.15</td>
<td>1.17</td>
</tr>
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<td></td>
</tr>
<tr>
<td></td>
<td>Water&lt;sup&gt;a&lt;/sup&gt;</td>
<td>MEA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>MEB&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(5-NO&lt;sub&gt;2&lt;/sub&gt;phen)&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>k = 2.76 x 10&lt;sup&gt;-4&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>k &gt; 3.0 s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>k &gt; 3.0 s&lt;sup&gt;-1&lt;/sup&gt;</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Fe(phen)&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>k = 3.2 x 10&lt;sup&gt;-5&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>k = 1.27 x 10&lt;sup&gt;-1&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>k = 2.84 x 10&lt;sup&gt;-1&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
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</tr>
<tr>
<td>Fe(4,7-dimethylphen)&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>k = 2.1 x 10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>γ&lt;sub&gt;1&lt;/sub&gt; = 1.51 x 10&lt;sup&gt;-2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>γ&lt;sub&gt;1&lt;/sub&gt; = 3.69 x 10&lt;sup&gt;-2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>γ&lt;sub&gt;2&lt;/sub&gt; = 8.06 x 10&lt;sup&gt;-4&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>γ&lt;sub&gt;2&lt;/sub&gt; = 8.95 x 10&lt;sup&gt;-2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
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</tr>
<tr>
<td></td>
<td>γ&lt;sub&gt;2&lt;/sub&gt; = 8.23 x 10&lt;sup&gt;-3&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>γ&lt;sub&gt;2&lt;/sub&gt; = 9.63 x 10&lt;sup&gt;-3&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
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</tr>
</tbody>
</table>

<sup>a</sup> [NaOH] = 2.97 x 10<sup>-3</sup> mol dm<sup>-3</sup>;  
<sup>b</sup> [NaOH] = 2.72 x 10<sup>-3</sup> mol dm<sup>-3</sup>.  

**TABLE 9.7**  
Kinetic data for reaction between hydroxide ions and iron(II) complexes in aqueous solution and in MEA and MEB at 298 K.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Water hydrolysis $10^3 k_1$/s$^{-1}$</th>
<th>[NaOH]/mol dm$^{-3}$</th>
<th>$10k_1$/s$^{-1}$ Hydroxide ions</th>
<th>$k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$ Cyanide ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous solution</td>
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</tr>
<tr>
<td>M.G.</td>
<td>2.09</td>
<td>0.0015</td>
<td>0.024</td>
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<tr>
<td>C.V.</td>
<td>0.11</td>
<td>0.0015</td>
<td>0.003</td>
<td>0.06</td>
</tr>
<tr>
<td>Microemulsion A</td>
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<tr>
<td>M.G.</td>
<td>20.2</td>
<td>0.0015</td>
<td>&gt;3.0</td>
<td>&gt;200</td>
</tr>
<tr>
<td>C.V.</td>
<td>0.017</td>
<td>0.000654</td>
<td>&gt;3.0</td>
<td>&gt;200</td>
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<tr>
<td></td>
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<td></td>
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<tr>
<td>Microemulsion B</td>
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<td></td>
</tr>
<tr>
<td>M.G.</td>
<td>9.79</td>
<td>0.0015</td>
<td>&gt;3.0</td>
<td>&gt;200</td>
</tr>
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<td></td>
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<td>0.0012</td>
<td>2.99</td>
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</tr>
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<td>0.0010</td>
<td>2.27</td>
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</table>

TABLE 10.2

Kinetic data for reactions of DNCB with hydroxide ions in MEA when $9 \times 10^{-3} \leq [\text{NaOH}] \leq 3 \times 10^{-2}$ mol dm$^{-3}$ at 298 K

<table>
<thead>
<tr>
<th>[NaOH]/mol dm$^{-3}$</th>
<th>$10^3k_1$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>8.77</td>
</tr>
<tr>
<td>0.028</td>
<td>9.37</td>
</tr>
<tr>
<td>0.026</td>
<td>8.52</td>
</tr>
<tr>
<td>0.023</td>
<td>8.42</td>
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<tr>
<td>0.020</td>
<td>7.86</td>
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<tr>
<td>0.018</td>
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<tr>
<td>0.0101</td>
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</tr>
<tr>
<td>0.009</td>
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</table>
### TABLE 10.3

Kinetic data for reactions of DNBC with hydroxide ions in M.E.A. where $3 \times 10^{-3} \leq [\text{NaOH}] \leq 7 \times 10^{-3}$ mol dm$^{-3}$ at 298 K [Scheme V (or VI)]

<table>
<thead>
<tr>
<th>[NaOH]/mol dm$^{-3}$</th>
<th>$10^3 \gamma_1$/s$^{-1}$</th>
<th>$10^3 \gamma_2$/s$^{-1}$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_1/a_2$</th>
<th>$\gamma_2/\gamma_1$</th>
<th>% contribution $\gamma_1$</th>
<th>% contribution $\gamma_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.007</td>
<td>8.08</td>
<td>2.59</td>
<td>0.12</td>
<td>0.57</td>
<td>0.80</td>
<td>0.21</td>
<td>0.32</td>
<td>17.35%</td>
<td>82.65%</td>
</tr>
<tr>
<td>0.005</td>
<td>9.15</td>
<td>2.00</td>
<td>0.12</td>
<td>0.68</td>
<td>0.88</td>
<td>0.18</td>
<td>0.22</td>
<td>15.25%</td>
<td>84.75%</td>
</tr>
<tr>
<td>0.003</td>
<td>5.24</td>
<td>0.84</td>
<td>0.13</td>
<td>0.42</td>
<td>0.66</td>
<td>0.31</td>
<td>0.16</td>
<td>23.66%</td>
<td>76.34%</td>
</tr>
</tbody>
</table>

Average $a_1/a_2$: 0.2313 ± 0.063  
Average $\gamma_2/\gamma_1$: 0.2362 ± 0.077  
Av. % contribution $\gamma_1$: 18.78% (± 3.6)  
Av. % contribution $\gamma_2$: 81.22% (± 3.6)
Appendix 9

Chapter 11 Data Tables
TABLE 11.1

First-order rate constants for reactions of Fe(4-Me.phen)$_3^{2+}$ with CN$^-$ ions and for aquation reactions of Fe(4-Me.phen)$_3^{2+}$ in aqueous solution at various temperatures

<table>
<thead>
<tr>
<th>Temp./K</th>
<th>$10^3 k_1$ with CN$^-$ ions/s$^{-1}$ ([CN$^-$] = 0.5 mol dm$^{-3}$)</th>
<th>$10^4 k_1$ for aquation/s$^{-1}$ ([H$_2$SO$_4$] = 0.5 mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.84</td>
<td>0.36</td>
</tr>
<tr>
<td>301</td>
<td>2.78</td>
<td>0.61$^a$</td>
</tr>
<tr>
<td>305</td>
<td>4.29</td>
<td>1.17$^a$</td>
</tr>
<tr>
<td>308</td>
<td>6.68</td>
<td>1.90</td>
</tr>
<tr>
<td>312</td>
<td>9.82</td>
<td>3.82$^a$</td>
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<td>315</td>
<td>10.65</td>
<td>5.51</td>
</tr>
<tr>
<td>318</td>
<td>16.42</td>
<td>8.94$^a$</td>
</tr>
</tbody>
</table>

$^a$ Interpolated data from graph of ln $k$ vs. $1/T$
TABLE 11.2

Second-order rate constants for reactions of Fe(4-Me-phen)$_3$ with CN$^-$ ions in aqueous solution at various temperatures

<table>
<thead>
<tr>
<th>T/K</th>
<th>$10^3 k_2$/$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>3.61</td>
</tr>
<tr>
<td>301</td>
<td>5.44</td>
</tr>
<tr>
<td>305</td>
<td>8.35</td>
</tr>
<tr>
<td>308</td>
<td>13.0</td>
</tr>
<tr>
<td>312</td>
<td>18.9</td>
</tr>
<tr>
<td>315</td>
<td>24.2</td>
</tr>
<tr>
<td>318</td>
<td>31.1</td>
</tr>
</tbody>
</table>

TABLE 11.3

Dependence of $\ln(k/T)$ on temperature, $T$, for reactions of Fe(4-Me-phen)$_3$ with CN$^-$ ions in aqueous solution (using $\ln(k/T) = \ln[k(\theta;\pi)/\theta] + a_1(T-\theta) + a_2(\pi-\pi)$). $\theta/K = 298.2$; $\pi/bar = 68$; $V_1^\pi = 18.02 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ - 11 data points; standard deviation = $1.27 \times 10^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimate</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln[k(\theta;\pi)/\theta]$</td>
<td>-7.3274</td>
<td>$5.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>$a_1/K^{-1}$</td>
<td>0.10704</td>
<td>$5.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>$a_2/bar^{-1}$</td>
<td>$-2.8065 \times 10^{-4}$</td>
<td>$9.2 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
TABLE 11.4

Derived activation parameters for reactions of Fe(4-Me-phen)$_3^{2+}$ with CN$^-$ ions in aqueous solution

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta^\circ H^\circ$(sln;θ;π)/kJ mol$^{-1}$</td>
<td>79.4 ± 4.3</td>
</tr>
<tr>
<td>$\Delta^\circ V^\circ$(sln;θ;π)/m$^3$ mol$^{-1}$</td>
<td>(6.96 ± 2.2) $\times 10^{-6}$</td>
</tr>
<tr>
<td>$[\partial ln(k[θ;π]/θ)/dT]$ at $V_1^*$</td>
<td>0.1044 ± 0.0052</td>
</tr>
<tr>
<td>$\Delta^\circ \psi(V_1^*)$/kJ mol$^{-1}$</td>
<td>77.22 ± 3.84</td>
</tr>
<tr>
<td>$[\partial ln(k[θ;π]/θ)/dp]$ at $V_1^*$</td>
<td>$1.83 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\Delta^\circ \phi(V_1^*)$/m$^3$ mol$^{-1}$</td>
<td>$-4.54 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
ABSTRACT

Rate constants for chemical reactions in various aqueous and microheterogeneous systems have been measured and analysed. A large part of the thesis is concerned with interpreting kinetic trends in two water-in-oil microemulsions. Kinetic data for inorganic reactions involving low-spin iron(II) di-imine complexes and for reactions involving the organic substrates, 2,4-dinitrochlorobenzene, crystal violet and malachite green in microemulsions have been collected and used to identify different structural zones in these solvent systems. The kinetic data are interpreted in terms of a model in which reaction occurs at an interphase.

Reactions involving cis-bis(pyridine)tetracarbonylmolybdenum(0) in oil-in-water, water-in-oil microemulsions and organic solvent mixtures have been studied.

Aquation reactions of iron(II) hexadentate Schiff base have been used to identify microheterogeneous phases in water-rich '2-butoxyethanol + water' mixtures.

Solvent effects on initial and transition states are discussed for reactions of iron(II) glyoxal bis-N methylamine with hydroxide ions in 'methanol + water' mixtures and reactions of iron(II) 1,10-phenanthroline with hydroxide ions in 'isopropanol + water' mixtures.

Transfer chemical potentials for single ions, in 'acetone + water' mixtures, have been estimated, using solubility data for salts in conjunction with the assumption that transfer chemical potentials for tetraphenylboronate and tetraphenylarsonium ions are equal.

Effects of added salt on the neutral hydrolysis of phenyldichloroacetate in aqueous solutions are examined in terms of solvent cosphere interactions between ions.

The temperature dependence of rate constants for reactions of iron(II) 4-methyl, 1,10-phenanthroline have been examined. The results are discussed in terms of isobaric, isothermal and isochoric activation parameters. The meaning of the term 'isochoric' is clarified in this context.