Studies of Solvation by Spectroscopic Methods

A Thesis submitted by

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STATEMENT

The experimental work described in this thesis was carried out solely by the author, except where otherwise stated in the text, in the Department of Chemistry of the University of Leicester during the period between March 1982 and March 1985.

The work in this thesis is not being concurrently presented for any other degree.

All work recorded herein is original unless otherwise stated in the text or by reference.

JUNE 1985

Signed: ..................................
Dedicated to my Parents,
without whose patience and inspiration
this work might not have been completed.

Thank You
"Science is the most intimate school of resignation and humility, for it teaches us to bow before the seemingly most insignificant of facts."

Miguel De Unamuno

'Tis a lesson you should heed,
Try, try again.
If at first you don't succeed,
Try, try again.

William Edward Hickson
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CHAPTER
1

Introduction
1.1 INTRODUCTION

The work presented in this thesis is aimed at investigating the potential of spectroscopic techniques to the understanding of the local structures present in solution, in particular, questions relating to solvation of neutral molecules and anions, and anion-cation interactions. To this end, a successful technique that utilises 'probe' molecules (and anions) in pure and binary mixed solvent systems has been pursued. Probe techniques have been used to great advantage on previous occasions.1-5

1.2 USE OF PROBES

1.2.1 The Concept

If a particular molecule (or ion) possesses an observable property that is sensitive to the components of its environment, then it may be used to monitor that environment.

1.2.2 Criteria for a Good Probe

a) The probe must be soluble in the various solvents studied.

b) The probe should be present in very dilute concentrations.

c) No chemical reaction should occur between the probe and solvents.

d) Some suitable observable spectroscopic 'label' must be present on the probe (e.g. infrared band, electronic transition, magnetically active nucleus, etc.), that changes systematically with the environment.

It is possible, in principle, to use almost any spectroscopic technique to study probes, although some care needs to be exercised in selecting the suitability of a particular technique (see Section 1.6). When dissolved in pure solvents, such probes have frequently been utilised to
provide the basis of the so-called empirical solvent scales, such as Z-values⁶ or Et-values.⁷

1.3 THE HYDROGEN BOND

1.3.1 The Need

Whenever such a 'probe' is present in solution, depending upon the nature of the solvent, various intermolecular interactions could be envisaged.

In fact, in the early part of the twentieth century, many suggestions had been made as to the nature of intermolecular associations in solvents. For example, it was recognised that polar solvents often contained separated positive and negative centres, thus having significant dipole moments. Association would thus be due to the attraction of dipoles between neighbouring molecules. Such ideas, however, did not resolve the many anomalies observed for molecules containing hydrogen atoms. Some of these included unique physical properties, altered electrical conductivity, shifts in the frequency of infrared and Raman bands, changes in solubility, etc. These findings, therefore, led Latimer and Rodebush⁸ to postulate the 'Hydrogen Bond'.

1.3.2 The Definition

Latimer and Rodebush introduced the concept of Hydrogen Bond (H-bond) in the following way:

".... in terms of the Lewis Theory, a free pair of electrons on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together."

According to Pimentai and McClellan,⁹ "A Hydrogen Bond exists when a hydrogen atom is bonded to two or more atoms".
1.3.3 Criteria for strong Hydrogen Bond (X-H\cdots Y) Formation

a) The hydrogen atom must be bound to an electronegative atom, i.e. X may be F, O, N, etc.

b) The Y atom must possess high electron density capable of interacting strongly with the acidic hydrogens.

c) The X-H bond and the axis of the lone-pairs must be nearly colinear.

1.3.4 Types of Hydrogen Bonds

Two kinds of hydrogen bonds are generally observed:

a) \textbf{Intermolecular Hydrogen Bonds}

This involves association of two molecules of the same or different substances, e.g. liquid water (Figure 1.1).

b) \textbf{Intramolecular Hydrogen Bonds}

This involves hydrogen bonds formed between groups within a single molecule, e.g. salicylic acid (Figure 1.2).

\[ (\text{fig. 1.1}) \quad (\text{fig. 1.2}) \]

All hydrogen bonds referred to the work in this thesis are of the former kind.
1.3.5 Nature of Hydrogen Bonds

Pauling first suggested that in a hydrogen bond X-H---Y, the hydrogen 1s orbital can form only one covalent bond with X and so the interaction with Y (electron donor) is largely electrostatic in character. Several features of H-bonds such as hydrogen bond energy, spectroscopic properties and others, can be interpreted on the basis of the electrostatic model.

It was realised, however, that the electrostatic theory was not completely satisfactory. For instance, if the electrostatic contributions alone were the major controlling factor in determining hydrogen bond energy, there should be a correlation between the strength of a hydrogen bond and the dipole moment of the electron donor. A ketone, therefore, should be a better donor than an ether and a nitrile better than a tertiary amine. Infrared spectroscopic studies show that the electron donating ability of a ketone and an ether are about the same, while a tertiary amine is a better donor than a nitrile. Also, the increase in intensity of the O-H stretching band on hydrogen bond formation is sometimes more than the increase expected on purely electrostatic grounds. Coulson has interpreted this behaviour as due to a charge movement to and from the donor, thus implying electron delocalisation. This suggests, therefore, that covalent contributions may be important in a hydrogen bond.

The covalent description has appeal from the standpoint of explaining some behaviour not satisfactorily explained by the electrostatic model. On the other hand, it leaves the difficulty of fitting extra valency into our present valence bond understanding of the covalent bond which is readily accomplished using the molecular orbital approach.
1.3.6 Importance of Hydrogen Bonds

Without the existence of the H-bond, life as we know it could not exist. Not only does it provide water with strange physical properties, it also plays a major part in the 'structure of life' itself. For example, the rôle of hydrogen bonds is of extreme importance in biological systems. They determine to a large degree the gross shape and structure of protein molecules and also the structures of the genetically important deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Also, it is well known that natural fibre has cellulose as one of its main components. Wood and many grasses are other important natural products with a high cellulose content. Cellulose is made up of saccharide units polymerised in chains by H-bonds.

1.3.7 Methods of Detection of H-Bonds

Numerous physical methods have been made available for hydrogen bond studies, such as X-ray diffraction, viscosity, solubility, etc. The work in this thesis, however, is concerned with the use of spectroscopic techniques, their importance being highlighted later.

1.4 STRUCTURE OF LIQUID WATER

Any discussion of hydrogen bonds brings to mind the unique chemical substance - water. Even a superficial study of liquid water suggests that life on this planet has been conditioned by its abnormal properties. It is well known that water forms a necessary constituent of the cells of all animals and plant tissues and that life cannot exist, even for a limited period, in its absence. Against this background, it must be pointed out that water, in addition to its enormous practical importance, is a very special substance in a scientific sense. Not only from view of its many anomalous properties but from the large number of
conflicting schools of thought that have emerged in attempting to unravel its structure.

Good quantum mechanical calculations for water monomers, dimers and oligomers (Del Bene and Pople,\textsuperscript{16} Hankins et al.,\textsuperscript{17} Kollman and Allen,\textsuperscript{18} Diercksen\textsuperscript{19}) exist. It seems that the conventional view of the water molecule, in which it is depicted as having a near tetrahedral array of two hydrogen atoms and two non-bonding electron pairs or 'lone-pairs' (Figure 1.3) is a reasonable one for structural considerations. This

![Figure 1.3](image)

FIGURE 1.3
The tetrahedral arrangement of atoms in water as dictated by hydrogen bonding.

suggests that the structure of water dimer is, in fact, linear (Figure 1.4a) which derives strong support from Tusi and Nixon\textsuperscript{20} using the matrix isolation technique coupled with infrared spectroscopy. It has been proposed that the cyclic dimer (Figure 1.4b) is preferred in fluid carbon tetrachloride.\textsuperscript{21} However, Symons and Atkins\textsuperscript{22} have suggested that the cyclic structure is a metastable transition state for linear dimer conversion.
FIGURE 1.4
Linear Water Dimer to Cyclic Dimer Transformation.

The key to understanding water is that the molecule is tetra-functional, with an equal number of acidic and basic groups which could ideally be placed for three-dimensional growth. For instance, in ice, the protons in the hydrogen bond are held directly between the oxygen atoms, and a more or less perfectly hydrogen bonded system occurs. As the temperature is raised, a phase change occurs and ice melts so that the symmetry is altered. It is still a matter of conjecture whether hydrogen bonds actually break or are drastically distorted; this leads to two main controversial models to describe the structure of liquid water, viz. 'the Continuum Model' and 'the Mixture Model'.

1.4.1 The Continuum Model

According to Kell, the Continuum Theory describes water as having essentially complete hydrogen bonding, at least at low temperatures, but as having a distribution of angles, distances and bond energies. The model requires the molecular interactions in hydrogen bonded network to have a smooth, single distribution ranging from the two extremes of 'ice-like' structure through to 'gas-phase like' interactions. This model further considers the average bond energy to change with temperature and pressure because of changes in the distribution of bond lengths and distortions of the angles. The melting of ice is viewed by this theory in terms of bending of H-bonds, which remain unbroken.
This model was probably the first to be considered in a simplified form as well as in a more detailed form. Pople and Bernal have proposed the presence of distorted hydrogen bonds as an interpretation of the radial distribution function diagrams derived from X-ray diffraction studies. Computer simulation techniques have recently been used. The Continuum Model further has been given a great deal of support by the work of Wall and Hornig, who have examined the Raman spectrum of HOD in liquid water. The vibrations of HOD molecule are uncoupled by deuteration. No distinct bands at different frequencies are observed for the O-H or O-D stretching vibrations. The authors have considered this as a strong evidence against the existence of two or at most a few distinct types of water molecules in water. Rather, there is a continuous distribution of frequencies with maxima at ca. 2516 cm^{-1} for O-D and 3439 cm^{-1} for O-H. A similar conclusion has been drawn by Falk and Ford using infrared spectroscopy. Naberukhin and Efimov have justified the Continuum Model in which they applied Zhukovskii's procedure to the temperature transformation of the contours of the stretching bands of HOD molecules in the infrared absorption and Raman spectra.

1.4.2 The Mixture Model

Kell defines the Mixture Model as being "understood to describe liquid water as an equilibrium mixture (or solution) of species that are distinguishable in an instantaneous picture". In Mixture theory, each water molecule might participate in from zero to four hydrogen bonds, so species with different numbers of hydrogen bonds are sometimes distinguishable. Whereas a Continuum Model considers the average bond energy to change, a Mixture Model implies different proportions of the species at different temperature and pressure. Hydrogen bond distortions
are ruled out thus entailing a large amount of bond breaking.

One of the most popular Mixture Models is probably the Cluster Model proposed by Frank and Wen.\textsuperscript{37,38} This model envisages water as existing in two states, one comprising large clusters of strongly bonded molecules and the other comprising dense regions of non-bonded molecules (Figure 1.5). A statistical thermodynamics treatment of the model by Lentz \textit{et al.}\textsuperscript{40} has led to the conclusion that clusters are indeed of great importance.

The Cluster Theory suggested that the formation of hydrogen bonds in water is a co-operativity effect and association of two water molecules by hydrogen bonding helps associate other water molecules. The concept that the strength of successive hydrogen bonds by a water molecule is not independent, was proposed in a qualitative way by Frank and Wen.\textsuperscript{37} Recent quantum mechanical calculations confirmed the existence of co-operativity, even though they disagree about its numerical magnitude. In fact, this is taken as a fundamental feature in many Mixture models.

Some workers, in order to explain density effects, have postulated water as having a hydrogen-bonded framework with monomeric water molecules in interstitial cavities.\textsuperscript{41,42} Pauling\textsuperscript{10} proposed that water formed Clathrate Cages with water molecules occupying interstitial sites (Figure 1.6).

One of the strongest points in favour of the Mixture Model stems from spectroscopy. The changes of shape of infrared and Raman\textsuperscript{43-47} bands with temperature (or pressure) have led a number of workers to conclude that different regions of the bands can give the concentrations of different species in chemical equilibrium. A major criticism to the Continuum Theory has been the indications of an isosbestic point, one of the basic criteria of the Mixture Model.\textsuperscript{45} However, ordinary ice Ih, in
FIGURE 1.5

The 'flickering cluster' model for the structure of water as proposed by Frank and Wen [Refs. 37, 38] showing two distinct regions for water: (a) monomeric water molecules; (b) clusters of polymeric water molecules hydrogen-bonded together. The diagrammatical representation shown here is by Nemethy and Scheraga [Ref. 39].
FIGURE 1.6
Possible framework of hydrogen-bonded water molecules [Ref. 10].

which all bonds are nearly equivalent, shows isosbestic points, with temperature changes, and they also occur in other solids where the structure is known to have only one component. 48

It seems fair, therefore, to say that proponents of the Mixture Theories have been most struck by the systematic changes observed in the spectra with temperature, which appear to indicate changes of composition, whereas proponents of Continuum Theories have been most struck by the need to explain the broadness of the bands and are agreed that this property implies a broad distribution of interaction configurations. The distinction between Mixture and Continuum theories may well also be clouded by differences in time-scales of a particular technique used. This view has been strongly emphasized by Eisenberg and Kauzmann. 49 For example, the OH-stretching vibration around ca. 3500 cm⁻¹ takes 10⁻¹⁴ sec; the dielectric relaxation time is in the order of 10⁻¹¹ sec. A process taking 10⁻¹² sec is slow compared with the OH vibration but fast compared to the dielectric relaxation.
1.4.3 The Adopted Model of Water Structure

The Mixture Model has been extended by Symons who introduced the concept of 'lone-pair free' and 'OH free' (Figure 1.7) groups, simply by identifying the species involved in the equilibrium that exists by definition in the Mixture Model. Symons postulates that water is a three-dimensional network involving such units linked together with 4, 5, 6 or 7 ring systems which are haphazardly strung together and not of any particular significance. However, in view of the continuous rapid motion of these molecules, the hydrogen bonds are subjected to constant strain. Thus they bend, stretch and occasionally break. When they break, the "ends" move away, so that there exists several protons and lone-pairs (these are designated respectively as (OH)free and (LP)free units in Figure 1.7) that are temporarily unable to form bonds. The major difference between water and a tightly-bound cross-linked polymer thus is that bonds are weak and are therefore continuously breaking and reforming on a time-scale in the region of 10^-11 seconds.

It is suggested that (OH)free and (LP)free units are the reactive species in liquid water. Such 'free' groups represent an extreme but defined limit, with the fully formed linear hydrogen bond as the other extreme. In between, there will surely be a range of bent and stretched
hydrogen bonds brought about momentarily and fortuitously because of the
demands and constraints of the surrounding three-dimensional structures.

If \((\text{OH})_{\text{free}}\) groups are present, there must be an equal number of non-
bonded \((\text{LP})_{\text{free}}\) groups.\(^{51}\) Spectroscopic evidence\(^{50}\) for \((\text{OH})_{\text{free}}\) units
is obtained from studies of first and second overtones of the \(\text{OH}\) stretch
of water. However, conceptual difficulties have been voiced because of
apparent absence of any such unique feature in the fundamental \(\text{OH}\)
stretching region of the infrared spectrum. It now seems to be accepted
that this is fortuitous: in the fundamental region, the oscillator
strengths for strongly \(H\)-bonded \(\text{OH}\) groups are greater than those for
weakly bonded groups, but in the \(2\nu_{\text{OH}}\) region, the reverse is true.
Unfortunately at present, there exists no spectroscopic method of
directly detecting \((\text{LP})_{\text{free}}\) features. However, presence of \((\text{LP})_{\text{free}}\)
units have been characterised by vibrational spectroscopy both in the
fundamental and \(2\nu_{\text{OH}}\) regions\(^{52}\) for methanol.

Symons' theory, now being accepted by other workers,\(^{53}\) is used as a
model throughout this work. Further work\(^2\) has illustrated the ability
of these groups to partake in hydrogen bonding with cosolvent molecules,
thus leading to the idea that the presence of \((\text{OH})_{\text{free}}\) and \((\text{LP})_{\text{free}}\)
species are very important when considering the properties of water.

\textbf{Aqueous Solvation - Electrolytes}

Figure 1.8 depicts a model\(^{37}\) of the way ions are thought to be
solvated. However, Symons\(^{51}\) disagrees with this view since in his view
it is incorrect to envisage the ion and its first hydration shell as an
entity separated from bulk water. Electrolytic solvation in water can
effectively be explained by the \((\text{OH})_{\text{free}}\) and \((\text{LP})_{\text{free}}\) hypothesis,
 together with continuous network bonding which includes cations and
anions.
FIGURE 1.8
Commonly invoked model for anion or cation hydration:
A - primary hydration $\text{H}_2\text{O}$ irrotationally bound;
B - disorganised $\text{H}_2\text{O}$; C - normal liquid $\text{H}_2\text{O}$.

Cations are electrophiles and will tend to coordinate to water molecules via lone-pairs of electrons (Figure 1.9a). That this is indeed the preferred mode of interaction is amply borne out by X-ray studies of salt hydrates, and there is no reason to suppose that this will not also occur in fluid solutions. The solvation of anions is complementary, hydrogen bonding to water occurring through $(\text{OH})_{\text{free}}$ groups (Figure 1.9b).

FIGURE 1.9
Cation and anion solvation by water.

It is probably of importance that there will normally be a rough balance in the number of $(\text{OH})_{\text{free}}$ groups generated during cation solvation and $(\text{LP})_{\text{free}}$ units formed by anion solvation. That this seems true is borne out experimentally.\(^\text{54}\)
b  **Aqueous Solvation - Non-Electrolytes**

Most polar aprotic solvents are bases. Water will normally only accept high concentrations of cosolvents if it forms hydrogen bonds therewith, since strongly structured water opposes the insertion of non-interacting molecules. By Symons' theory, the solvation of bases (B) in aqueous solutions is governed by the scavenging of (OH)\text{free} groups, generating (LP)\text{free} species in the process.

\[
(H_2O)_{\text{bulk}} + :B \rightleftharpoons O-H\cdots-B + (LP)_{\text{free}} \quad \cdots (1.10)
\]

bulk water base base bound lone-pair bulk water species

1.5 **STRUCTURE OF METHANOL**

Methanol can be treated as a simple derivative of water with one of the protons replaced by an alkyl group. In fact, the proton donating capability of methanol monomer is similar to water,\textsuperscript{55} despite suggestions to the contrary.\textsuperscript{56} The structure of liquid methanol is far simpler than water. Studies of methanol have been of interest in the expectation that any gain in its understanding would help in the water study.

It has been suggested that the majority of species present in liquid methanol at room temperatures can be represented by rings or chains of four to seven molecules.\textsuperscript{57} Possible evidence for the presence of rings is derived from the low heat of melting and high latent heat of boiling.\textsuperscript{10} However, studies of the crystal structure of solid methanol\textsuperscript{58,59} shows a linear arrangement of methanol molecules (Figure 1.11) and, hence, it is probable that liquid methanol contains similar chains.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{-----OH-----OH-----OH-----} \\
\end{align*}
\quad \cdots (1.11)
\]

One difference between methanol and water is the almost complete
absence of an (OH)_{free} band in the 2\nu_{OH} region for methanol.\textsuperscript{60} This is probably because (OH)_{free} groups are rapidly scavenged by the large excess of lone-pairs not normally used for hydrogen bonding (Scheme 1.12 - for clarity (LP)_{free} groups are confined to terminal methanol molecules only).

\[
\text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\
\begin{array}{c}
\text{-----OH-----OH-----} \\
+ \quad \text{(OH)$_{free}$} \\
\Rightarrow \\
\text{-----OH-----OH-----}
\end{array}
\]

\[(\text{ii})\]

\[
\begin{array}{c}
\text{H} \\
\text{O-Me}
\end{array}
\]

Spectroscopic evidence for (LP)_{free} groups is mainly from infrared spectroscopy.\textsuperscript{52} The basis of detection of such terminal molecules lies in the fact that the hydrogen bonds that they form [(ii) - Scheme 1.12] are expected to be weaker than the normal hydrogen bonds within the polymer chains and therefore distinguishable spectroscopically from bulk methanol (Figure 1.13). This is a crucial aspect of methanol and

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.13.png}
\caption{Infra-red spectrum for methanol + triethylamine in the (OH) stretch region, showing the band in the 3440 cm\textsuperscript{-1} region assigned to (LP)$_{free}$ or 'terminal' methanol molecules.}
\end{figure}
water structure\textsuperscript{51} which, although obvious, is frequently ignored. These important co-operativity effects of H-bond strengths are illustrated in Figure 1.14. Bonds (i), (ii) and (iii) are progressively stronger, with

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{OH}---\text{OH} & \quad \text{OH}---\text{OH}---\text{OH}---\text{OH} \\
\text{(i)} & \quad \text{(ii)} & \quad \text{(iii)}
\end{align*}
\] (1.14)

(iii) approximately equal to "bulk" bond. The strengths of (i) in the 'dimer' is approximately half that of (iii), as revealed by infrared band shifts.\textsuperscript{61}

When basic (B) aprotic solvents are added, (OH)\text{free} groups are scavenged and (LP)\text{free} groups are generated in the process (Scheme 1.15).

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{(MeOH)bulk + } : \text{B} & \quad \text{OH}---\text{B} + \text{OH}--- \\
\text{(OH)bound} & \quad \text{(LP)free}
\end{align*}
\] (1.15)

1.6 EXPERIMENTAL TECHNIQUES FOR PROBE STUDIES

Depending upon the nature of the probes, a large number of spectroscopic techniques may be used. It is not the primary intention here to discuss the theoretical background to the techniques which is amply spelt out in numerous text books. The accent is therefore centred on their applicability to solvation studies of probe systems.

1.6.1 Infrared Spectroscopy

The specific nature of the various infrared bands make it a very powerful technique. Some oscillators, e.g. P=O, C=O, etc., are particularly sensitive to hydrogen bonding and dipolar interactions. Hydrogen bonding interactions $\beta$ usually lead to bond weakening $\alpha$, the effect which is felt in the absorption frequency which is shifted to
lower frequencies. The major advantage of infrared spectroscopy lies

\[
\begin{array}{c}
\alpha \\
\beta \\
H
\end{array}
\]

\[\rightarrow \text{P-O} \quad \text{---------} \quad \text{HO} \quad \rightarrow\]

in the fact that it 'sees' a largely static system, very much on the slow-exchange side, so that precise solvation features may be distinguished.

There are, however, sometimes insurmountable problems when using infrared spectroscopy. As most probes are used in very dilute solutions, the oscillator being observed must give rise to a reasonably strong absorption band. Solvents too have their own absorption spectrum in the infrared regions and hence must be chosen so that their main absorption bands do not overlap with those of the probe under study. Raman spectroscopy may often be a good alternative. However, information from both these techniques is complicated if the studied absorption consists of features spaced so close together as to make resolution impossible. Curve resolution techniques (see Chapter 2) may offer a partial solution to this problem. There are considerable advantages in the use of infrared methods for monitoring probes in binary mixed solutions\(^2,62\)

1.6.2 NMR (Nuclear Magnetic Resonance) Spectroscopy

Magnetic resonance techniques are complementary to infrared techniques. The use of NMR methods in solvation of probe systems is based upon the fact that the nucleus under observation is shielded differently depending upon its environment. Thus, solvent interactions at a phosphate linkage may be gauged using \(^{31}\text{P}\) resonance. In contrast to infrared spectroscopy,

\[\rightarrow \text{P}^{31} \rightarrow \text{O} \quad \rightarrow\]

NMR techniques detect a largely dynamic system, almost always on the
fast-exchange side. This means, therefore, that when NMR shifts are monitored, weighted-average information results, whereas infrared (or ultraviolet) spectroscopy provides, in favourable cases, separate pieces of information from all the different solvates formed by the probe. So long as this is borne in mind, it is difficult to predict which measurement is the most useful. This technique has been applied extensively in this laboratory.  

1.6.3 Ultraviolet Spectroscopy

Although early applications of spectroscopy to solvation studies were mainly in this area, it has since proved to be less widely applicable. Probably one major responsible factor has been the generally broad band widths arising from electronic transitions, so that shifts need to be large to be detected. This technique has recently been applied successfully to the solvation of DTBN (ditertiary-butyl nitroxide) probe. Amongst the ions, the iodide anion has been most studied.

1.6.4 ESR (Electron Spin Resonance) Spectroscopy

ESR spectroscopy has effectively been used in the solvation studies of paramagnetic species. The technique, however, suffers from disadvantages that are identical to NMR since discernible features often arise from rapid exchange, a lot of useful information being lost as a consequence.

1.7 SOLVENT SCALEx

1.7.1 Introduction

The fact that chemical reactions are significantly affected by the solvent in which they take place has been realised for over 100 years. It would therefore seem desirable to be able to predict these effects
and, to this end, many investigations have been undertaken.\textsuperscript{72-75} 

Probably the earliest scheme for solvent classification was provided by Bronsted,\textsuperscript{76} who differentiated solvents in terms of protic and aprotic. The classically measured quantities for solvents such as dipole moments $\mu$ or dielectric constant $\varepsilon$, only appear to apply to the behaviour of selected groups of solvents. Some correlations between these parameters and the other measured quantities that have a wider application appears to exist\textsuperscript{77} but must be treated with caution when specific interactions occur.

Because of the difficulties involved with classical and theoretical quantities, many workers have turned to the more empirical approach of measuring solvent behaviour as a measure of such parameters as rate constants for known reactions, electronic transitions or infrared shifts for reference compounds, etc. Numerous empirical scales have now been published,\textsuperscript{78-80} the majority based on spectroscopic measurements.

A universal solvent polarity scale would be useful. However, such a scale does not exist at the present time; being generally overcast by its limitations, difficulties and drawbacks. Of the many empirical scales that exist, this thesis makes frequent reference to Acceptor Number and Donor Number scales, and attempts to comment on their applicability. It is pertinent, however, to survey a few other important solvent scales.

1.7.2 Z-Values

Kosower\textsuperscript{81} proposed a scale of 'solvent polarity' based on the UV spectrum of 1-ethyl-4-carboxythoxypyridinium iodide (1.16).

The Z-value for a solvent is defined as the transition energy (in kcal mol\textsuperscript{-1}) of the longest wavelength absorption band of 1-ethyl-4-carboxythoxypyridinium iodide in that solvent. The band appears to arise
from contact ion-pairs (Figure 1.16), since it only appears in relatively concentrated solutions. The solvent induced changes in the charge transfer energy are considered to be an empirical measure of the electrophilic properties of the solvent, since solvent interactions occur via electrophilic attack at the iodide ion of the ion-pair (Figure 1.16). The range of existing Z-values have been reviewed and extended.82

1.7.3 $E_r$-Values

A very similar scale to that of Kosower was proposed by Dimroth and Reichardt.7 $E_r$-values are based on the energy of the lowest electronic transition of pyridinium-N-phenol betaine (Figure 1.17). This has a large $\pi$ electron system and although neutral overall has a highly basic oxygen site. Its behaviour is expected to be similar to that of pyridinium iodide (Figure 1.16). Solvent attack occurs electrophilically (acceptor property of the solvent) at the highly basic oxygen atom which is sterically well accessible. The UV spectrum may be studied since it is quite sensitive to this attack.
1.7.4 Y-Values

An earlier system devised for following the electrophilic properties of solvents was given by Winstein and Grunwald, the so-called Y-value. The Y-value is defined by equation 1.18

\[ Y = \log \left( \frac{K_S}{K_{SO}} \right) \]  

where \( K_S \) and \( K_{SO} \) denote the first order rate constants for the solvolysis of t-butyl chloride in a solvent \( S \) and the standard solvent \( SO \) (EtOH : \( \text{H}_2\text{O} = 4 : 1 \) by volume).

\[ (\text{CH}_3)_3\text{CCl} \rightarrow (\text{CH}_3)_3\text{C}^+\text{Cl}^- \rightarrow \text{products} \]  

\[ \text{ion-pair polar transition} \]  

Since the tertiary carbon atom is usually strongly shielded towards solvent attack, stabilisation of the transition state will depend essentially on the interaction with the halide ion, i.e. on the electrophilic properties of the solvent.

1.7.5 \( \alpha \) and \( \delta \) Scales

Taft and co-workers used what they called a "solvatochromic comparison method" in order to produce scales of hydrogen bonding capability of solvents. In essence, this is based upon the idea that a plot of spectral shifts for an electrophilic probe against those for a nucleophilic probe in non-hydrogen bonding solvents will lie off the line, the magnitude of their deviation from the line being a measure of their hydrogen bonding capability either as a donor or acceptor.

The direction of deviation from the regression line would depend upon whether the hydrogen bond former is an electron donor or acceptor. For most applications, it is easier to use the plot of an amphiphilic probe against that of either the electrophilic or nucleophilic probe. Thus a single deviation is observed for hydrogen bonding due to the electron
1.7.6 Donor Numbers (DN) and Acceptor Numbers (AN)

The concept that solvent interactions are akin to the classical Lewis acid-base situation was proposed by Gutmann and co-workers. They suggested that solvent attack on a solute could be described by Scheme 1.20:

\[
\text{nucleophilic } \delta^+ \rightarrow \delta^- \text{ electrophilic}
\]

\[
\text{S} \rightarrow \text{A} \rightarrow \text{B} \rightarrow \text{S}
\]

\[
\text{ELECTRON PAIR DONOR} \quad \text{ELECTRON PAIR ACCEPTOR}
\]

\text{Scheme 1.20}

The nucleophilic character of a solvent is described by a Donor Number. It is defined as "the molar enthalpy value for the reaction of the donor with antimony pentachloride SbCl}_5 as a reference acceptor in a 10^{-3} M solution of 1,2-dichloroethane".

\[
D: + SbCl}_5 \rightleftharpoons D:SbCl}_5 \ (\Delta H \equiv \text{DN}) \quad \ldots \ (1.21)
\]

It is assumed that 1:1 adducts are formed. Recently, Marcus has reviewed the existing list of DN for various solvents. Reasonable correlations between solvent Donor Numbers and magnetic resonance shifts of various nuclei such as $^{32}$Na, $^{19}$F, $^{29}$Si and also $^{59}$Co in solvents are known.

The measure of the electron acceptor strengths of various solvents was pursued using a probe that acted as a strong electron donor. Triethylphosphine oxide (Et}_3PO) was chosen as the model substrate since it fulfilled important requirements. This base contains only a single basic centre, namely the oxygen atom, whereas the acidic centre of the molecule, the phosphorus atom is protected against nucleophilic solvent
attack by the oxygen and the three largely inert alkyl groups.

The Acceptor Number defined by equation 1.22 is based on the $^{31}P$ chemical shift of Et$_3$PO in some solvent ($\delta_{corr}$), extrapolated to zero concentration and referred to an infinitely dilute solution of the Et$_3$PO in n-hexane, the denominator being the corresponding shift value for an infinitely dilute solution of antimony pentachloride-triethylphosphine oxide adduct in 1,2-dichloroethane (AN of the adduct arbitrarily assigned a value of 100, n-hexane of course being assigned zero).

Owing to the excellent solubility and stability of the Et$_3$PO, acceptor numbers can be directly measured for all types of solvents.$^{93}$

Gutmann$^{75}$ has summarised the correlations between AN scale and a variety of other solvent scales which includes: Kosower's Z-values, Dimroth-Reichardt E$_T$-values, WINstein-Grunwald Y-values, free energy of solvation of Cl$^-$ anion, $^{13}$C shifts of C=O group of acetone and others.$^{94,95}$

Further, since AN scale has previously been applied with considerable success in this laboratory,$^3,64$ it has been the primary solvent scale used throughout in the thesis.
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95. V. GUTMANN, 
CHAPTER 2

Experimental Techniques
2.1 **PURIFICATION OF MATERIALS**

Most organic solvents were purified and dried according to standard procedure.\(^1\) Generally, these required fractional distillation off some appropriate drying agent, e.g. calcium hydride, under nitrogen. Water, however, was purified by deionisation followed by a secondary treatment using a Millipore 'Milli-Q' system.

All materials and non-aqueous solvents were stored in a dry atmosphere in a dry box prior to use.

2.2 **SAMPLE PREPARATION AND HANDLING**

Samples were prepared fresh by volume or weight whichever was convenient for the materials being used. When necessary, all mixing and transferring of materials was conducted in a dry box under an inert atmosphere (dry nitrogen). To minimise any errors due to deterioration, all spectra were recorded immediately after preparation.

For monitoring the behaviour of the solute (a probe) in a binary mixed solvent system \(A\)+\(B\), a simple standard procedure was followed:

a) A suitable dilute concentration of probe (usually around 1\% \(\text{v/v}\)) was prepared in 10 ml of \(A\) and 10 ml of \(B\).

b) These solutions were then mixed to give a range of different concentrations.

c) The same mixtures were prepared using pure \(A\) and pure \(B\); these solutions were then used as references (for instance in double beam spectrometers).

2.3 **SPECTROSCOPIC TECHNIQUES**

a) **Infrared Spectroscopy**

Infrared spectra were recorded on a Perkin-Elmer 580\(^2\) machine. This
is a double beam recording spectrometer with scale expansion facilities on ordinate and abscissa and pre-selectable modes for optimum resolution and/or noise level. For many of the spectra, an accuracy of within ±0.5 cm⁻¹ was achieved for the peak position ($v_{\text{max}}$).

The cells used were generally of the demountable type, with windows chosen depending upon the spectral region. For most measurements above 1000 cm⁻¹, calcium fluoride plates were used. Pathlengths were adjusted using PTFE (poly tetrafluoroethylene) spacers, a path of 0.025 cm being found most suitable. Variable temperatures were obtained using a 'SPECAC 20000' vacuum jacketed cell holder and proportional controller. It was possible to hold the temperature to ±1°C in the range -200 to +250°C. Low temperatures were achieved with the aid of liquid nitrogen and heating by using the built-in cell heater.

b) Ultraviolet Spectroscopy

All spectra in these regions were recorded on a Perkin-Elmer Hitachi 340 spectrometer. This is a double beam spectrometer which is capable also of recording near infrared and visible spectra. The 2600 to 800 nm (1 nm = 10⁻⁹ m) region is designated the near infrared region and uses a lead sulphide detector. 850 to 190 nm is the visible and ultraviolet region using a photomultiplier detector. In the machine, the near infrared and visible radiation is obtained by means of a tungsten filament bulb, the source of ultraviolet radiation being a deuterium lamp. Facilities for both ordinate and abscissa scale expansions are provided.

Cells used were made of silica glass with a fixed pathlength of 1 cm.

c) Nuclear Magnetic Resonance Spectroscopy

Depending upon the nature of the work being undertaken, several types of spectrometers were employed. Proton ($^1\text{H}$) work was conducted on a 'JEOL PS-100' spectrometer. This is a 100 MHz spectrometer operating in
the continuous wave mode. 5 mm outer diameter (OD) tubes were used
generally with a tetramethylsilane (TMS) reference (Appendix B).

A 'JEOL FX-60' spectrometer was used for $^{13}\text{C}$ and $^{31}\text{P}$ work. This is
a 60 MHz (proton) spectrometer operating with a pulsed Fourier transform
mode technique and having variable temperature capability. Fourier
transform spectroscopy is a recent development which involves application
of a strong rf pulse to the sample, the resultant spectral response
pattern being recorded in the computer memory. This is then subjected
to a mathematical treatment whereby the signal-to-noise ratio is enhanced.
10 mm OD tubes were used with coaxial inserts for referencing. To ensure
field stability, a deuterium lock signal was incorporated into the
external solution. All $^{31}\text{P}$ measurements were done using 85% phosphoric
acid in $\text{D}_2\text{O}$ as an external reference. $^{17}\text{O}$ NMR measurements were done at
Warwick University on a Bruker WM-400 spectrometer. This is a 400 MHz
(proton) Fourier transform instrument having a superconducting magnet
and variable temperature facilities. Since the samples examined
contained natural abundant $^{17}\text{O}$ levels, long accumulations were necessary
to produce good spectra. Referencing was by computer storage of the
$\text{D}_2^{17}\text{O}$ signal. 10 mm OD tubes were used for measurements.

2.4 INFRARED SPECTRAL BAND DECONVOLUTION

Appendix C provides a brief discussion of the relevant techniques
involved. The Dupont 310 Curve Resolver and the VIDCA program were
extensively used for infrared band analysis.

2.5 GENERAL COMMENTS

All instruments were operated following standard procedures and
according to manufacturers' instructions. In order to reduce experimental
errors to a minimum, care was taken over all aspects of the work, particularly in the preparation of samples and the cleanliness of equipment, cells, etc.
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CHAPTER 3

Solvation of Neutral Phosphates
3.1 INTRODUCTION

Amongst the large variety of compounds, the greatest significance in biochemical processes is possessed by phosphate derivatives with the ester bonds on the phosphorus atoms. These compounds have also long been known for their remarkable extractant properties.\textsuperscript{1,2} Distribution experiments\textsuperscript{3,4} have indicated that the base strengths of neutral organophosphorus compounds decrease from phosphine oxides to phosphinates, phosphonates and phosphates. These findings are also consistent with infrared measurements involving association of phosphoryl compounds with various proton donors.\textsuperscript{5-8} Substituent effects\textsuperscript{6,7} have been invoked to explain these differences in base strengths, as they have also been to rationalise the alkaline hydrolysis\textsuperscript{9-11} of a series of organohalophosphorus compounds.

Vibrational spectroscopy has extensively been used in studies involving phosphoryl compounds. Dahl \textit{et al.}\textsuperscript{12} have shown that there is a pronounced tendency for the (P-O) vibration to occur at lower frequencies for a stronger donor (except for those containing N-P and S-P bonds); further, the spectra are complicated by the presence of rotational conformers\textsuperscript{13,14} but as yet, no single structural assignment has found wide acceptance.\textsuperscript{15} Both metal ions\textsuperscript{16} and relatively polar solvents\textsuperscript{17,18} have been known to displace the (P-O) ν to lower frequencies.

Although magnetic resonance techniques involving \textsuperscript{31}P NMR have long been applied to studies of phosphoryl compounds, the potential of \textsuperscript{17}O NMR\textsuperscript{19,20} is only recently realised. Thus, despite extensive research on these systems, our understanding of the solvation of these compounds is very limited. This work therefore is primarily aimed at probing various phosphate compounds using spectroscopic techniques that had
been applied to triethylphosphine oxide.\textsuperscript{21} In subsequent discussions, frequent reference has been made to this compound both from the view of its structural similarity and also from its significance in the determination of solvent acceptor numbers (A.N.).\textsuperscript{22}

3.2 EXPERIMENTAL

Trimethylphosphate (TMP), tri n-butylphosphate (TBP), dimethylmethylphosphonate (DMMP), hexamethylphosphoric triamide (HMPA) were the highest grade commercially available, and were purified by vacuum fractional distillation over CaH\textsubscript{2}. Triethylphosphine oxide (Et\textsubscript{3}PO), which contained traces of benzene, was purified by sublimation at room temperature in a vacuum.

Preparation of O,O,S-Trimethyl Phosphorothioate (TMPS)

TMPS (II) was prepared\textsuperscript{23} from triethylammonium salt of O,O-dimethylphosphorothioate (I) by methylation using MeI in methanolic solutions when triethylammonium iodide (III) was precipitated. The TMPS (II) formed was subsequently separated and purified by vacuum fractional distillation.

\[
\begin{align*}
\text{S} & \quad \text{HNEt}_3 \\
\text{MeO-P-O} & \quad \text{SMe} \\
\text{O-Me} & \quad \text{MeI} \\
\text{(I)} & \quad \text{MeO-P=O} \quad + \quad \text{Et}_3\text{NH}^+\text{I}^- \\
\text{(II)} & \quad \text{(III)} \\
\end{align*}
\]

(I) was prepared by the following reaction scheme

\[
\begin{align*}
\text{O} & \quad \text{HNEt}_3 \\
\text{-P-H} & \quad + \quad \text{S} \quad + \quad \text{Et}_3\text{NET} & \quad \rightarrow \text{MeO-P-S} \\
\text{O-Me} & \quad \text{O-Me} \\
\text{(I)} & \quad \text{(I)}
\end{align*}
\]
Solutions were prepared by volume using Eppendorf pipettes. The probe concentration was kept at a minimum (ca. 1% v/v) except in experiments involving $^{17}$O NMR where this was increased to ca. 5% v/v. Infrared spectra were recorded on a double beam Perkin-Elmer model 580 spectrometer using demountable cells with 25 µm pathlength teflon spacers between CaF$_2$ plates. Temperature measurements were performed with the aid of SPECAC temperature controller. UV spectra were run on a Hitachi model 340 spectrometer using a 1 cm silica cuvette. $^{31}$P NMR spectra were measured on a Jeol FX60 Fourier Transform spectrometer with phosphoric acid (85% v/v in D$_2$O) as an external reference with D$_2$O lock signal. All chemical shifts were corrected for volume susceptibility which were available from literature.$^{24-26}$ Low temperature $^{31}$P resonance studies were conducted with a phosphoric acid reference in CD$_2$Cl$_2$. Measurements of $^{17}$O resonance were performed at Warwick University on a Bruker WM 400 MHz Fourier Transform spectrometer, with chemical shifts computed from an external water reference. This was changed to dioxane and subsequently to methanol in low temperature measurements. The proton-phosphorus coupling constants were determined on Jeol PS100 NMR spectrometer with TMS as an internal reference. Infrared bands were resolved using a computer program.

3.3 RESULTS AND DISCUSSION

3.3.A Trimethylphosphate (TMP)

3.3.A.1 Pure Solvent Systems

In general, infrared spectra of TMP in pure solvents in the P-O stretch regions comprise more than one band (Fig. 3.1), the feature 'X' being associated with a methyl rocking vibration.$^{27}$ The vibrational spectra of TMP$^{27-30}$ and other phosphate esters$^{13,14}$ have been studied in detail both in the liquid and solid phases and the presence of rotational
Infrared spectra for dilute solutions of TMP in a water, b methanol and c acetonitrile in the P-O stretch regions, showing features assigned to the high frequency conformer (a) and low frequency conformer (b). [Band X is discussed in the text.]
conformers (a and b) has been generally suggested to explain the presence of two bands for the (P-O) vibration. This feature is also indicated in gas phase studies of TMP. The doublet bands in carbon tetrachloride were found to be independent of dilution. However, the relative proportion of the components are solvent dependent as indicated (Table 3.1) (the high frequency component of the doublet presumably is the relatively more polar, being particularly favoured in a polar environment).

Conformer preference is also expected to be a function of temperature. This is demonstrated for carbon tetrachloride solutions (Figure 3.2) where the band profile exhibits large changes. Clearly, the high frequency component is favoured at low temperatures. However, this behaviour is less marked in methanolic (Figure 3.3) and aqueous (Figure 3.4) solutions. It is not the objective to establish the structure of the conformers involved since, this has been the subject of numerous views. 13,15,30,32

Table 3.1 presents the phosphoryl stretching frequency (P-O) $\nu_{\text{max}}$ of TMP in a range of pure solvents plotted against the $^{31}$P chemical shift values. The obvious advantage of infrared spectroscopy over magnetic resonance methods for this compound is quite apparent. NMR probes provide only a single narrow line which arises because of rapid time-

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
<th>Ratio of Peak Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>High $\nu$ : Low $\nu$</td>
</tr>
<tr>
<td>Isooctane</td>
<td>1.96</td>
<td>0.93 : 1</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.24</td>
<td>1.14 : 1</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>2.64</td>
<td>1.40 : 1</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>7.58</td>
<td>1.60 : 1</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.70</td>
<td>1.78 : 1</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>37.50</td>
<td>2.12 : 1</td>
</tr>
</tbody>
</table>
FIGURE 3.2

Effect of temperature on the infrared spectra of TMP solutions in tetrachloromethane in the (P-O) stretch regions.
FIGURE 3.3
Effect of temperature on the infrared spectra of TMP solutions in methanol in the (P-O) stretch regions.
FIGURE 3.4
Effect of temperature (°C) on the infrared spectra of TMP solutions in water in the (P-O) stretch regions.
FIGURE 3.5
Plot of $^{31}\text{P}$ resonance shifts versus (P-O) stretch frequency for TMP in dilute solutions in a range of pure solvents.

KEY
1 Cyclohexane
2 Triethylamine
3 Tetrachloromethane
4 Tetrahydrofuran (THF)
5 Acetone
6 Acetonitrile (MeCN)
7 Nitromethane
8 Dimethylsulphoxide (DMSO)
9 Methylenechloride
10 Trichloromethane
11 Tert-Butanol
12 Iso-Propanol
13 Ethanol
14 Methanol (MeOH)
15 Ethane-Diol (DIOL)
16 Water (H$_2$O)
17 Trifluoroethanol
18 Hexafluoroisopropanol

HIGH FIELD

---

1300
1280
1260
1240
1220
1200

12.8
12.6
12.4
12.2
12.0

0.8
1.6
2.4
3.2

31P Shift / ppm

---
averaging, an aspect which obscures a good deal of useful information. In contrast, infrared probes have the advantage of providing separate features for distinct species, provided of course, they are not broad so as to make resolution difficult. The points depicted (●) denote the weighted mean values for the infrared bands since the NMR results are weighted means.\(^{21}\) The low frequency shift of the (P-O) vibration from aprotic to protic solvents can be explained by the weakening of the (P-O) bond during interaction at the phosphoryl oxygen site. In marked contrast to the trends in the infrared, the \(^{31}\text{P}\) resonance is almost solvent insensitive, so that the NMR shifts are thought to be of no real significance. Correlations between infrared and NMR features have previously been established for triethylphosphine oxide and other probes,\(^{33}\) but in these cases both are very sensitive to solvation. Lack of \(^{31}\text{P}\) resonance sensitivity has also been reported for this probe over a range of acid concentrations\(^{34}\) and phosphoric acid.\(^{35}\) Similar trends are also found for tri n-butylphosphate (TBP) in solvents (Figure 3.6).

The trends in the (P-O) \(\nu_{\text{max}}\) for TMP are shown in Figure 3.7 plotted as a function of Gutmann's solvent acceptor numbers\(^{22}\) (A.N.), which are based on the \(^{31}\text{P}\) chemical shift of Et\(_3\)PO in the solvent concerned. However, Et\(_3\)PO forms three hydrogen bonds in water and is disolvated in alcohols.\(^{21}\) Using the shifts deduced for similarly bonded Et\(_3\)PO molecules, a good correlation is achieved. There are four correlating lines, two \((a, b)\) for the aprotic solvents and the other two \((a', b')\) for the protic solvents, arising as a result of the two conformers. It is sufficient to note from the AN correlation that solutions of TMP in protic solvents are hydrogen bonded (two in water and one in alcohols generally) with mixtures of conformers, the high frequency conformer
FIGURE 3.6
Plot of $^{31}$P resonance shift versus (P-O) stretch frequency for TBP in dilute solutions in a range of pure solvents. 
[Key as for Figure 3.5]
FIGURE 3.7
Correlation between $\nu_{P-O}$ for TMP and solvent acceptor number, after adjusting to give the same solvation numbers as Et$_3$PO. [Key as for Figure 3.5]
Lines a, b connect data for aprotic solvents and a', b' for protic solvents.
One of our major concerns is the possible involvement of ether oxygen sites in solvation. It might be anticipated that $^{17}$O NMR spectroscopy could shed light about the environment of these oxygen sites. The results of $^{17}$O shifts are thus presented in Figure 3.8(i), the corresponding $^{31}$P resonance being shown in Figure 3.8(ii) for comparison. Although the $^{17}$O shifts are much larger than the $^{31}$P shifts, the trends bear little relation to the infrared results or to any simple theory. However, the $^{31}$P-$^{17}$O coupling constants of the phosphoryl group clearly decreases in the protic media (Table 3.2). Since hydrogen bonding tends

to make the four oxygen atoms more nearly equivalent, the bond angles may possibly alter slightly towards producing a tetrahedral structure. The $^{31}$P-$^1$H coupling constants were, however, found to be insensitive to solvent effects. Figure 3.8(iii) depicts the $^{17}$O shifts induced in the P-O-C linkage. These trends although definitive, being shifted to high fields in the protics, are not a conclusive evidence for the participation by the ether oxygens since the trends may equally be assigned to bond angle or electron density changes that would arise from interactions at the more basic phosphoryl site. Unlike the infrared spectra in the P-O stretch regions, the $^{17}$O resonance for TMP in CH$_2$Cl$_2$ was found to be

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$^{31}$P-$^{17}$O (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbontetrachloride</td>
<td>2.9</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>2.8</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>2.8</td>
</tr>
<tr>
<td>Methanol</td>
<td>2.4</td>
</tr>
<tr>
<td>Deuterium Oxide</td>
<td>2.4</td>
</tr>
</tbody>
</table>
FIGURE 3.8
Comparison of (i) $^{17}P$, (ii) $^{31}P$ and (iii) $^{17}P-C$ resonance shifts for TMP in several solvents.
temperature insensitive. This was also true for the solutions of TMP in CH\(_2\)Cl\(_2\), MeOH and mixtures of CH\(_2\)Cl\(_2\) and ethylene glycol, monitoring the \(^{31}\)P resonance. It is thus concluded that both \(^{31}\)P and \(^{17}\)O resonance techniques seem to fail in pure solvent studies of TMP.

3.3.A.2 Methanol + Aprotic Solvent Systems

A set of infrared spectra for dilute solutions of TMP in MeOH + THF, MeOH + MeCN and MeOH + CCl\(_4\), mixed systems are presented in Figures 3.9, 3.10 and 3.11 respectively. Since the spectra in the protic solvents are complicated (Figure 3.7), it is appropriate to analyse the results in terms of solvation by individual conformers. If it is accepted that TMP is mono-solvated in MeOH (with a mixture of high [a\(_1\)] and low [b\(_1\)] frequency conformers), as inferred from the AN plot, the trends in the MeOH-rich regions could satisfactorily be explained by a loss of [b\(_1\)] with concomitant growth of species around ca. 1268 cm\(^{-1}\) (assigned to features [a\(_1\)] and [b\(_0\)], which denote respectively the high frequency mono hydrogen-bonded and low frequency 'free' conformers). The latter generates the high frequency 'free' conformer [a\(_0\)]. It may be noteworthy that the mono-solvated species in CCl\(_4\) solutions is retained even in CCl\(_4\) rich regions. This is because CCl\(_4\) is a relatively inert solvent (donor number = 0\(^{36}\)) in comparison with either MeCN or THF.

3.3.A.3 Water + Base Systems

The \(^{31}\)P chemical shifts are shown as a function of the mole fraction (mf) of added aprotic solvents in Figure 3.12(i). Note that towards the rich base regions, there is hardly any significant change in resonance. Much of water chemistry is thought to be dominated by the equilibrium (1).\(^{37}\)

\[(\text{OH})_{\text{free}} + (\text{LP})_{\text{free}} = (\text{H}_2\text{O})_{\text{bulk}} \quad \text{.... (1)}\]
FIGURE 3.9
Infrared spectra for dilute solutions of TMP in the ν(P-O) regions in MeOH + THF systems. [Significance of a0, b0, al and bl is discussed in the text.]
FIGURE 3.10
Infrared spectra for dilute solutions of TMP in the v(P-O) regions in MeOH + MeCN systems.
FIGURE 3.11
Infrared spectra for dilute solutions of TMP in the ν(P-O) regions in MeOH + CCl₄ systems.
$^{31}$P resonance shifts for TMP in water + base systems as a function of the mole fraction of base.

**FIGURE 3.12(i)**

- + HMPA
- × DMSO
- △ THF
- ○ MeCN
- ■ MeOH
When basic aprotic solvents are added, they scavenge \( (\text{OH})_{\text{free}} \) groups and generate \( (\text{LP})_{\text{free}} \) groups from bulk water via equilibrium (1). In the 0-0.2 mf base region [Figure 3.12(ii)], the shifts induced by added base can be interpreted by the loss of water molecules bonded to the probe by the reaction of the \( (\text{LP})_{\text{free}} \) species. This is nicely illustrated by the rapid initial high field shift induced by the very strong base HMPA. Clearly, the weak base MeCN, is very inefficient at affecting water desolvation. The behaviour of the strong base DMSO is however contrary to expectation. Shifts for the tetrabutylammonium salts are dominated by the chloride ion that scavenges \( (\text{OH})_{\text{free}} \) units (the cation effectively remaining dormant), the slope of the line being a measure of anion solvation. Assuming the chloride ion to be hexa-hydrated in water, the results suggest a solvation number of nearly 5 for HMPA, a figure which is also expressed by other workers. This scheme however assigns a higher solvation number for the hydration of THF than normally accepted. Sodium salts with bulky anions (the anion participation being only minor) would increase the \( (\text{OH})_{\text{free}} \) concentration by scavenging \( (\text{LP})_{\text{free}} \) groups. Since \(^{31}\text{P}\) resonance is sensitive to loss in \( (\text{OH})_{\text{free}} \) groups, such salts are not expected to display significant effects on the resonance as typified by sodium hexafluoro arsenate (\( \text{NaAsF}_6 \)). However, the anomalous behaviour of sodium tetraphenylborate (\( \text{NaPhiB} \)) may be noted. This prompted the study to be extended to probing \( \text{Et}_3\text{PO} \) (Figure 3.13) where the \(^{31}\text{P}\) resonance is known to be sensitive. The similarity in the response of \( \text{NaPhiB} \) to this probe is interesting since this behaviour is not born out of \(^{31}\text{P}\) resonance insensitivity. The influence of benzene ring currents may be a possibility. Trends for the other salts are as expected, the results indicating comparable solvation numbers for the \( \text{Na}^+ \), \( \text{Cl}^- \) and \( (\text{MeO})_2\text{PO}_2^- \) ions in water. \(^{31}\text{P}\) resonance has thus proved satis-
FIGURE 3.12(ii)

$^{31}$P resonance shifts for TMP in water + base systems as a function of the mole fraction of base over a limited range.
FIGURE 3.13

$^{31}\text{P}$ resonance shifts for Et$_3$PO in water + base systems as a function of the mole fraction of base.
factory over a limited concentration region for binary mixed solutions of TMP, although discrepancies have been observed for DMSO and THF systems.

Infrared spectroscopy reveals the presence of four well defined bands for the systems. The spectra for H$_2$O + THF solutions [Figure 3.14(i)] were computer synthesised using a set of four bands [Figure 3.14(ii)] and these were used to follow the growth and loss of species with increase in concentration of the cosolvent. For qualitative purposes, the assumptions made are that the extinction does not change significantly from one solvent to the other, and that [a2] (assigned to the high frequency di-hydrated conformer) is the predominant species in aqueous solutions. Analogous treatment was used to monitor changes for H$_2$O + MeCN mixtures [Figure 3.15(i) and Figure 3.15(ii) respectively]. The initial loss of band [a2] and the growth of band [b1] (assigned to a low frequency mono-hydrated conformer) occurs much faster for the comparatively stronger base THF than MeCN. For MeCN, some disolvate is retained almost throughout but this is clearly lost in the ca. 0.55 mf region for THF. Similarly for MeCN, the mono-hydrate [b1] reaches a maximum in the 0.4 mf regions which is much later than that for THF. As for methanolic systems, the assignment of bands around ca. 1273 cm$^{-1}$ is rather difficult. In these regions, species such as [a1] and [b0] (which are respectively due to the high frequency mono-solvated conformer and low frequency 'free' conformer) are thought to prevail. As expected of a relatively stronger base, [a1] in THF environment attains a maximum sooner than does the weak base MeCN. It is concluded from these mixed solvent systems that TMP is di hydrogen-bonded in water.

3.3.A.4 Water + Methanol Systems

Figures 3.16(i) and 3.16(ii) present a set of trends for dilute
FIGURE 3.14(i)
Infrared spectra for dilute solutions of TMP in water + THF systems in the \nu(P-O) regions.
[Significance of a0, b0, a1, b1 and a2 is discussed in the text.]
FIGURE 3.14(ii)

Trends in the intensities of the deconvoluted $\nu (P-O)$ bands for TMP in water + THF systems shown as a percentage of maximum.
[a and b refer to high $\nu$ and low $\nu$ conformers respectively.]
FIGURE 3.15(i)
Infrared spectra for dilute solutions of TMP in water + MeCN systems in the ν(P-O) regions.
FIGURE 3.15(ii)

Trends in the intensities of the deconvoluted ν(P-O) bands for TMP in water + MeCN systems shown as a percentage of maximum.
FIGURE 3.16(i)
Infrared spectra for dilute solutions of TMP in water + methanol systems in the ν(P-O) regions.
FIGURE 3.16(ii)
Trends in the intensities of the deconvoluted ν(P-O) bands for TMP in water + methanol systems, shown as a percentage of maximum.
solutions of TMP in H$_2$O + MeOH mixed systems. The changes with increasing concentrations of MeOH can be accommodated in terms of three hydrogen-bonded conformers, the high frequency di-bonded [a2], the low frequency mono-bonded [b1] and the high frequency mono-bonded [a1].

In this connection, it is noteworthy that for aqueous systems (and methanolic systems), there are small but distinct shifts of the infrared bands assigned to the different hydrates as the concentration of the cosolvent was increased. These shifts can be understood in terms of the loss of tertiary and secondary solvation. The situation, which is simpler for MeOH than for water, is depicted in terms of structures (IV), (V) and (VI). Structure (IV) represents the situation for dilute solutions in MeOH. With increasing concentrations of cosolvent, methanol molecules are removed from the chains. Conversion of (IV) to (V) would weaken hydrogen bonds to TMP and hence the band for (IV) will shift to higher frequencies. Obviously, this shift which is small compared with the loss of primary solvation is also responsible for the difficulty in resolving such bands. This process of desolvation is continued until the limiting structure (VI) is reached. These shifts have been allowed for in the peak height plots.

One of the main aspects of these results has been the remarkable insensitivity of the $^{31}$P resonance. In the hope of finding a possible cause for this lack of sensitivity, a systematic investigation of
structurally similar compounds was undertaken.

3.3.B Dimethylmethyl Phosphonate (DMMP)

3.3.B.1 Pure Solvent Systems

Figure 3.17 presents a typical set of infrared spectra for dilute solutions of DMMP in several solvents, these are again characterised by the presence of multiple bands, which have been partly attributed to the presence of rotational conformers. The bands around ca. 1312 cm\(^{-1}\) and ca. 1185 cm\(^{-1}\) respectively are assigned to methyl vibrations. It is noteworthy that for DMMP, conformer preference at room temperature is reversed to those observed in TMP. This preference for the low frequency component is also reflected on cooling (Figure 3.18). However, the high frequency conformer seems favoured in a polar environment (Table 3.3) (which is similar to TMP).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
<th>Ratio of Peak Intensities low v : high v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbontetrachloride</td>
<td>2.24</td>
<td>6.50 : 1</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.28</td>
<td>3.30 : 1</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>5.62</td>
<td>2.63 : 1</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>7.58</td>
<td>2.39 : 1</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.70</td>
<td>1.33 : 1</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>35.90</td>
<td>1.17 : 1</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>37.50</td>
<td>1.10 : 1</td>
</tr>
</tbody>
</table>

Figure 3.19 displays \((P\text{-}\text{O)}\ \nu_{\text{max}}\) plotted as a function of the measured \(^{31}\text{P}\) chemical shifts in a range of solvents. Such correlations between NMR and infrared have been previously reported. That the single NMR signal detected is a rapid time-averaged value for the various conformers, at least in aprotic solvents, is also illustrated from the temperature dependence of the \(^{31}\text{P}\) resonance (Figure 3.20) that shifts to
FIGURE 3.17
Infrared spectra for dilute solutions of DMMP in a water, b methanol and c hexane in the P-O stretch regions, showing features assigned to the high frequency conformer (a) and low frequency conformer (b). [Band X is discussed in the text.]
FIGURE 3.18

Effect of temperature on the infrared spectra of pure DMMP in the (P-O) stretch regions.

Cooling Cycle: +30 → -5 → -30 → -45 → -75 → -95 → -108 °C
FIGURE 3.19

Correlation between $^{31}$P resonance shifts and $\nu$(P-O) for DMMP in dilute solution in a range of pure solvents.

[Key as for Figure 3.5]

$\text{a}$ and $\text{b}$ refer to high and low frequency conformers respectively.

($\text{H}_2\text{O}$ resonance from $\text{P}^+$ = +38.47 ppm)
FIGURE 3.20
Effect of temperature on the $^{31}$P resonance shift for pure DMMP.
low fields on cooling. Note that this is to be expected from the correlation when infrared features (Figure 3.18) are subject to low temperatures.

In protic solvents, trends can generally be understood by phosphoryl bond weakening caused as a result of hydrogen bonding. As a consequence, the \( v_{\text{max}} \) shifts to lower frequencies. Since this weakening involves a decrease in electron density in the P-O linkage, the phosphorus nucleus is effectively deshielded and resonates at relatively lower fields. One of the benefits of the correlation is that non-averaged shifts for individual species can be predicted with some confidence. An important observation thus, is the enhanced \(^{31}\text{P} \) resonance sensitivity for DMMP over TMP. This particularly favours the former in solvation studies involving NMR.

A very popular solvation parameter used to correlate solvent shifts is the acceptor number\(^{22} \) (AN). In marked contrast to TMP, there are only two correlating lines (Figure 3.21), one for the high frequency conformer (a) and the other for the low frequency conformer (b). One notes similarity in the slopes of lines for the aprotic and protic solvents, and conclude that this presents a rather serious limitation on the utility of acceptor numbers. The spectra for aqueous solutions is a single band, assigned to a high frequency conformer which is tri hydrogen-bonded. Shifts for alcoholic solutions fit best when a mixture of conformers is invoked (low frequency di-bonded, low and high frequency mono-bonded conformers), the position in diol thought to arise mainly from mixtures of di and mono solvates.

3.3.B.2 Methanol + Aprotic Mixed Systems

The \(^{31}\text{P} \) chemical shifts are depicted as a function of the mole fraction (mf) of added aprotic solvent in Figure 3.22(i). Note that in the 0-0.2
Correlation between υ_{P-O} for DMP and solvent acceptor number, after adjusting to give the same solvation number as Et₃PO.

(Line a connects data for high \( \nu \) conformer and line b for low \( \nu \) conformer.)
$^{1}P$ resonance shifts for DMP in methanol + base systems as a function of the mole fraction of base.
mf base regions, the shifts induced by added base depends on the order expected from base strength.\textsuperscript{36} Trends in the infrared are monitored for MeOH + THF, MeOH + MeCN and MeOH + CCl\textsubscript{4} systems in Figures 3.23(i), 3.24(i) and 3.25(i) respectively, and the computer-synthesised curves depicted in Figures 3.23(ii), 3.24(ii) and 3.25(ii) respectively. The rate of initial loss of band \([b_2]\) (assigned to a di hydrogen-bonded low frequency conformer) and the growth of band \([b_1]\) (assigned to a mono hydrogen-bonded low frequency conformer) seems dictated by the strength of respective bases. This is also reflected in the trends for the \([b_1]\) species which attains a maximum only much later for CCl\textsubscript{4} compared to the other bases. The \([a_1]\) band is assigned to a mono-solvated high frequency conformer present in pure MeOH. However, this is made ambiguous in mixed systems by \([b_0]\) (due to low frequency 'free' conformer), which is the dominant species in pure aprotic solvent spectra. Using the correlation (Figure 3.19) and the computer-synthesised curves, the \(^{31}\text{P}\) shifts have been estimated for THF and MeCN systems in Figure 3.22(ii), which compare reasonably with the experimental results [Figure 3.22(i)].

Trends in the 0-0.2 mf regions could be understood by desolvation of methanol molecules as the cosolvent (B) accumulates in the system. The most likely process being:

\[
\text{B + (MeOH)}_{\text{bulk}} \rightleftharpoons \text{B(MeOH)} + (\text{LP})_{\text{free}} \quad \text{.... (2)}
\]

which is followed by:

\[
(\text{LP})_{\text{free}} + R_3\text{PO(MeOH)}_2 \rightleftharpoons (\text{MeOH})_{\text{bulk}} + R_3\text{PO(MeOH)}_1 \quad \text{.... (3)}
\]

and later, direct processes such as:

\[
\text{B + R}_3\text{PO(MeOH)}_2 \rightleftharpoons (\text{MeOH})\text{B + R}_3\text{PO(MeOH)}_1 \quad \text{.... (4)}
\]

However, if the added base is fully solvated, it would be unavailable for direct reactions (as in equilibrium 4) so that the reaction involving \((\text{LP})_{\text{free}}\) would predominate.
FIGURE 3.23(i)
Infrared spectra for dilute solutions of DMMP in the v(P-O) regions in MeOH + THF systems. [Significance of a0, b0, b1 and b2 is discussed in the text.]
FIGURE 3.23(ii)

Trends in the intensities of the deconvoluted $\nu$(P-O) bands for DMMP in MeOH + THF systems, shown as a percentage of maximum.
**FIGURE 3.24(i)**

Infrared spectra for dilute solutions of DMMP in the ν(P-O) regions in MeOH + MeCN systems.
FIGURE 3.24(ii)
Trends in the intensities of the deconvoluted $\nu(P-O)$ bands for DMMP in MeOH + MeCN systems, shown as a percentage of maximum.
**FIGURE 3.25(i)**

Infrared spectra for dilute solutions of DMMP in the \(\nu(P-O)\) regions in MeOH + CCl₄ systems.
FIGURE 3.25(ii)

Trends in the intensities of the deconvoluted ν(P-O) bands for DMMP in MeOH + CCl₄ systems, shown as a percentage of maximum.
3.3.B.3 Water + Aprotic Solvent Systems

Depicted in Figure 3.26(i) are the \(^{31}\)P shifts induced by the cosolvent where, in the 0-0.1 mf regions, the shifts produced by DMSO and THF are identical. That for DMMP itself is greater whilst that for HMPA is even more rapid. In these initial regions, the data for gradients, normalised to a DMMP value of 3, are as follows:

MeCN 2.0, THF 2.6, DMSO 2.6, HMPA 4

The DMMP value of 3 arises from work discussed later in the thesis. These trends can be considered in the light of concepts of \((OH)_{\text{free}}\) and \((LP)_{\text{free}}\) groups. In the 0.2-0.8 mf regions, the curves for the aprotic bases separate in the order expected in terms of their base strengths. Since there is only a comparatively limited supply of water, the trends could be depicted in terms of competitions such as:

\[
B(H_2O) + R_3PO(H_2O)_3 \rightleftharpoons B(H_2O)_2 + R_3PO(H_2O)_2 \quad \ldots \quad (5)
\]

and

\[
B + R_3PO(H_2O)_2 \rightleftharpoons B(H_2O) + R_3PO(H_2O) \quad \ldots \quad (6)
\]

Clearly, MeCN being a weaker base is a very ineffective solvent remover compared to the stronger bases such as HMPA. The 0.8-1.0 mf cosolvent range represents a region where the influence of the cosolvent is being felt most strongly.

These trends are well supported by the infrared results presented for THF and MeCN systems [Figures 3.27(i) and 3.28(i) respectively], which require the need of 5 bands [Figure 3.27(ii) and 3.28(ii) respectively]. As required by the \(^{31}\)P shift results, the initial loss of band [a3] (assigned to a high frequency tri-hydrated conformer) and the growth of band [b2] (assigned to a low frequency di-hydrated conformer) are governed by base strength, THF [Figure 3.27(ii)] generates the latter species much more rapidly than MeCN [Figure 3.28(ii)]. Similarly, for
Figure 3.27(a): Infrared spectra for dilute solutions of DMP in the v(P-O) region in water + THF system.
FIGURE 3.27(ii)
Trends in the intensities of the deconvoluted $\nu(P-O)$ bands for DMMP in water + THF systems, shown as a percentage of maximum.

![Graph showing trends in the intensities of deconvoluted $\nu(P-O)$ bands for DMMP in water + THF systems. The graph plots peak height against mole fraction of THF, with different bands labeled as a0, a3, b0, b1, and b2.](image-url)
FIGURE 3.28(i)
Infrared spectra for dilute solutions of DMMP in the ν(P-O) regions in water + MeCN systems.
FIGURE 3.28(ii)
Trends in the intensities of the deconvoluted $\nu$(P-O) bands for DMMP in water + MeCN systems, shown as a percentage of maximum.
MeCN, the di-hydrate attains a maximum later in contrast to THF. For MeCN, [bl] (assigned to a low frequency mono-hydrate conformer) only maximises at ca. 0.8 mf of MeCN, whereas for THF, this is reached at ca. 0.75 mf. Trends in the very rich aprotic solvent regions are dominated by the growth of 'free' conformer bands ([a0] and [b0] which are respectively the high and low frequency conformers). It is thought, however, as for methanolic systems, [b0] may have a contribution from [al] (assigned to a high frequency mono hydrogen-bonded conformer) over the range for mixed solutions.

Using the correlation (Figure 3.19), and the trends [Figures 3.27(ii) and 3.28(ii)], it is thought possible to estimate the NMR shift values in this way [Figure 3.26(ii)] which agree quite well with experimental results [Figure 3.26(i)]. It is emphasized, however, that without the infrared information, the NMR shifts could be interpreted in a wide variety of ways. Further, the band assignments for conformers in the infrared is based mostly on relative shifts, and there could be no guarantee that the correct assignment was used.

3.3.B.4 Water + Methanol Mixed Systems

Changes for H₂O + MeOH mixed systems which are presented in Figure 3.29(i) display the presence of four distinct bands [a3, b2, bl, al] whose loss and growth is being followed in Figure 3.29(ii), the predicted ³¹P resonance being displayed in Figure 3.26(ii).

3.3.C O,O,S-Trimethylphosphorothioate (TMPS)

3.3.C.1 Pure Solvent Systems

The study of TMPS is important from the view of the structural similarity with TMP. Generally, infrared spectra for dilute solutions of TMPS is composed of more than one band (attributed to conformer presence in the spectra for the aprotic solvents). These have been
FIGURE 3.26(ii)
Reconstruction of $^{31}$P resonance shifts, using infrared data of Figures such as 3.27(ii) and 3.28(ii), and the correlation of Figure 3.19.
Infrared spectra for dilute solutions of DWP in the $\nu (P-O)$ regions in water + methanol systems.
FIGURE 3.29(ii)
Trends in the intensities of the deconvoluted v(P-O) bands for DMMP in water + methanol systems, shown as a percentage of maximum.
depicted in Figure 3.30 as a function of the $^{31}\text{P}$ resonance shift values. As before, only a single NMR feature was detectable for the solutions. The correlation displays yet another interesting behaviour of the $^{31}\text{P}$ resonance.

The $(\text{P-O}) \nu_{\text{max}}$ for TMPS is presented against acceptor numbers in Figure 3.31. The plot suggests similarity in the solvation for both TMPS and DMMP probes. A high frequency tri hydrogen-bonded conformer in water, and a low frequency conformer (invoking a mixture of di and mono hydrogen-bonding) being favoured for solutions in ethane-diol and methanol. The absence of another feature in the MeOH spectra (comparing that for DMMP) is presumably due to differences in base strength.

3.3.D Hexamethylphosphoric Triamide (HMPA)

HMPA is one of the most strongly basic dipolar aprotic solvents, employed extensively in respect of its solvent properties. Normant has provided an exhaustive review on this compound.

3.3.D.1 Pure Solvent Systems

Figure 3.32 depicts a set of dilute solution spectra for HMPA in representative solvents. In the 1200 cm$^{-1}$ regions, the spectra are complicated by (C-N) vibrations (band X) and a (P-O) stretch vibration (band a), both being sensitive to solvent effects (seemingly indistinguishable in the aprotic media). It is particularly noted that the spectra are further made ambiguous by other features (unassigned). It is unlikely that these are due to traces of water since careful drying did not remove the bands. This obviously presents a serious limitation in attempts to quantify infrared measurements so that some of these deductions may possibly be called into question.

The $(\text{P-O}) \nu_{\text{max}}$ are plotted against the $^{31}\text{P}$ chemical shifts in Figure 3.33. For solutions of methanol, the two bands detected in the infrared
FIGURE 3.30
Correlation between $^{31}\text{P}$ resonance shifts and $v(\text{P-O})$ for TMPS in dilute solution in a range of pure solvents.
[Key as for Figure 3.5]
(Line a connects data for high ν conformer and line b for low ν conformer.)

FIGURE 3.31
Correlation between ν(P-O) for TMPS and solvent acceptor number, after adjusting to give the same solvation numbers as Et₃PO.
[Key as for Figure 3.5]
Infrared spectra for dilute solutions (1% v/v) of HMPA in a water, b methanol and c acetonitrile in the P-O stretch regions, showing features (a) assigned to a solvate. [Band X is discussed in the text.]
FIGURE 3.33
Correlation between $^{31}$P resonance shifts and $\nu$(P-O) for HMPA in dilute solution in a range of pure solvents.
[Key as for Figure 3.5]
spectra are included in the correlation (Figure 3.33) together with points (a) representing the weighted mean values. Trends for the (P-O) $\nu_{\text{max}}$ as a function of acceptor numbers is displayed in Figure 3.34. For the alcohols, assignments of the high frequency band to the mono hydrogen-bonded and the low frequency band to the di hydrogen-bonded species are favoured, a tri-hydrate being proposed in aqueous solutions. This represents a significant result since identical solvation at the phosphoryl oxygen site is indicated for both HMPA and Et$_3$PO bases. Similar deductions could be arrived at for the $^3$P resonance (Figure 3.35) based on two correlating lines [one for the aprotic solvents $a$ and the other for the protic solvents $b$]. However, if these arguments are based on a single correlating line $a$, then it is necessary to postulate a higher solvation number than Et$_3$PO in the protic solvents. Such solvation is possible if N-interaction (the P-N function is known to display high basic character) is also invoked. The site of protonation, viz. O- vs N- is a point of long-standing controversy.

3.3.D.2 Methanol + Aprotic Solvent Systems

The $^3$P chemical shifts are shown as a function of the mole fraction (mf) of added aprotic solvent in Figure 3.36. In contrast with the behaviour displayed by Et$_3$PO or DMMP, the shifts induced by MeCN, THF and DMSO are identical in the very rich MeOH regions. This could possibly be taken as evidence for N-interaction, so that the initial effect of added cosolvent is primarily concerned with removing solvent molecules bonded at the N- site. However, beyond ca. 0.2 base mf, the curves separate in the order expected in terms of base strengths.

The infrared spectral trends in Figures 3.37, 3.38 and 3.39 show the presence of three bands for the systems. These are assigned to the di[2]- and mono[1]- hydrogen-bonded species (around ca. 1146 cm$^{-1}$ and
FIGURE 3.34

Correlation between $\nu(P-O)$ for HMPA and solvent acceptor numbers.

[Key as for Figure 3.5]
Plot of $^{31}$P resonance shift versus solvent acceptor number showing the effect of assuming higher basicities of HMPA. [Key as for Figure 3.5]

Line a connects data for aprotic solvents and b for protic solvents.
FIGURE 3.36

$^{31}\text{P}$ resonance shifts for HMPA in methanol + base systems as a function of the mole fraction of base.
FIGURE 3.37
Infrared spectra for dilute solutions of HMPA in the ν(P-O) regions in MeOH + MeCN systems.
**FIGURE 3.38**

Infrared spectra for dilute solutions of HMPA in the ν(P-O) regions in MeOH + THF systems.
**FIGURE 3.39**
Infrared spectra for dilute solutions of HMPA in the $\nu$(P-O) regions in MeOH + DMSO systems.
ca. 1173 cm$^{-1}$ respectively), the 'free'[0] state (around ca. 1200 cm$^{-1}$) being complicated by the presence of another band as discussed before. On this assignment, it is sufficient to postulate that methanolic solutions of HMPA are comprised of a mixture of di- and mono- hydrogen bonded structures. With added aprotic base, the trends can be understood by the loss of the di-solvate [2], with concomitant growth of the mono-solvate [1], the changes being exclusively dominated by the 'non-bonded' state [0] towards the base end. As before, the primary rôle of (LP)$_{\text{free}}$ units in desolvation is proposed.

3.3.D.3 Water + Other Solvent Systems

As for methanolic systems, one again observes (Figure 3.40) the apparently curious result that MeCN, THF and DMSO have the same initial effect on the dehydration of water molecules bonded to HMPA. Beyond ca. 0.3 water mf however, the shifts seem dictated by base strength.

Presence of four distinct species are clearly indicated for solutions of HMPA in H$_2$O + THF binary systems (Figure 3.41). These are assigned respectively to the tri[3]- (at ca. 1119 cm$^{-1}$), di[2]- (at ca. 1145 cm$^{-1}$), mono[1]- (at ca. 1165 cm$^{-1}$) and the non-bonded[0] species around ca. 1205 cm$^{-1}$. The exceptionally large shift of the tri-hydrate species from the di-hydrate may be noted; this may reflect involvement of nitrogen sites also in solvation studies of HMPA.

Trends for HMPA in H$_2$O/MeOH mixed systems (Figure 3.42) clearly indicate the involvement of three distinct species, the tri-hydrate dominating the pure water spectra, and the di- (+mono-) hydrogen-bonded dominating those for pure MeOH.

One of the main observations has been the apparent rôle of structural symmetry around the phosphorus nucleus in dictating the $^{31}$P resonance sensitivity. This is amply displayed for the compounds in Figure 3.43,
FIGURE 3.40

$^{31}$P resonance shifts for HMPA in water + base systems as a function of the mole fraction of base.
Infrared spectra for dilute solutions of DMEA in the ν(P-O) region in water + THF systems.

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</table>

Figure 3.41
**FIGURE 3.42**
Infrared spectra for dilute solutions of HMPA in the ν(P-O) regions in water + methanol systems.
FIGURE 3.43
Plot showing relative $^{31}$P resonance shifts and $v$(P-O) for the phosphate compounds in dilute solution in several solvents. [Key as for Figure 3.5]
(Reference: 85% $\nu$ $H_3PO_4$)
the major shift being to low fields for the probes (relative to TMP). Noteworthy is the fact that the greater NMR sensitivity correlates with the observed large low field shifts.

Comparison of the relative $^{31}$P resonance sensitivity suggests that TMP (and TBP) possesses about ca. 10% sensitivity of Et$_3$PO, those for the others lying midway, the sensitivity increasing in the order:

$$\text{TMP} \approx \text{TBP} < \text{HMPA} < \text{DMMP} \approx \text{TMPS} < \text{Et}_3\text{PO}$$

The behaviour of the (P-O) stretch frequency (Figure 3.44) in contrast, are markedly different, the sensitivity increasing in the order:

$$\text{TMP} \approx \text{TMPS} < \text{DMMP} \approx \text{Et}_3\text{PO} < \text{HMPA}$$

These trends are clearly independent of base strengths (Figure 3.45). It is most interesting to note, however, that $\Delta\nu_{\text{MeOH}}$ (representing the shift of monomeric MeOH in CCL$_4$) correlates reasonably well with $\Delta\nu_{(P-O)}$ (depicting the shift induced in the (P-O) frequency by MeOH relative to that induced in CCL$_4$). $\Delta\nu_{\text{MeOH}}$ may qualitatively be accepted as a measure of base strengths.

It may now be possible to understand at least partly, the apparent lack of $^{31}$P resonance sensitivity for TMP, which progressively increases for the other phosphates. These shifts may be dominated by the paramagnetic term, which is dictated by the availability of low-lying excited states (Appendix A).

Figure 3.46 shows, indeed, that for the limited range of compounds such as TMP, DMMP and Et$_3$PO, as the $n-\pi^*$ absorption moves to longer wave-length (smaller $\Delta E$), the phosphorus nucleus is deshielded and resonates at lower fields, that for TMP (which is practically transparent in the UV) is strongly shielded and resonates at relatively much higher fields. HMPA and TMPS (which may be complicated by nitrogen and sulphur respectively) are rather different and, therefore, not commented upon.
FIGURE 3.44(i)
Plot of (P-O) stretch frequency for Et₃PO versus (P-O) stretch frequency for A TMP and B DMMP in several solvents. [Key as for Figure 3.5]
FIGURE 3.44(ii)
Plot of (P-O) stretch frequency for Et$_3$PO versus (P-O) stretch frequency for A TMPS and B HMPA in several solvents. [Key as for Figure 3.5]
FIGURE 3.45
Plot showing the shifts induced in the (P-O) frequency for several bases by MeOH, relative to that induced in CCl₄, (Δνₚ₋₀) versus the shift for monomeric MeOH in CCl₄, solutions (Δνₘₑₒ₉).
FIGURE 3.146
UV spectra for solutions of TMP (0.25% Vs), DMP (0.25% Vs), HMPS (0.25% Vs), and PPO (arbitrary concentration) in water.
3.4 CONCLUSIONS

Spectra of phosphate solutions studied, are generally complicated by
the presence of rotational conformers which indicate strong temperature
preference. These have presented a particularly complex problem in the
interpretation of spectra. It has, however, been possible to reproduce
NMR shifts for mixed solvent systems using infrared/NMR correlations.
Reasonable solvation numbers have been established for the probes using
mixed solvent techniques. These seem to be dictated by base strength.
Vibrational spectroscopy has indicated the solvation of HMPA at the
phosphoryl function to be analogous with that for Et\textsubscript{3}PO. However,
evidence is presented to suggest possible participation by N- sites
also.

One of the most significant limitations has been highlighted in the
use of \textsuperscript{31}P NMR in solvation studies involving TMP and other similar
compounds. The \textsuperscript{31}P resonance sensitivity follows the n-\pi* absorption
so that the shifts may be governed by the paramagnetic (Ramsey) term.

Accepter Number is a solvent scale that is applicable to solvated
states that are similar to those for Et\textsubscript{3}PO. It is stressed that this
represents a rather serious limitation to its use generally.
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REFERENCES TO CHAPTER 3 (Continued)

23. Many thanks are due to Dr. P. M. Cullis at Leicester University for providing this compound.
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CHAPTER 4

Solvation of Phosphate Mono-anions
4.1 INTRODUCTION

Nucleic acids and their derivatives are natural multi-site ligands; hence, the interaction of these molecules with both natural and foreign species has stimulated great interest using a variety of techniques.¹ The exact nature and site of metal binding in complexes of nucleotides is not yet firmly established. A decision regarding the nature of the binding in such compounds requires further work. Probably, the single most important finding has been that the phosphate group interaction dominates, and that the bases play a secondary, or sometimes insignificant rôle. Experimental information about the hydration of the phosphate group comes mostly from studies of phospholipids. Although the literature is relatively abundant,²⁻⁸ it does not precisely stipulate the solvation structures nor the number of water molecules involved during hydration. For sake of simplicity, this work concentrates on the phosphate group and explores possibilities in the use of dimethylphosphate mono-anion (DMP⁻) and other related anions, as model systems to represent the phosphate structure in biological systems. The basic character of phosphate ions is relatively higher in comparison with others, i.e.

\[ H_2PO_4^- \rightarrow HSO_4^- \rightarrow ClO_4^- \]

DMP⁻ possesses a near tetrahedral geometry,⁹⁻¹² the anionic oxygens being the most favourable site for hydration and cation interactions,¹³,¹⁴ the ester oxygens being virtually uninvolved.¹⁴,¹⁵

\[
\begin{array}{c}
\text{O}^5^- \\
\text{O} \\
\text{O} \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

Theoretical investigations¹⁴ of the solvation of DMP⁻ reveals that up to
six water molecules could be accommodated around the anionic oxygens (the most stable hexa-hydrate being a symmetric disposition of three \( H_2O \) molecules around each oxygen). This agrees with similar deductions from infrared studies involving humidity measurements\(^{16}\) of the phosphate group of nucleic acids.

Metal ion interactions with the phosphate mono-anion have received considerable attention. Theoreticians\(^{17-19}\) predict water bonding to be so strong that the most favourable structure in aqueous solutions involves phosphate-water-cation (through water interaction) species. This view is also borne out experimentally in crystal structures of nucleotides.\(^{20}\) Recently, \(^{31}\)P resonance\(^{21}\) has been used to follow cation interactions at the phosphoryl oxygens. It may be recalled (Chapter 3) that information available from magnetic resonance techniques although precise, is quite limited because of rapid time-averaging.

4.2 EXPERIMENTAL

Trimethylphosphate \([(\text{MeO})_3\text{PO}]\) and dimethoxymethyl phosphonate \([(\text{MeO})_2(\text{Me})\text{PO}]\) were commercially available and purified by vacuum distillation over calcium hydride. Tetrabutylammonium chloride which contained impurities was purified by solvent extraction in an acetone/ether mixture. Both dimethylphosphite \([(\text{MeO})_2(\text{H})\text{PO}]\) and diphenylphosphinic acid \([(\text{Ph})_2(\text{OH})\text{PO}]\) were obtained commercially and used directly.

Dimethylphosphate mono-anion (DMP\(^-\)) \([(\text{MeO})_2\text{PO}_2^-]\) was prepared quantitatively from trimethylphosphate by alcoholysis with sodium hydroxide in methanol. The reaction mixture was refluxed for 3 hours and left for 48 hours for completion. The sodium salt was finally recovered by evaporation of MeOH on a rotor vapour and subsequently crystallised.
Methoxymethylphosphate mono-anion (MMP⁻) [(MeO)(Me)PO₂⁻] was prepared from dimethoxymethyl phosphonate as previously described.

Diphenylphosphate mono-anion (Ph₂PO₂⁻) was prepared by the reaction of diphenylphosphinic acid with freshly prepared sodium methoxide.

Dimethylthiophosphate mono-anion (DMSP⁻) [(MeO)₂P(O)S⁻] was obtained by the reaction of dimethylphosphite, sulphur and sodium methoxide. The salt was purified by crystallisation from methanolic solutions.

Tetrabutylammonium salts were prepared by repetitive displacement of the sodium salts by tetrabutylammonium chloride in methanol. All the other salts used in the work were commercially obtained and dried.

Solutions were prepared by volume (containing fixed weight of probe) using Eppendorf pipettes. The solution of the probe was kept at a minimum except in the aprotic solvents where this was increased for spectroscopic detection.

Infrared spectra were recorded on a Perkin-Elmer model 580 spectrometer using demountable cells with 25 μm teflon spacers between CaF₂ plates. UV spectra were run on a Hitachi model 340 spectrometer using 1 cm silica cells. ³¹P measurements were performed on a Jeol FX60 Fourier Transform spectrometer with phosphoric acid (85% v/v in D₂O) as an external reference with a D₂O lock signal.

4.3 RESULTS AND DISCUSSION

4.3.1 Pure Solvent Systems

Vibrational spectra of the mono-anions - dimethylphosphate²³,²⁴ (DMP⁻), methoxymethylphosphate²³,²⁴ (MMP⁻) and dimethylthiophosphate²⁴ (DMSP⁻) have been well studied. Their respective infrared absorption spectra in dilute solutions of water are displayed (Figure 4.1). For DMP⁻ and MMP⁻, since the two P-O stretching modes are coupled, two absorption bands are
FIGURE 4.1
Infrared spectra for solutions of a NaDMP, b NaMWP and c NaWSP in water in the (P-O) stretch regions.
detected for the P-O vibration which are respectively due to the asymmetric ($v_3$) and symmetric ($v_1$) stretch vibrations. DMSP$^-$ is a typical decoupled system where the stretch modes behave almost as independent group vibrations. The comparison with the latter suggests that, on decoupling, the $v_3$ frequency of DMF$^-$ is shifted towards the mean position for the coupled bands. A common feature in the spectra is the presence of band 'X' that has been identified as a methyl rocking vibration. Otherwise, there seems to be a major contribution from only one species in water (the exception being the POS$^-$ system where the aquo-complex is thought to be a mixture of solvates).

The solvent-induced shifts in the $v_3$ frequency for DMP$^-$, MMP$^-$ and DMSP$^-$ are depicted in Figure 4.2, the $^{31}$P resonance shift also being monitored. Although the figures shown pertain only to the sodium salts, the results for t-butyl ammonium salts were found to be identical. It was most unfortunate, however, that the $v_1$ absorption for the coupled systems (and the P-S absorption for DMSP$^-$) were mostly masked by solvent bands and, therefore, not extensively monitored. It is observed that hydrogen bonding induces a marked low frequency infrared shift relative to DMSO. Infrared results suggest that the overall effects of water and methanol on the ions are fairly comparable. This unusual feature of the ions when compared to some neutral probe systems probably means that the solvation numbers are the same in these solvents. Despite the limitations conferred by solubility, it is most interesting to note the gain in $^{31}$P resonance sensitivity on going from DMP$^-$ to MMP$^-$.

Similar observations were made in studies involving $^{31}$P resonance shifts of a range of neutral phosphate probe systems (Chapter 3). The overall sensitivity of NMR is clearly much smaller than infrared, so that the use of infrared spectroscopy in further work relating to these ions is
FIGURE 4.2
Correlations between (P-O) stretch and $^{31}$P shifts for a DMP$^-$, b MMP$^-$ and c DMSP$^-$ in various solvents (● representing the weighted-mean value for the infrared result).
strongly recommended.

The lack of \(^{31}\)P resonance sensitivity in solvents for DMP\(^-\) may be
governed by the absence of low-lying excited states (Appendix A). This
is qualitatively demonstrated in the UV absorption spectra for the
limited number of compounds (Figure 4.3). There is a clear shift to
low frequencies at the onset of absorption in the order

\[
\text{DMP}^- < \text{MMP}^- < \text{DMSP}^-.
\]

However, although MMP\(^-\) shows a clear increase in \(^{31}\)P sensitivity, this
is apparently reduced for the sulphur derivative.

4.3.2 Water + DMSO Mixed Systems

A set of infrared spectra for dilute solutions of DMP\(^-\) in H\(_2\)O/DMSO
binary mixed systems are presented in Figure 4.4. The narrow band
profile described in the pure DMSO spectrum is characteristic of
aprotic solvents and suggests the presence of relatively weakly perturbed
anion structures in such solutions. This is in marked contrast to the
spectrum in pure water which is broad, indicative of the presence of a
range of different hydrates.

Initial additions of water to DMSO solutions distinctly generates an
isosbestic point for the \(v_3\) band at \(\text{ca.}\ 1250 \text{ cm}^{-1}\), with a band at \(\text{ca.}\ 1248 \text{ cm}^{-1}\) (1) assigned to the monohydrate (I).

\[
\text{P} \quad \text{O} \\
\text{O} \quad \text{HOH}
\]

Further increase in water concentration produces hydrated species with
band maxima at \(\text{ca.}\ 1239\ (2), 1230\ (3), 1222\ (4), 1213\ (5)\) and, possibly,
1203 (6) cm\(^{-1}\) respectively. Most noteworthy is the shift accompanying
the bonding of the first water molecule (\(\Delta l = 6 \text{ cm}^{-1}\)) which is clearly
FIGURE 4.3
UV spectra for solutions of phosphate mono-anions in water.
FIGURE 4.4
Infrared spectra for solutions of Ba₄N⁺ DMP⁻ (0.00533 g/ml) in the (P-O) stretch regions in water + DMSO systems.
smaller than that for the bonding of the second water molecule ($\Delta 2 = 9$ cm$^{-1}$). This differs markedly from normal behaviour where the perturbation accompanying the formation of the first hydrogen bond is greater than the second. It is suggested that these observations reflect the need to consider solvent effects on the degree of coupling between the (P-O) vibrational modes. Importance of coupling has been stressed in the case of water dissolved in an inert medium (such as CCl$_4$) and monitoring the changes in the hydroxyl frequency shift induced by added base (B). These results for water are summarised [Figure 4.5(a)] for comparative purposes.

The phosphate ion in pure DMSO environment can virtually be regarded unperturbed, and thereby characterised by strong coupling between the (P-O) modes. When this is mono-hydrated (I) by interaction with water, the modes are somewhat decoupled, and the $\nu_3$ frequency is displaced slightly ($\Delta 1$) towards $\nu_{\text{free}}$ ($\nu_f$). Band (I) around ca. 1248 cm$^{-1}$ can be attributed to the stretching of the 'free' (P-O) bond. Full coupling, however, is restored (since the symmetry is regained) when the di-hydrate structure (II) is formed. This constitutes a major perturbation for the $\nu_{\text{free}}$ band, such that it is accompanied by a large shift ($\Delta 2$). These initial changes are schematically depicted for the $\nu_3$ frequency in Figure 4.5(b); trends in the $\nu_1$ band unfortunately being masked by solvent absorptions. It is concluded that the 1:1 species (I) is associated through a hydrogen bond involving only one of the P-O bonds of the phosphate ion, the other bond remaining virtually 'free'; furthermore, this species gives way at higher water concentration to one involving 1:2 species (II), there being no evidence to suggest that a species such as (III) is a major contributor in solution.

Shifts ($\Delta$'s) accompanying subsequent additions of water are quite

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FIGURE 4.5(a)
Effect of bases (B) on the OH frequencies of H$_2$O
[results from Refs. 21, 28].

FIGURE 4.5(b)
Shifts in the $\nu_3$ frequency accompanying the solvation
of DMP$^-$ as deduced from Figure 4.4.
comparable, making identification of the precise hydrate structure
difficult. It is, however, concluded that DMP\(^-\) ion has a maximum
solvation number of 5 or possibly 6 in water.

Since spectral changes in the \( \nu_3 \) frequency for MMP\(^-\) anion (Figure
4.6) in similar systems are poorly defined, two schemes have been used
to define the changes:

a. assuming a 5-6 solvation number in water (Figure 4.7a)
b. assuming a 4-5 solvation number in water (Figure 4.7b).

Noteworthy are the trends in the induced shifts:

\[ \Delta 1 < \Delta 2, \quad \Delta 3 < \Delta 4, \quad \Delta 5 < \Delta 4 \]

This alternation behaviour can again be linked to the changes in coupling
accompanying solvent interactions. The high solvation numbers (between
5 and 6) suggested for DMP\(^-\) and MMP\(^-\) mono-anions in water is also
consistent with other findings\textsuperscript{14-16} (see also Chapter 3).

Results for DMSP\(^-\) in similar solutions are in marked contrast with
those for the other two anions (Figure 4.8a). In this case, only three
hydrogen bonded solvates are detected, the pure aqueous solution con­
taining a mixture of the di- and tri-hydrates. For this system, it has
not been possible to comment upon the solvation at sulphur from existing
results. However, the solvation at the phosphoryl oxygen site and the
resulting shifts are expected to be almost independent of any solvation
at the P-S bond since DMSP\(^-\) is not easily polarisable, as evidenced from
FIGURE 4.6
Infrared spectra for solutions of Na\textsuperscript{+} MP\textsuperscript{-}
(0.00264 g/mL) in the (p-O) stretch regions
in water + DMSO systems.
FIGURE 4.7(a)
Shifts in the ν₃ frequency accompanying the solvation of MMP⁻ as deduced from Figure 4.6, the maximum solvated state being the hexa-hydrate.
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FIGURE 4.7(b)
Shifts in the ν₃ frequency accompanying the solvation of MMP⁻ as deduced from Figure 4.6, the maximum solvated state being the penta-hydrate.
FIGURE 4.8(a)
Infrared spectra for solutions of Na⁺DMSP⁻ (0.00654 g/ml) in the (P-O) stretch regions in water + DMSO systems.
the results of optical spectra in Figure 4.3. The shifts induced for the 'symmetrically solvated' MMP⁻ ion agree reasonably with trends for the (P-O) stretch frequency of DMSP⁻ in water/DMSO systems (Figure 4.8b). Since for DMSP⁻, there are fewer solvates involving the PO⁻ unit and the shifts are large, band assignments are relatively clear cut. The result that this oxygen binds up to three water molecules strongly supports similar conclusions for the PO₂⁻ ions.

4.3.3 Methanol + DMSO Mixed Systems

Figure 4.9a displays the trends for MMP⁻ ion in MeOH/DMSO solutions. In contrast to the trends in the DMSO-rich regions, the changes towards pure alcohol regions are ill-defined. A probable factor responsible for this ambiguity may be the co-operativity effect of methanol. Depending upon whether the maximum solvation number in pure MeOH is 5 or 4, two schemes have been proposed. These are presented in Figures 4.9b and 4.9c respectively. A noteworthy point is the perturbation accompanying 'asymmetric bonding' which is clearly smaller than that for the 'symmetric bonding'. The trends in the latter correlate reasonably with those for the (P-O) stretch frequency of DMSP⁻ ion (Figure 4.10a and b respectively) in similar systems.

4.3.4 Water + Methanol Mixed Systems

Figure 4.11 depicts trends in the ν₃ frequency for DMP⁻ in water + methanol systems. Most noteworthy is the fact that the band is narrower in methanol (compared to water), suggestive of a more precise solvation. The changes which are better defined for MMP⁻ (Figure 4.12) show clear signs of a decrease in the average solvation number from water to MeOH. These trends in the water-rich regions compare well with those accompanying initial additions of DMSO to aqueous solutions (see Figures
FIGURE 4.8(b)
Comparison of the shifts of various solvated states for MMP⁻ and DMSP⁻ mono-anions, as deduced from Figures 4.6 and 4.8(a).
FIGURE 4.9(a)
Infrared spectra for solutions of Na\textsuperscript{+} MP (0.00264 g/ml) in the (P-O) stretch regions in methanol + DMSO systems.
FIGURE 4.9(b)
Shifts in the $v_3$ frequency accompanying the solvation of MMP$^-$ as deduced from Figure 4.9(a), the maximum solvation number being five.
FIGURE 4.9(c)

Shifts in the $\nu_3$ frequency accompanying the solvation of MMP$^-$ as deduced from Figure 4.9(a), the maximum solvation number being four.
FIGURE 4.10(a)
Infrared spectra for solutions of Na\(^+\) DMSP\(^-\) (0.0113 g/ml) in the (P-O) stretch regions in methanol + DMSO systems.
Comparison of the shifts of various solvated states for MMP$^-$ and DMSP$^-$ mono-anions, as deduced from Figures 4.9(a) and 4.10(a).
<table>
<thead>
<tr>
<th>Soln.</th>
<th>m.f. MeOH</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>2</td>
<td>0.399</td>
</tr>
<tr>
<td>3</td>
<td>0.611</td>
</tr>
<tr>
<td>4</td>
<td>0.818</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
</tr>
</tbody>
</table>

**FIGURE 4.11**
Infrared spectra for solutions of Bu₄N⁺ DMP⁻ (0.00986 g/ml) in the (P-O) stretch regions in water + methanol systems.
FIGURE 4.12
Infrared spectra for solutions of Na"MMP" (0.00876 g/ml) in the (P-O) stretch regions in water + methanol systems.
4.4 and 4.6 respectively). It is therefore suggested that the sixth water molecule (forming a part of the 5-6 mixed solvation) in pure water is weakly bonded and is rapidly lost to produce the more precise penta-hydrate (being characterised by a relatively narrow band).

4.3.5 Salt Effects

The phosphate mono-anions were found to exhibit a rather strong dependence on the presence of cations in solution. Although at any concentration there exists a range of cation-anion environments, preferred types of ion interactions have been postulated. In principle, two types of 'ion-pairs' have been distinguished:

a) the 'solvent-separated ion-pairs' where the ions are separated by one or several layers of solvent molecules.

b) the 'contact ion-pair' where the ion is in direct contact with each other.

a Mg\(^{2+}\) Effect

Figure 4.13 depicts the influence of magnesium perchlorate on the \(v_3\) phosphoryl stretch frequency for DMP\(^-\). The role of Mg(ClO\(_4\))\(_2\) in methanol is at least two-fold:

(i) It may simply remove solvent molecules because of the high solvation numbers of magnesium\(^{29}\) and perchlorate\(^{30}\) ions. This should result in a high \(v\) shift for the band in methanol.

(ii) Ion-pair formation between the phosphate and Mg\(^{2+}\) is expected to occur. This can take at least three forms - solvent-shared ion-pairs (IV), monodentate contact (V) or bidentate contact (VI) ion-pairs.

Observations of a low \(v\) shift for structures such as (IV) is expected if there is no loss of solvation, since hydrogen bonds such as 'a' are
**FIGURE 4.13**

Effect of Mg(ClO$_4$)$_2$ on the infrared spectra of Na$^+$DMP$^-$ in methanol (0.0123 g/ml) in the $\nu_3$ (P-O) stretch regions.

<table>
<thead>
<tr>
<th>Soln.</th>
<th>m.f. Mg(ClO$_4$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>2</td>
<td>0.0017</td>
</tr>
<tr>
<td>3</td>
<td>0.0029</td>
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<tr>
<td>4</td>
<td>0.0037</td>
</tr>
<tr>
<td>5</td>
<td>0.0086</td>
</tr>
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</table>
known to be strengthened by the secondary effect of Mg$^{2+}$. However, no such features are actually observed. It must therefore be assumed that there is some compensative loss of hydrogen bonding at one or both of the oxygens. Hence, there may have been no net shift, so that the normal band (S) at ca. 1209 cm$^{-1}$ contains a contribution from species (IV), with band (1) at ca. 1241 cm$^{-1}$ assigned specifically to species (IV). An alternative assignment would identify band (1) at ca. 1241 cm$^{-1}$ to a monodentate (V) and (2) at ca. 1287 cm$^{-1}$ to the bidentate (VI) contact ion-pairs.

The latter assignment is strongly supported by the Mg$^{2+}$ perturbation in a DMSO environment ($\Delta = 78$ cm$^{-1}$, $\Delta$ referring to the shift measured from the MeOH band) (Figure 4.14) which is similar to that in a methanol environment, i.e. the effect of Mg$^{2+}$ on $\beta$ seems identical in DMSO (VII) and MeOH (VIII) environments.

However, since $\beta$ is dependent upon the nature of the cation and the solvent, this is not a necessary condition. In fact, for the present case, it is a matter of coincidence that the effects on $\beta$ are similar. Thus, in methanolic solutions, with (2) assigned to a bidentate ion-pair
FIGURE 4.14
Effect of $\text{Mg(ClO}_4\text{)}_2$ on the infrared spectra of $\text{Bu}_4\text{N}^+\text{DMP}^- \text{in DMSO (0.0061 g/mL) in the}$
$v_3 (\text{P-O}) \text{stretch regions.}$
If 'α' is strengthened, 'β' is weakened (and vice versa)

(VII) (VIII)

and (1) therefore probably due to a monodentate contact ion-pair, then (S) could be assessed as due in part to solvent-shared ion-pairs. The presence of the latter species is inferred since such structures are expected in methanolic solutions. Similar conclusions could be construed for the MMP⁻ mono-anion (Figure 4.15). In support of this assignment, it is further observed that the bands assigned to monodentate (1) and bidentate (2) contact ion-pairs are independent of the Mg²⁺ ion concentration. Analogous behaviour was also displayed by Ph₂PO₂⁻ mono-anions.

If these assignments are correct, it is noted that a bidentate contact ion-pair (VI) induces a higher frequency shift than a monodentate contact ion-pair (V). It is proposed that this observation may possibly be related to a change in the bond angle θ accompanying bidentate interaction (i.e. it is a structural change).

The behaviour of DMSP⁻ mono-anion with Mg²⁺ (Figure 4.16) (in contrast to the previous cases) is interesting since the changes involve only two bands. The 1142 cm⁻¹ band is assigned to the normal anions and possibly to solvent-shared ion-pairs and that at 1182 cm⁻¹ to monodentate contact ion-pairs. There is no evidence to suggest a bidentate ion-pair. However, it is noteworthy that the shift induced for the monodentate ion-pair for the PO₂⁻ systems (Δ = 32 cm⁻¹) differs from that for the
**Figure 4.15**

Effect of Mg(ClO$_4$)$_2$ on the infrared spectra of Na$_2$MgF$_4$ in methanol (0.009 g/ml) in the $\nu_3$ (P-O) stretch regions.

<table>
<thead>
<tr>
<th>Soln.</th>
<th>m.f. Mg(ClO$_4$)$_2$</th>
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</thead>
<tbody>
<tr>
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<td>0.00168</td>
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<td>5</td>
<td>0.00218</td>
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</table>
FIGURE 4.16
Effect of Mg(ClO$_4$)$_2$ on the infrared spectra of Na$^+$ DMSP$^-$ in methanol (0.0213 g/ml) in the (P-O) stretch regions.
POS$^-$ systems ($\Delta = 40 \text{ cm}^{-1}$). This is possibly because for the PO$_2^-$ systems, the P-O vibration is a coupled vibration and is therefore sensitive to changes induced at the other P-O bond. Such a question, however, is of little relevance for the POS$^-$ systems where the (P-O) vibration is virtually independent of the (P-S) vibration.

It is most important to draw attention to the contradiction that hydrogen bonding induces a marked low frequency shift in the $\nu_3$ vibration and metal ion bonding to a high $\nu$ shift. That this is also true for the POS$^-$ systems suggests that these observations are not coupling dependent.

It is stressed that this behaviour is unusual when compared to other known systems such as ketones, esters, amides, nitriles, phosphine oxides and anions such as RCOO$^-$ and CN$^-$ where the directions of shifts for hydrogen bonding and metal ion bonding are the same.

b Ca$^{2+}$ Effect

Calcium ion effects on the PO$_2^-$ systems (Figures 4.17 and 4.18 respectively) in MeOH are comparable. One possible tentative assignment could be the bidentate structure assigned to the feature at high frequency (2), with (1) assigned to a monodentate contact ion-pair species, so that the solvent-shared ion-pair species is not discretely visible. For DMSP$^-$ ion (Figure 4.19), the new feature at ca. 1168 cm$^{-1}$ may be assigned to a monodentate ion pair. Contrary to effects displayed by Mg$^{2+}$, the perturbation induced for PO$_2^-$ systems by Ca$^{2+}$ in DMSO (Figure 4.20, $\Delta = 61 \text{ cm}^{-1}$) differs markedly from that in a MeOH environment ($\Delta = 50 \text{ cm}^{-1}$), a behaviour which probably indicates differing cation-solvating propensities of DMSO and MeOH. From existing results for PO$_2^-$ and POS$^-$ systems, it can further be seen that Mg$^{2+}$ exerts a relatively stronger perturbation than Ca$^{2+}$ cation. This finding is also
FIGURE 4.17
Effect of Ca(ClO$_4$)$_2$ on the infrared spectra of Na$^+$ DMP$^-$ in methanol (0.015 g/ml) in the $\nu_3$ (P-O) stretch regions.
FIGURE 4.18
Effect of Ca(ClO₄)₂ on the infrared spectra of Na⁺ MMP⁻ in methanol (0.00955 g/ml) in the ν₃ (P-O) stretch regions.
FIGURE 4.19
Effect of Ca(ClO₄)₂ on the infrared spectra of Na⁺ DMSP⁻ in methanol (0.0219 g/ml) in the (P-O) stretch regions.
FIGURE 4.20
Effect of Ca(ClO₄)₂ on the infrared spectra of Bu₄N⁺ DMP⁻ in DMSO (0.0051 g/ml) in the ν₃ (P-O) stretch regions.

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<td>3</td>
<td>0.000240</td>
</tr>
<tr>
<td>4</td>
<td>0.000860</td>
</tr>
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</table>
FIGURE 4.21
Effect of Zn(ClO$_4$)$_2$ on the infrared spectra of Na$^+$ DMP$^-$ in methanol (0.0181 g/ml) in the $\nu_3$ (P-O) stretch regions.
FIGURE 4.22
Effect of LiCl on the infrared spectra of Na$^+$ MMMP$^-$(2) in water (0.0098 g/ml) in the $\nu_3$ (P-O) stretch regions.

<table>
<thead>
<tr>
<th>Soln.</th>
<th>m.f. LiCl</th>
</tr>
</thead>
<tbody>
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<tr>
<td>2</td>
<td>0.00019</td>
</tr>
<tr>
<td>3</td>
<td>0.00076</td>
</tr>
<tr>
<td>4</td>
<td>0.00095</td>
</tr>
</tbody>
</table>
FIGURE 4.23
Effect of KCl on the infrared spectra of Na$^+$ MMP$^-$ in water (0.014 g/ml) in the $\nu_3$ (P-O) stretch regions.
FIGURE 4.24
Effect of CaCl\textsubscript{2} on the infrared spectra of Na\textsuperscript{+} MMP\textsuperscript{-} in water (0.0162 g/ml) in the \nu\textsubscript{3} (P-O) stretch regions.
predicted theoretically.\textsuperscript{43}

\textbf{c Zn\textsuperscript{2+} Effect}

Figure 4.21 depicts the response of the $v_3$ (P-O) frequency for DMP$^-$ anion to the presence of Zn$^{2+}$ in methanolic solutions. The assignment of the high frequency band to the bidentate contact ion-pair (based on induced shift), and the low frequency feature to the monodentate ion-pair is favoured. However, the alternative assignment involving a monodentate and solvent-shared ion-pair species is also possible.

In biological systems, only water needs to be considered. Since these studies have shown very little effects of salts on phosphate ions in water (Figures 4.22, 4.23 and 4.24 respectively), it is suggested that solvent-shared ion-pairs are the favourable species formed in aqueous solutions. This observation finds wide support from experimental\textsuperscript{20} and theoretical workers.\textsuperscript{17-19}

Vibrational spectroscopy has thus proved useful in monitoring ion interactions at the phosphate group. These results should pave the way to studies of ion interactions at the phosphate group of deoxyribonucleic acid (DNA).

\textbf{4.4 CONCLUSIONS}

It is observed that hydrogen bonding interactions induce a clear low frequency shift in the (P-O) $v_3$ vibration for PO$_2^-$ systems and (P-O) vibration for POS$^-$ systems. For PO$_2^-$ anions, the coupling between the (P-O) stretch vibrations appears to be solvent sensitive.

Contrary to the shift induced by hydrogen bonding, the shift accompanying metal ion bonding is anomalous, being shifted to higher frequencies. It is emphasized that this behaviour is unusual and differs from that observed for other known systems. Various forms of ion-pairs, namely
'solvent-separated', 'monodentate' and 'bidentate' contact ion-pairs have been invoked to explain the spectral changes induced by metal ions. It is suggested that, in aqueous solutions, 'solvent-separated' ion-pairs are the favourable species.
REFERENCES TO CHAPTER 4

REFERENCES TO CHAPTER 4 (Continued)

22. Many thanks are due to Dr. P. M. Cullis at Leicester University for making available this compound.


34. M. C. R. SYMONS, Unpublished results.


41. See Chapter 6.


CHAPTER 5
Solvation of Esters
5.1 INTRODUCTION

The work on esters is a part of a systematic study of the solvation of a variety of carbonyl probe molecules undertaken in this laboratory. Esters are of fundamental importance in a large number of biochemical processes. The main technique employed is vibrational spectroscopy which had proved extremely useful in the study of the solvation of acetone\(^1\) and amide\(^2\) probes.

Although the behaviour of esters is expected to be similar to that of other carbonyl derivatives, the influence of the alkoxy (or aryloxy) linkage needs consideration. One possible advantage of esters over many other similar compounds as revealed by band assignments in the infrared\(^3-5\) is the possibility of monitoring both the \((\text{C}=\text{O})\, \nu\) and \((\text{C}-\text{O})\, \nu\) vibrations simultaneously. Esters have been a subject of numerous investigations using a variety of techniques. Most have been devoted to the study of:

a) substituent effects on carbonyl frequencies and intensities,\(^6\)

b) solvent effects on carbonyl frequencies,\(^7\) \(^1^3\)C NMR shifts\(^8\) and ultraviolet \((n-\pi^*)\) transitions,\(^9\)

c) carbonyl frequency shifts during metal complex formation,\(^1^0\)

d) basicity and site of interaction\(^5,1^1\) and their conformations both by theoretical and experimental methods.\(^1^2-1^4\)

It is important for the following discussion to be aware of the complexities imposed by esters when analysing the results derived from vibrational spectroscopy.

One potentially complicating factor relates to the possibility of conformer equilibria. Such an equilibrium is expected on theoretical grounds to be:
but which is experimentally difficult to observe. The cis conformer is expected to be more stable. Jones and Owen have provided a comprehensive review of past work. A large energy barrier has been reported in simple esters by ultrasonic studies although this is small in the esters of formic acid. A single molecular conformer for methylacetate (Me.CO.OMe) has been suggested by George et al., from temperature and dipole moment measurements. For dimethylcarbonate (MeO)₂CO, a single conformer is suggested from electron diffraction and dipole moment data. This view is also supported by Collingwood et al., although Katon et al. have indicated the presence of trans conformer in very low concentrations. Thus, the role of conformers is unlikely to be significant to this discussion.

The other is concerned with complications in the vibrational spectra arising from nearby bands. Spectra of both (Me.CO.OMe) and (MeO)₂CO are well assigned in the infrared. In the carbonyl stretch region, these assignments indicate possible weak bands around ca. 1700 cm⁻¹ and ca. 1725 cm⁻¹ respectively. The consequences of these are dealt with in subsequent sections. However, for the two esters, no such complications are reported in the (C-O) v stretch regions.

5.2 EXPERIMENTAL

Methylacetate and dimethylcarbonate were the highest grade commercially available, and were purified by fractional distillation over CaH₂. Non-aqueous solvents were purified by normal techniques. Solutions were
prepared by volume using Eppendorf pipettes. The ester concentration was kept at a minimum except in experiments involving $^{13}$C NMR where this was increased to ca. 10% (V/V).

Infrared spectra were recorded on a double beam Perkin-Elmer model 580 spectrometer using demountable cells with 25 μm pathlength teflon spacers between CaF$_2$ plates. UV spectra were run on a Hitachi model 340 spectrometer using a 1 cm silica cuvette. $^{13}$C NMR spectra in H$_2$O were measured on a Jeol FX60 Fourier Transform spectrometer using a D$_2$O lock signal. Infrared bands were resolved using a Dupont-310 Curve Resolver.

5.3 RESULTS AND DISCUSSION
5.3.1 Pure Solvent Systems

C=O Shifts

The peak maxima for a series of esters in a range of solvents is depicted in Figure 5.1. In all cases, symmetrical bands are observed for the vibration in aprotic solvents. This is contrary to the findings in protic solvents where the spectra are complicated by band multiplicities. Nonetheless, there is a definite low frequency trend from aprotic to protic solvents. Also noteworthy are small yet significant differences amongst the esters studied as regards their regions of carbonyl stretch, there being a trend to high frequencies on going from acetone to the esters. Table 5.1 depicts the effect of added base on the shift of monomeric MeOH ($\Delta \nu$) in an inert medium. $\Delta \nu$ can be used as a measure of base strengths of these solutes towards hydrogen-bond formation. The carbonyl absorption frequency for the various esters are clearly independent of base strength. However, their absorption frequencies could satisfactorily be explained in terms of electronic effects of attached substituents.
FIGURE 5.1
Carbonyl band positions for various esters in dilute solutions (1% v/v) in the C=O stretch regions I Acetone, II Methylacetate, III Methylbenzoate, IV Dimethylcarbonate.

KEY
1 Hexane
2 Triethylamine
3 Carbontetrachloride
4 Tetrahydrofuran
5 Acetonitrile (MeCN)
6 Hexamethyl-phosphoric Triamide
7 t-Butanol
8 Chloroform (d)
9 Nitromethane
10 Dimethylsulphoxide (DMSO)
11 Ethanol
12 Methanol (MeOH)
13 Ethane Diol
14 Water (D₂O)
15 Hexafluoroisopropanol
16 Trifluoroethanol

Wavenumber / cm⁻¹
1750 1730 1710 1690
### TABLE 5.1

Frequency shift $\Delta\nu$ of monomeric MeOH in CCl$_4$ and carbonyl stretch frequency for various esters

<table>
<thead>
<tr>
<th>ESTER</th>
<th>$\Delta\nu$ (cm$^{-1}$)</th>
<th>(C=O)$\nu_{\text{max}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Acetone</td>
<td>120.0</td>
<td>1721.5</td>
</tr>
<tr>
<td>II Methylacetate</td>
<td>82.0</td>
<td>1754.0</td>
</tr>
<tr>
<td>III Methylbenzoate</td>
<td>80.0</td>
<td>1734.0</td>
</tr>
<tr>
<td>IV Dimethylcarbonate</td>
<td>72.5</td>
<td>1753.0</td>
</tr>
</tbody>
</table>

**C-O Shifts**

Figure 5.2 displays the corresponding (C-O) band maxima for the esters. The solvent pattern resembles that for (C=O) $\nu$ but the shift is opposite. The relationship between the two is clearly demonstrated in Figure 5.3 where the solvent shift for (C=O) $\nu$ and (C-O) $\nu$ is plotted for Me.CO.CMe. It is interesting to note that the band multiplicity of (C=O) frequency in protics is also echoed in the (C-O) vibration. The position for DMSO deviates most strongly from the correlating line. The following explanation for the opposing shifts is suggested.

![Chemical Structure](attachment:image.png)

In the case of esters, the carbonyl oxygen is thought to be the predominant site of interaction. During such an interaction, the hydrogen bond $\alpha$ between the carbonyl oxygen and the hydroxyl proton is strengthened.

As a consequence:

a) $\beta$ is weakened - producing (Figure 5.1) a low frequency carbonyl shift from aprotic to protic solvents.

b) $\gamma$ is strengthened - resulting in a high frequency shift (Figure 5.2).
FIGURE 5.2
Carbonyl band positions for various esters in dilute solutions (1% v/v) in the C-OR stretch regions.
[Key as for Figure 5.1]
FIGURE 5.3
Correlation between the C=O stretching mode and the C=O mode for methylacetate in a range of solvents.
[Key as for Figure 5.1]
However, if interaction occurred at the ether oxygen, the reverse would hold. The results so far presented accord best with the carbonyl oxygen as the only likely protonation site in solution. This claim is well supported from most studies\textsuperscript{9-11,23} although ether oxygen interaction is also proposed in matrix isolation studies.\textsuperscript{24}

The band multiplicity encountered (Figure 5.1) is assigned to the presence of more than one solvated species formed as a consequence of donor-acceptor interaction. Since esters are electron donors via the carbonyl oxygen, the shift should bear relation with solvent acceptor numbers (AN).\textsuperscript{25,26}

Figure 5.4 displays the results for Me.CO.OMe and (MeO)\textsubscript{2}CO as a function of the (P-O) stretch frequency of triethylphosphineoxide (Et\textsubscript{3}PO),\textsuperscript{27} a correlation of the latter and Gutmann's acceptor number\textsuperscript{25-26} having previously been established.\textsuperscript{27} One of the many outcomes of the latter work was the success in quantifying the shift corresponding to a particular solvate, thereby predicting the di- and mono-solvates at ca. 1125 cm\textsuperscript{-1} and ca. 1153 cm\textsuperscript{-1} respectively. For the two esters, the best fit to the data requires a mixture of di + mono solvates in D\textsubscript{2}O and fluoroalcohols, a mixture of mono + free solvates in MeOH, EtOH, ethane-diol and in t-butanol. Esters are presumably mono-bound in chloroform solutions.

The relative sensitivity of the carbonyl band maxima for the esters is illustrated (Figure 5.5). Although the solvent sensitivity of acetate and carbonate are comparable, that of acetone is much less pronounced. It emerges that neither the inductive effect of the substituents nor the relative base strength are a major contributing factor to this trend. The similarity with acetone which only has one site for hydrogen bonding, as underlined by the correlation, further suggests that solvation must
FIGURE 5.4
Correlations between $\nu_{C=O}$ for methylacetate and dimethylcarbonate and the $\nu_{P-O}$ for Et$_3$PO after adjusting to give the same solvation numbers for the esters and Et$_3$PO.
[Key as for Figure 5.1]
FIGURE 5.5
Plot of C=O stretch frequency of a acetone, b methylacetate and c dimethylcarbonate in various solvents versus $\nu_{C=O}$ of acetone. [Key as for Figure 5.1]
also be comparable for the probes.

The discussion so far has stressed the importance of electronic effects within the carbonyl group during solvent perturbations. One of the immediate consequences of such effects would be to modify the electron distribution around the carbonyl carbon. Figure 5.6 presents such a relation between the solvent induced carbonyl band maxima and the $^{13}\text{C}$ resonance shifts\(^8\) for a few probes. The single NMR signal obtained for the compounds in MeOH is a result of rapid time averaging of the signals due to various species and therefore indicates a major disadvantage of the technique. For ester solutions in MeOH and D\(_2\)O, the weighted mean of the band maxima is plotted since, NMR results are weighted mean. The plot is similar to that for the organic phosphates (Chapter 3). Both Me\(_2\)CO and Me.CO.OMe have low field resonances in protic solvents which correlates well with the infrared results. The $^{13}\text{C}$ shift for the carbonate on the other hand is almost solvent insensitive and the plot is of no significance. The gradual change in sensitivity from acetone to dimethylcarbonate has been interpreted by Maciel and Natterstad\(^8\) in terms of inductive effects of substituents alone. Although it is not the primary concern to discover reasons for the NMR shifts, it is interesting to note that the $^{13}\text{C}$ sensitivity varies inversely with the energy of the $n\rightarrow \pi^*$ transitions (Figure 5.7) for Me\(_2\)CO ($\nu_{\text{max}} \approx 37879$ cm\(^{-1}\)), Me.CO.OMe ($\nu_{\text{max}} > 45455$ cm\(^{-1}\)) and (MeO)\(_2\)CO ($\nu_{\text{max}} > 50000$ cm\(^{-1}\)). These are 'magnetic' transitions and therefore play an important rôle in the 'paramagnetic' (Ramsay) contribution to the chemical shift.

5.3.2 Methanol + Aprotic Solvents

The variation in (C=O) $\nu$ and (C-O) $\nu$ for mixed solvent systems is discussed. A typical set of spectra for acetate and carbonate in a system MeOH + DMSO is given in Figures 5.8 and 5.9 respectively. Trends
FIGURE 5.6
Correlations between the C=O stretch frequency and $^{13}$C shifts for a acetone, b methylacetate and c dimethylcarbonate.
[Key as for Figure 5.1 - $^{13}$C data from this work and Ref. 8]

(Chemical shift with respect to shift of neat solute.)
FIGURE 5.7
UV spectra for dilute solutions (0.2% v/v) for a acetone, b methylacetate and c dimethylcarbonate in water.
FIGURE 5.8α
Infrared spectra $\nu_C=0$ for dilute solutions of methylacetate in methanol + DMSO systems.
Infrared spectra $\nu_{C=O}$ for dilute solutions of dimethylcarbonate in methanol + DMSO systems.

![Graph showing infrared spectra](image)

<table>
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<th>Soln.</th>
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<td>0.793</td>
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in MeOH + MeCN systems were similar. Adopting the simplest possible approach, the changes can be accommodated in terms of an equilibrium involving two species which denote respectively the 'free' (ii) and the mono hydrogen-bonded (i) species. The frequency difference between the

\[
\begin{align*}
\text{(ii)} & \quad \text{R} \quad \text{C} \quad \text{O} \\
\text{(i)} & \quad \text{R} \quad \text{C} \quad \text{O} \quad ----\text{H-O} \quad \text{Me}
\end{align*}
\]

'free' ester in hexane and the 'free' ester in methanol suggests that the 'free' ester may be subject to some interaction in methanol. The features located at ca. 1705 cm\(^{-1}\) and ca. 1727 cm\(^{-1}\) for Me.CO.OMe and (MeO)\(_2\)CO in MeOH respectively are not derived from solvation and are therefore disregarded in this discussion; their origin however being indicated later.

C=O Regions

In order to obtain estimates of the relative concentrations of the individual solvates, it is necessary to know the absorbancies for each band. These values are normally obtained from the spectra for the probes in the pure solvent systems, but since the spectra for alcoholic (and aqueous) solutions comprise multiple bands, assigned to the different solvates, it was not possible to use this procedure directly for these solvents. It is therefore arbitrarily assumed that the maximum absorbances for the di- and mono-hydrates in water, and the mono-solvate in methanol are equal. Adopting this procedure, spectra for methanolic systems were computer analysed to yield plots such as in Figures 5.10.

The changes for the two esters can be interpreted in terms of the following reaction scheme involving desolvation by added cosolvent, which is clearly dictated (Figures 5.10) by base strength. Although the major
FIGURE 5.10(a)
Trends in the intensities of the deconvoluted $\nu(C=O)$ bands for methylacetate in MeOH + DMSO systems, shown as a percentage of maximum; (i) mono-hydrogen bonded ester, (ii) 'free' ester.
FIGURE 5.10(b)
Trends in the intensities of the deconvoluted $\nu(C=O)$ bands for dimethylcarbonate in MeOH + DMSO systems, shown as a percentage of maximum; (i) mono-hydrogen bonded ester, (ii) 'free' ester.
FIGURE 5.10(c)

Trends in the intensities of the deconvoluted ν(C=O) bands for methylacetate in MeOH + MeCN systems, shown as a percentage of maximum;
(i) mono-hydrogen bonded ester, (ii) 'free' ester.
FIGURE 5.10(d)

Trends in the intensities of the deconvoluted $\nu(C=O)$ bands for dimethylcarbonate in MeOH + MeCN systems, shown as a percentage of maximum; (i) mono-hydrogen bonded ester, (ii) 'free' ester.
change involves the removal of hydrogen bonds to the ester, it is important also to consider the direct interaction of the aprotic base on the ester. Reaction (1) occurs rapidly because of a higher base strength of DMSO compared to the ester, producing the 'free' (non-hydrogen bonded) acetate species at ca. 1747 cm\(^{-1}\) which (with the rapid loss of the mono-solvate) is shifted to ca. 1736 cm\(^{-1}\) in pure DMSO. The latter could be understood in terms of a specific dipolar influence of the aprotic base such as in (IV). A similar trend is also observed for the carbonate.

Analogous conclusions may be drawn for methanolic systems involving MeCN (Figure 5.11). An important implication of the results therefore is that 'free' ester is much more strongly perturbed in an environment of DMSO (and MeCN) than that of MeOH environment.

It is appropriate at this point to comment on the feature at ca. 1705 cm\(^{-1}\) for methylacetate solutions in MeOH. It is proposed that this is not a species which can be assigned to a disolvate for the following reasons:

a) On adding basic solvents, there is no evidence for the growth of the mono-solvate at ca. 1730 cm\(^{-1}\) in the MeOH rich regions which
FIGURE 5.11
Infrared spectra $\nu_{C=O}$ for dilute solutions of methylacetate in MeOH + MeCN systems.
would be expected in the event of a loss of a di-solvated species. Since the conversion of the mono-solvate to 'free' ester occurs concurrently, this is not a necessary requirement. However, it is noted that there is a good isosbestic point during this conversion, so there does not seem to be any growth in total absorbance.

b) The rate of loss of the feature is much slower than that of the mono-solvate.

c) The relative shifts of the position of the feature from the mono-solvate and the mono-solvate from that of the free hexane position are comparable. This is out of line for a di-solvate since the perturbation accompanying the first hydrogen-bond is expected to be greater than that of the second.

This feature in Me.CO.OMe is related to a Me-O stretch vibration. Similarly, the feature at ca. 1727 cm\(^{-1}\) in the case of \((\text{MeO})_2\text{CO}\) is not assigned to a di-solvate. No attempt is made to assign these weak bands, whose contribution was subtracted from the spectra prior to band analysis.

C-O Regions

The weak band around ca. 1290 cm\(^{-1}\) for the acetate in MeOH is fairly solvent sensitive. This has been assigned to a Me-C deformation vibration.\(^5\) However, no such complexity is indicated in the spectra for the carbonate. Although the changes observed in Figures 5.88 and 5.98 are a consequence of conjugation, they clearly affirm the mono + free solvation view in MeOH for the two probes. Also, the specific dipolar influence of DMSO on the ether oxygens is unlikely, as indicated by the rather 'weak' perturbation of DMSO compared to 'free' MeOH in this region.
FIGURE 5.86
Infrared spectra $\nu_C-\nu_R$ for dilute solutions of methylacetate in methanol + DMSO systems.
[Key as for Figure 5.8a]
FIGURE 5.9b
Infrared spectra $\nu_{C-OR}$ for dilute solutions of dimethylcarbonate in methanol + DMSO systems.
[Key as for Figure 5.9a]
Comparison of the MeOH bands for the esters suggests a larger proportion of mono-solvate in the acetate. This is consistent with a higher basic character of this ester over the carbonate.

5.3.3 Water + Aprotic Solvents

C=O Regions

Solutions of esters in water display two bands. Figures 5.12(a) and 5.13(a) depict a typical set of spectra in the (C=O) ν regions for Me.C0.OMe and (MeO)₂CO respectively, in D₂O/MeCN mixed systems. Trends in D₂O + DMSO systems were similar. The spectra were computer analysed using three bands to yield plots such as in Figure 5.14. The trends for the esters can be explained in terms of the solvated species (iii), (ii) and (i) which are respectively the 'free', the mono- and the di-hydrogen bonded species. The mono-solvated species such as (ii) is expected to resemble that for MeOH. This is clearly indicated in the mono-solvate band maxima around ca. 1730 cm⁻¹ and ca. 1745 cm⁻¹ for the acetate and the carbonate respectively.

\[
\begin{align*}
(iii) & \quad (ii) & \quad (i) \\
R & \quad R & \quad R' \\
C & \quad C & \quad C \\
O & \quad O & \quad O \\
R' & \quad R' & \quad R'' \\
\end{align*}
\]

The hydrogen-bonded species (i) is located around ca. 1704 cm⁻¹ and ca. 1744 cm⁻¹ respectively for the esters. It should, however, be pointed out that the band profile in these regions should be interpreted as being complicated by a weak band whose contribution has been arbitrarily subtracted in the analysed plots. The shift of the mono-
Infrared spectra $\nu_{\text{C}=\text{O}}$ for dilute solutions of methylacetate in $\text{D}_2\text{O} + \text{MeCN}$ systems.
FIGURE 5.13a
Infrared spectra $v_C=0$ for dilute solutions of dimethylcarbonate in $D_2O + MeCN$ systems.
FIGURE 5.14(a)
Trends in the intensities of the deconvoluted ν(C=O) bands for methylacetate in D₂O + DMSO systems, shown as a percentage of maximum; (i) di-hydrate, (ii) mono-hydrate, (iii) 'free' ester.
FIGURE 5.14(b)

Trends in the intensities of the deconvoluted \( \nu(C=O) \) bands for dimethylcarbonate in D\(_2\)O + DMSO systems, shown as a percentage of maximum; (i) di-hydrate, (ii) mono-hydrate, (iii) 'free' ester.
FIGURE 5.14(c)
Trends in the intensities of the deconvoluted $\nu$(C=O) bands for methylacetate in $\text{D}_2\text{O} + \text{MeCN}$ systems, shown as a percentage of maximum;
(i) di-hydrate, (ii) mono-hydrate, (iii) 'free' ester.
Trends in the intensities of the deconvoluted $\nu(C=O)$ bands for dimethyl carbonate in $D_2O + MeCN$ systems, shown as a percentage of maximum: (i) di-hydrate, (ii) mono-hydrate, (iii) 'free' ester.
solvate band for the acetate and less so for the carbonate can be explained by the loss of secondary solvation as depicted in (V), (VI) and (VII) respectively.

\[
\begin{align*}
\text{(V)} & \quad \text{R} & \quad \text{C} & \quad \text{O} & \quad \text{H} & \quad \text{O} \\
\text{(VI)} & \quad \text{R} & \quad \text{C} & \quad \text{O} & \quad \text{H} & \quad \text{O} \\
\text{(VII)} & \quad \text{R} & \quad \text{C} & \quad \text{O} & \quad \text{H} & \quad \text{O}
\end{align*}
\]

**C-O Regions**

The overlays in Figures 5.12(β) and 5.13(β) for Me.CO.OMe and (MeO)₂CO respectively again suggests the involvement of three species. The shifts arising from the mono-bound species (ii) around ca. 1265 cm⁻¹ and ca. 1302 cm⁻¹ respectively for the esters notably agree with the MeOH mono hydrogen-bonded states. Also for the two esters, the perturbation caused by the first hydrogen-bond formation is much larger than the second as expected.

Results for esters in pure water are interesting since they show the presence of two distinct bands assigned to the di- and mono-hydrate. In a lot of previous work,² single absorption for dilute solutions of the dipolar aprotic base in water have been found. The results are thus important since it was always accepted that water formed only the hydrate with maximum solvation number. Interconversion between the mono- and non-bonded forms differ markedly from that observed for the corresponding methanol systems [Figures 5.10(c) and 5.14(c)]. This implies that water is a much stronger proton donor than methanol. However, each water
Infrared spectra $v_{C-OR}$ for dilute solutions of methylacetate in $D_2O + MeCN$ systems.

[Key as for Figure 5.12a]
Infrared spectra νC=O for dilute solutions of dimethylcarbonate in D₂O + MeCN systems.
[Key as for Figure 5.13a]
molecule provides two -OH units and can form hydrogen bonds to two bases (B---HOH---B). Thus in the high mole fraction (base) region, the potential ability for water to form hydrogen bonds to the probe molecules is double that of methanol. It was therefore necessary to plot the changes in concentration of the three solvates as a function of the concentration of (OH) groups (Figure 5.14e). Displayed in this way, it can be seen that the differences between methanol and water in the aprotic-rich region are greatly reduced. This should have been expected in the light of previous results concerning the interaction of water and methanol with anions in tetrachloromethane, which showed that the monomer molecules are comparable hydrogen-bond donors. It is believed that water forms a di-solvate and not methanol because of the presence of a large excess of (OH)$_{\text{free}}$ groups in liquid water. Partly because of the three-dimensional structure and partly because the average water molecule forms four hydrogen bonds, there are a large number of defects in liquid water, governed by the equilibrium (2).

\[ (\text{H}_2\text{O})_{\text{bound}} = (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}} \]  

Methanol has less reason to form such defects because the motional stresses and requirements are less. Furthermore, because of the large concentration of lone-pairs of electrons [(LP)$_{\text{free}}$] not involved in the 'linear' hydrogen-bonded structure of methanol, (OH)$_{\text{free}}$ groups that are formed are almost entirely bonded to give weakly-bound units with a reduced reactivity. It is suggested that it is the presence of (OH)$_{\text{free}}$ groups with a high reactivity that contributes to the tendency for water to form two hydrogen-bonds to esters. As a basic aprotic solvent is added to the system, so the concentration of (OH)$_{\text{free}}$ groups falls, together with the tendency to form a dihydrate.
FIGURE 5.14(e)
Trends in the intensities of the deconvoluted $\nu$(C=O) bands for methylacetate in D$_2$O + MeCN systems, shown as a function of the mole-fraction of OH groups; (i) di-hydrate, (ii) mono-hydrate, (iii) 'free' ester.
FIGURE 5.15g
Infrared spectra $\nu_{C=O}$ for dilute solutions of methylacetate in D$_2$O + MeOH systems.
FIGURE 5.158
Infrared spectra $\nu_{C-OR}$ for dilute solutions of methylacetate in $D_2O$ + MeOH systems. [Key as for Figure 5.15a]
FIGURE 5.16
Trends in the intensities of the deconvoluted $\nu(C=O)$ bands for methylacetate in $D_2O + MeOH$ systems, shown as a percentage of maximum; (i) di-hydrogen bonded, (ii) mono-hydrogen bonded, (iii) non-hydrogen bonded ester.
5.3.4 Water + Methanol Systems

Figure 5.15 for methylacetate in this system further reinforces di + mono solvation in water and mono + free solvation in MeOH. Curve analysis (Figure 5.16) shows that there is a steady loss of the di-hydrate (i) and a steady growth of the non-hydrogen bonded species (iii). The mono-hydrogen bonded species (ii) reaching a maximum concentration at ca. 0.5 mole fraction regions (R$_2$CO---HOH and R$_2$CO---HOME are indistinguishable). All three components co-exist in this middle region but the mono-solvate dominates.

5.4 CONCLUSIONS

Probe studies of esters using vibrational spectroscopy has revealed the carbonyl oxygen as the only predominant site of hydrogen bonding in solution. The reverse shift observed for the (C=O) feature can be understood in terms of this solvation only since there is no evidence to propose hydrogen bonding to the ether oxygen, although this cannot be ruled out.

Further, this work has been important in filling the gap left over by previous work,$^2$ thereby making possible the study of carbonyl derivatives as a group. Summarised below are the solvation numbers for the compounds in water and methanol. The results unequivocally suggest base strength as a primary factor governing the solvation of carbonyl compounds.

<table>
<thead>
<tr>
<th></th>
<th>ESTERS</th>
<th>ACETONE$^2$</th>
<th>AMIDES$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>mono + di</td>
<td>di</td>
<td>di</td>
</tr>
<tr>
<td>MeOH</td>
<td>free + mono</td>
<td>free + mono mostly</td>
<td>mono + di</td>
</tr>
</tbody>
</table>

Trends in $^{13}$C shifts follow the energy of n-$\pi^*$ absorption for the compounds.
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CHAPTER 6

Solvation of Carboxylate Anions
6.1 INTRODUCTION

The carboxylate anion, involved in the structures of numerous compounds of biological interest (for instance at the C terminal group of proteins), participates in a number of intermolecular interactions involving water and cations. Simple acetate and benzoate anions which are representatives of the equivalent biological carboxylic function have been selected for this study to probe solvent and cation interactions. It must be emphasized, however, that these anions are by no means substitutes for real biological systems although, under the experimental conditions, the conclusions should have considerable relevance.

That the oxygen is the predominant site of interaction in the case of carboxylate anions is shown theoretically\(^1\) and, for example, from known crystal structures of formic,\(^2\) acetic\(^3\) and benzoic\(^4\) acids. Extensive infrared studies have been made on metal complexes of carboxylic acids. Spectral studies using KBr discs have indicated that the asymmetric (\(v_3\)) carbonyl vibration is the more sensitive to metal interactions. Several authors have attempted to relate this with a physical property of the metal. Theimer and Theimer\(^5\) have claimed that the radius of the metal ion is the main factor governing the frequency, whereas Kagarise\(^6\) found that there was a dependence of frequency on the electronegativity of the metal. However, Ellis and Pyszora\(^7\) have suggested that the (C-O) vibrational frequency is a complicated function of the mass, radius and electronegativity of the metal.

Based on the evidence of X-ray analysis, a carboxylate anion such as acetate is known to co-ordinate to a metal (M) in one of the following ways:
The effect of changing the metal ion on the COO stretching frequencies must be different for each structural type mentioned above. For example, in a series of metal complexes of amino acids having structure I, the (C-O) \( \nu_3 \) is displaced to higher frequencies and the (C-O) \( \nu_1 \) to lower frequencies, with increase in the strength of metal ion. This trend is not seen in a series of compounds having the symmetrical structure (III) where both COO stretching bands are known to be shifted in the same direction. Warrier and Krishnan have proposed a bidentate structure (II) for a range of metal salts of trichloro acetate. For such structures, with increase in the strength of the metal ion, they have suggested that the (C-O) \( \nu_3 \) shifts to lower frequencies and the (C-O) \( \nu_1 \) to higher frequencies from the value for sodium trichloroacetate in KBr disc.

The magnitude of the separation between the frequencies \( \nu_3 \) and \( \nu_1 \) in metal complexes has been related to the strength \(^{10,11}\) of the metal-oxygen bond although possible dependence on the carboxylate bond angle \(^{12}\) is also suggested. Spinner \(^{13}\) has examined the effect of substituents on the frequencies. The carboxylate anion is, however, much less investigated in solution using vibrational spectroscopy, although this phase is of greater biological relevance.

6.2 EXPERIMENTAL

All salts used throughout this study were the highest grades commercially available. Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer using demountable cells with CaF\(_2\) plates and 25 \( \mu \)m
teflon spacers. In work involving salt perturbations in methanolic solutions, the pathlength of the cells was increased to compensate for loss in oscillator strength resulting from working with low salt concentrations. This was necessary to avoid crystallisation.

6.3 RESULTS AND DISCUSSION

6.3.1 Pure Solvent Systems

Infrared spectra of acetate\textsuperscript{14,15} and benzoate\textsuperscript{16-18} anions are characterised by absorptions around ca. 1500 cm\textsuperscript{-1} and ca. 1400 cm\textsuperscript{-1}, which are assigned respectively to the asymmetric (\(v_3\)) and symmetric (\(v_1\)) carbonyl stretch vibrations. A typical spectrum for the acetate ion in D\textsubscript{2}O solutions is presented in Figure 6.1a. Band "X" was found to be insensitive to solvent effects and is believed to be a combination band of C-C stretching (~920 cm\textsuperscript{-1}) and in-plane OCO-rocking (~470 cm\textsuperscript{-1}) modes.\textsuperscript{15} The spectra for the benzoate ion (sodium salt) in D\textsubscript{2}O and DMSO solutions that are depicted in Figure 6.1b indicate additional features around ca. 1600 cm\textsuperscript{-1} (Y) and ca. 1358 cm\textsuperscript{-1} (Z) respectively. The spectra for tetrabutylammonium salts were identical. Green et al.\textsuperscript{16} have assigned "Y" to a benzene ring vibration. The significance of "Z" is discussed in the text.

The effects of the solvents on the shifts for the absorptions are illustrated in Figure 6.2. It can be seen that the sensitivity of the \(v_3\) and \(v_1\) vibrations to solvents are comparable. Most noticeable is the strong solvent isotope effect for MeOH and MeOD which is larger than normally encountered. This means that the results for D\textsubscript{2}O cannot be equated to those expected for H\textsubscript{2}O which, unfortunately, cannot be obtained because of strong solvent absorption. The \(v_3\) frequency is displaced towards lower energy in the strongly hydrogen-bonding solvents.
FIGURE 6.1
Infrared spectra for solutions of a acetate ion in D$_2$O, b benzoate ion in D$_2$O and DMSO (d$^6$) in the (C=O) stretch regions. [Bands X, Y and Z are discussed in the text.]
FIGURE 6.2
Plot depicting $\nu_3$ (C-O), $\nu_1$ (C-O) and $\Delta\nu$ ($\Delta\nu = \nu_3 - \nu_1$) for solutions of tetrabutyl ammonium salts of $a$ acetate and $b$ benzoate ions in various solvents.

KEY

- $a$ Hexafluoro Isopropanol
- $b$ Trifluoroethanol
- $c$ Water (D$_2$O)
- $d$ Ethane Diol
- $e$ Methanol-d (MeOD)
- $f$ Methanol (MeOH)
- $g$ Ethanol-d (EtOD)
- $h$ Ethanol (EtOH)
- $i$ Chloroform
- $j$ Dimethylsulphoxide (DMSO)
- $k$ Acetonitrile (MeCN)
- $l$ Acetone
- $m$ Methyl Acetate
- $n$ Tetrahydrofuran (THF)
- $o$ Carbon Tetrachloride (CCl$_4$)
such as water and fluoro-alcohol. These observations are understandable in terms of hydrogen-bonding at the carbonyl oxygen site(s). The results for acetate ion in CCl₄ should probably be ignored, the problem being to ensure the complete absence of water. However, there could be a weak charge-transfer interaction with CCl₄ which might induce a shift.

On the contrary, the behaviour of ν₁ is clearly the opposite, being displaced to higher frequencies in the protic media. This change is the same as that observed for metal bidentate co-ordination, where both oxygens are equally affected. A cyclic interaction (IV) has been proposed theoretically for the hydration of the formate ion¹,¹⁹ by a

![IV](image)

single water molecule but such an interaction is most unlikely for the ions in bulk water and impossible for the alcohols. The solvent trends in the ν₃ and ν₁ vibrations therefore require some other explanation.

Changes in the bond angle OCO may make some contribution to this behaviour. It could, however, be argued from the analysis of X-ray crystallographic data (Table 6.1) that even actual protonation required

| Carboxylate Bond Angle OCO |  
|---------------------------|---
| CH₃COOH³                | 122.0° |
| CH₃COO⁻²⁰               | 123.4° |
| HCOOH²                  | 123.0° |
| HCOO⁻²¹                 | 124.0° |

**TABLE 6.1**

Tabulation of bond angles for carboxylic acids and related ions
to produce the respective acids hardly alters $\delta CO$, and hence that hydrogen-bonding is unlikely to cause a significant change therein.

For such systems, it is always important to consider the symmetry of the ions and its influence on the effects of coupling between the C-O stretch modes. Sodium acetate is therefore schematically compared with other related compounds (Figure 6.3a). The carboxylate function of sodium acetate (NaAc) is expected to be symmetrical. Although no detailed structural data are presently available on NaAc, the X-ray analysis of sodium formate\textsuperscript{21} definitely indicates that the formate ion is symmetrical. On the other hand, the monomer of acetic acid, isolated in an argon matrix at low temperatures,\textsuperscript{22} is highly asymmetric. It may thus be concluded that asymmetry would tend to displace the (C-O) $\nu_3$ to higher frequencies and (C-O) $\nu_1$ to lower frequencies, relative to the value for the symmetrical structure. Of interest is the fact that the overall effects of actual protonation and methylation on the carbonyl frequencies are quite comparable. Analogous deductions could be made for the benzoate anion (Figure 6.3b).

Figure 6.4 displays the shifts for the $\nu_3$ frequency plotted against the corresponding $\nu_1$ frequency for the acetate ion. It can generally be noted that protic and aprotic solvent data stand well apart: otherwise, there is a reasonable linearity for the sets of solvents used.

It is noteworthy that there are linear correlations between the $\nu_1$ and $\nu_3$ shifts for MeCO$_2^-$ and PhCO$_2^-$, as shown in Figure 6.5. The slopes of these lines are quite close to unity, which suggests comparable solvation for the acetate and benzoate anions.

Figure 6.6 illustrates the frequency shifts plotted as a function of solvent acceptor number.\textsuperscript{23} It is recalled that acceptor numbers are based on the $^{31}$P chemical shift measurement of triethylphosphine oxide...
FIGURE 6.3
Comparison of the (C-O) stretch frequencies of the ions with related compounds.
FIGURE 6.4
Plot of $v_3$ (C-O) stretch frequency versus $v_1$ (C-O) stretch frequency of Bu$_4$N$^+$ MeCO$_2^-$ in several solvents. [Key as for Figure 6.2]
Correlations between $v_3$ (C-O) and $v_1$ (C-O) stretch frequencies for acetate and benzoate ions in several solvents.

[Key as for Figure 6.2]
FIGURE 6.6
Plot of $v_3$ (C-O) stretch frequency of a acetate ion and b benzoate ion versus solvent acceptor numbers. [Key as for Figure 6.2]
referred to an infinitely dilute solution in hexane. Unfortunately, it is not possible to use such correlations for ions as effectively as those for neutral molecules, since there are no good values for the unperturbed ions. There is a good correlation amongst the protic solvents, but this does not extend to data for the aprotic solvents. Because of the stronger oscillator strengths of the \( v_1 \) and \( v_3 \) bands of PhCO\(_2\)\(^-\) than of MeCO\(_2\)\(^-\) ions, it was decided that the former be used for further detailed study.

6.3.2 Water + DMSO Mixed Systems

Figure 6.7a displays a set of infrared spectra for the \( v_3 \) stretch frequency for the benzoate anion in D\(_2\)O + DMSO systems. Contrary to the band profile in pure DMSO which is narrow and symmetric, that in aqueous solution is broad indicative of mixed solvation for this ion. Most marked are the trends in the DMSO-rich regions where the bands are hardly accompanied by any significant shifts (up to ca. 0.503 mf D\(_2\)O). It is proposed that this lack of change may be controlled by two opposing interactions:

a bonding of one water molecule to produce an asymmetric solvated species (V) - this is thought to induce a high frequency shift, as in the case of full protonation.

\[
\begin{align*}
\text{O} & \quad \text{DOD} \\
\text{C} & \\
\text{O} & \\
\text{O} & \quad \text{DOD}
\end{align*}
\]

(V)

b bonding of the second water molecule which would restore the symmetry (VI) - this is assumed to displace the band back to lower frequencies.

Changes accompanying further additions of water are relatively clear.
FIGURE 6.7(a)
Infrared spectra for solutions of sodium benzoate (0.0098 g/ml) in the $\nu_3$ (C-O) stretch regions in water ($D_2O$) + DMSO systems.
with bands shifted to lower frequencies. It is tentatively proposed.
that in pure aqueous solutions the spectra are dominated by a mixture
of tetra- (VIII) and tri- hydrates (VII), the latter being the dominant
hydrate at ca. 0.800 m\text{D}_2\text{O}. A solvation number of 4 has been reported
for the acetate ion in aqueous solutions from compressibility measure-
ments.\textsuperscript{24}

It is interesting to note that the asymmetrically solvated ion (V)
gives a high $\nu_3$ shift from the DMSO value, however the asymmetrically
solvated species (VII) does not exhibit such behaviour, rather a low $\nu_3$
position at ca. 1553 cm$^{-1}$. It is probable that the already solvated
carboxylate ion (VI) has a coupling that is less sensitive to the
environment.

The corresponding trends in the $\nu_1$ vibration are illustrated in
Figure 6.7b. It is imperative to this discussion that the origin of the
bands in pure DMSO be established.

The possibility of ion-pairing is considered less likely due to the
similarity of the spectra for sodium and tetrabutylammonium salts; also
the use of the sodium selective (benzo-15-crown-5) ether failed to alter
materially the spectrum for the sodium salt. That this peak (ca. 1357
cm$^{-1}$) is not considered as due to a C-H oscillator of the solvent is
confirmed by its presence when deuterated DMSO is used. Temperature
variation, failing as it does to alter the spectral envelope, would seem
to indicate that these peaks are not due to the "reinforced dipolar" and
FIGURE 6.7(b)
Infrared spectra for solutions of sodium benzoate (0.0098 g/ml) in the ν₁ (C-O) stretch regions in D₂O + DMSO systems.
[Key as for Figure 6.7(a)]
"free" species in equilibrium. These peaks are not considered to be water solvate species in view of the fact that stringent drying methods were employed during this investigation and the introduction of controlled amounts of water into the system failed to enhance either bands as would have been expected. The peak at ca. 1357 cm$^{-1}$ might conceivably be considered to be due to Fermi resonance; however, this possibility would not appear to be borne out by experimental observation. Were the peak due to Fermi resonance, the close proximity of a neighbouring fundamental band would be expected to cause an increase in the "Fermi" peak intensity - this is not seen to be the case. The difficulty in accurately assigning the ca. 1357 cm$^{-1}$ peak remains. However, if this band is accepted as representing a weak oscillator$^{16,17}$ which is not pertinent to the relevant discussion, the explanations offered are acceptable.

If the $v_1$ absorption in pure DMSO (at ca. 1379 cm$^{-1}$) arises from an unperturbed and, therefore, symmetrical carboxylate function, then the initial low $v_1$ shift observed for the band in the rich DMSO regions may be understood by the formation of an asymmetric solvated state ($V$) as a result of hydrogen bonding by one water molecule. However, beyond 0.200 mf D$_2$O, the $v_1$ band progressively shifts to higher frequencies to ca. 1375 cm$^{-1}$ at 0.503 mf D$_2$O. It is thought that this behaviour occurs as a consequence of the symmetrical hydrate structure ($VI$). Changes accompanying subsequent additions of water that involve band shifts are rather difficult to interpret.

### 6.3.3 Methanol + DMSO Mixed Systems

Figure 6.8a displays the results of the $v_3$ carbonyl absorption for the benzoate anion in MeOH + DMSO solutions. It is observed that the band in pure DMSO is displaced slightly to higher frequencies (ca. 1564 cm$^{-1}$)
FIGURE 6.8(a)
Infrared spectra for solutions of sodium benzoate (0.0097 g/ml) in the $\nu_3$ (C-O) stretch regions in MeOH + DMSO systems.
during initial additions of MeOH to DMSO solutions. It is proposed that this arises as a result of a loss of the symmetric structure to produce the mono-hydrogen bonded species (IX). At higher concentration of MeOH, this band is shifted back again to lower frequencies to the pure MeOH value. It is suggested that the major contributor to the pure MeOH spectra arises from the di-solvate (X) (possessing a symmetrically solvated structure) so that equilibrium (a) dominates.

\[
\begin{align*}
\text{Me} & \text{O---HO---Bulk} \\
\text{C} & \text{O---HO---Bulk} \\
\text{Me} & \text{O---HO---Bulk} \\
\text{Me} & \text{O---HO---Bulk} \\
\end{align*}
\]

\[\text{Me} \quad \text{C} \quad \text{O} \quad \text{Me} \quad \text{Me} \]

\[\text{IX} \quad \text{X} \quad \ldots \quad (a)\]

However, the asymmetry of the band profile in pure MeOH suggests the possible presence of tri-solvate also.

Changes in the \(\nu_1\) vibration in similar solutions (Figure 5.8b) are identical to those for water systems. It is proposed that the initial low frequency shift observed for the band in the DMSO regions arises from asymmetry (IX). However, this is progressively displaced to higher frequencies when symmetrical species (X) is regained. Studies of this system is thus significant in assigning mostly a di-solvation for the carboxylate anion in methanol. These findings are consistent with results for lithium acetate,\(^{25}\) where a solvation number between 1 and 2 has been deduced for the acetate ion in methanol.

6.3.4 Water + Methanol Mixed Systems

For the benzoate anion, trends for the \(\nu_1\) frequency in protic mixed systems (Figure 6.9a) are rather less definitive. However, if it is accepted that this probe is tetra-solvated in D\(_2\)O, then it could be seen, on increasing MeOD concentrations, that this band is shifted progressively
**FIGURE 6.8(b)**
Infrared spectra for solutions of sodium benzoate (0.0097 g/ml) in the v1 (C-O) stretch regions in MeOH + DMSO systems. [Key as for Figure 6.8(a)]
FIGURE 6.9(a)
Infrared spectra for solutions of sodium benzoate (0.0105 g/ml) in the \( \nu_3 \) (C-O) stretch regions in D\(_2\)O + MeOD systems.
to higher frequencies, narrowing slightly in this process. A unique isosbestic point is noted at ca. 1550 cm\(^{-1}\). In these regions, equilibrium such as (b) involving the tri- and tetra- hydrogen bonded species is thought to prevail. It has not been possible to distinguish between

\[\text{H}_2\text{O-H}_2\text{O-H}_2\text{O} \quad \rightleftharpoons \quad \text{H}_2\text{O-H}_2\text{O-H}_2\text{O} \]  

water and methanol molecules in the above scheme since the hydrogen-bonding strengths of water and methanol are quite similar.\(^\text{26}\) It is proposed that the peak corresponding to 0.209 mf D\(_2\)O be assigned mainly to a tri-solvate, so that the changes at the MeOD-rich regions may then be understood as arising from di- and tri- solvates.

Trends in the \(\nu_1\) frequency in similar solutions are depicted in Figure 6.9b. Most marked is the lack of shift in the MeOD-rich regions. This could possibly be viewed as further evidence for the mixed solvation (di + tri) proposed for methanolic solutions. However, beyond 0.300 mf D\(_2\)O, there is a clear change to the pure D\(_2\)O value indicative of a different solvation in D\(_2\)O than methanol.

6.3.5 Salt Effects

The effectiveness of vibrational spectroscopy in monitoring ion interactions at the phosphate group was shown in Chapter 4. Although in solution, various forms of cation-anion environment are thought to exist, one can invoke specific structures, in particular solvent-separated ion-pairs and contact ion-pairs.

Figure 6.10 depicts the effect of calcium perchlorate [Ca(Cl\(_\text{O}_4\))\(_2\)] on the \(\nu_3\) absorption spectra. The role of Ca(Cl\(_\text{O}_4\))\(_2\) in methanol could be viewed in two ways:
FIGURE 6.9(b)
Infrared spectra for solutions of sodium benzoate (0.0105 g/ml) in the $v_1$ (C-O) stretch regions in $D_2O + MeOD$ systems.
[Key as for Figure 6.9(a)]
Table 6.10

<table>
<thead>
<tr>
<th>Soln.</th>
<th>m.f. Ca(ClO$_4$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00000</td>
</tr>
<tr>
<td>2</td>
<td>0.00026</td>
</tr>
<tr>
<td>3</td>
<td>0.00052</td>
</tr>
<tr>
<td>4</td>
<td>0.00104</td>
</tr>
<tr>
<td>5</td>
<td>0.00156</td>
</tr>
<tr>
<td>6</td>
<td>0.04935</td>
</tr>
</tbody>
</table>

FIGURE 6.10

Effect of Ca(ClO$_4$)$_2$ on the $\nu_3$ (C-O) frequency for solutions of Bu$_4$N$^+$/PhCO$_2^-$(0.0132 g/ml) in methanol. [Features due to a and b are discussed in the text.]
(i) Because of the relatively high solvation numbers of calcium\(^{27}\) and perchlorate\(^{28}\) ions, it may simply remove solvent molecules attached to the carboxylate groups. For example, if the carboxylate anion which is thought to be mostly di-solvated in MeOH, is depicted as in XI (S\(_1\) being the primary molecules bonded directly to the anion), then increasing the Ca\(^{2+}\) concentration would remove methanol molecules (such as S\(_2\)). The chain would ultimately terminate in a methanol molecule that forms only one hydrogen-bond (XII). This behaviour is expected to displace the \(\nu_3\) band to higher frequencies, as is observed on adding DMSO, which has the same desolvating effect. Since the shifts are to low frequencies such desolvation cannot be of major importance.

(ii) Ion-pair formation between the carboxylate and Ca\(^{2+}\) ions is expected to occur. This can take at least three forms - solvent-shared ion-pairs (XIII), monodentate contact (XIV) or bidentate contact (XV) ion-pairs.
FIGURE 6.11
Effect of \( \text{Zn(ClO}_4\text{)}_2 \) on the \( \nu_3 \) (C-O) frequency for solutions of \( \text{Bu}_4\text{N}^+\text{PhCO}_2^- \) (0.014 g/ml) in methanol.
FIGURE 6.12
Plot showing the limiting shifts induced in the (C-O) stretch frequencies of the benzoate ion in methanolic solutions by metal ions.
FIGURE 6.13
Effect of LiClO₄ on the v₃ (C-O) frequency for solutions of Bu₄N⁺ PhCO₂⁻ (0.013 g/ml) in methanol.
If there is no loss of solvation, structures such as XIII are expected to induce a low $v_3$ shift since $'a'$ is thought to be strengthened by the secondary effect of metal ions such as $Ca^{2+}$.

It is seen that the spectra in the $v_3$ regions (Figure 6.10) are dominated mostly by two features, $a$ and $b$ around ca. 1560 cm$^{-1}$ and ca. 1548 cm$^{-1}$ respectively. At higher salt concentrations (such as 0.00104 m$^{-1}$ salt), band $a$ could be attributed to a solvent-shared ion-pair since such structures are expected in methanolic solutions.

Similar arguments may be used to explain the effects displayed by $Zn^{2+}$ (Figure 6.11). Although $a$ may be assigned as due to a solvent-shared ion-pair, the bidentate structure (XV) for $b$ is thought to be favoured on the evidence of a bidentate structure as indicated for zinc acetate by X-ray analysis.$^{29}$

According to Nakamoto,$^{11}$ a bidentate (XV) type of interaction is expected to displace the $v_3$ vibration to lower frequencies and $v_1$ vibration to higher frequencies. The limiting shifts at high salt concentrations for the vibration are therefore depicted in Figure 6.12. Indeed, it is seen that for $Zn^{2+}$ and $Ca^{2+}$, this is the case. The comparative shifts observed for both $Ca^{2+}$ and $Zn^{2+}$ corroborate the assignment of feature $b$ at ca. 1548 cm$^{-1}$ generated in the presence of $Ca^{2+}$ (Figure 6.10) as due to a bidentate contact ion-pair. In marked contrast to the other metal ions, the effect of $Li^+(Figure 6.13)$ is negligible. It is suggested that, if anything, solvent-shared ion-pairs are the most probable species formed by this metal ion.

6.4 CONCLUSIONS

It is generally observed that protic solvents induce a low frequency shift in the asymmetric (C-O) vibration and high frequency shift in the
symmetric (C-O) vibration. This apparent convergence of the shifts from aprotic to protic solvents is not yet completely understood. However, mixed solvent studies have revealed, partly, the importance of the symmetry of the carboxylate group in dictating the observed shifts. In aqueous solutions, it is thought that the benzoate anion is mostly tetra-hydrated and mostly di-hydrogen bonded in methanolic solutions. Metal ions were found to have a pronounced effect on the carbonyl stretch vibration in solution. In marked contrast to phosphate mono-anions (Chapter 4), metal ions in solution induce a low frequency shift in the (C-O) \( \nu_3 \) vibration.
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CHAPTER 7

Solvation of Nitro Compounds
7.1 INTRODUCTION

This work aims at extending the study to yet another linkage of wide occurrence, the nitro group. Nitrogen oxides are of particular interest both from the view of their rôle, undesirable though it be, in atmospheric pollution and their importance to industry. Nitromethane (MeNO₂) is a typical compound selected as a probe for this study.

X-ray and electron diffraction techniques suggest a symmetrical planar structure, with a C₂ symmetry (from microwave spectroscopy) for this molecule.

Spectroscopy has figured prominently in a vast amount of previous work. The use of ultraviolet spectroscopy has been mostly limited to the study of solvent effects on electronic transitions for a series of nitro derivatives. MeNO₂ has long been employed as a primary standard in studies involving nitrogen magnetic resonance. The effect of solvents on nitrogen resonance shifts for nitromethane and related compounds has recently been studied by Witanowski et al. Lambert and Roberts have indicated the importance of the paramagnetic term in dictating these shifts. Vibrational spectroscopy has been used extensively in the past to study the rôle of substituents in influencing the (N-O) stretch frequency and infrared intensities; it has also been the technique used in the present study to investigate the solvation of nitromethane. However, complications that arise as a consequence of changes in coupling between the two N-O oscillators to which the technique would be strongly sensitive, cannot be ignored. It was therefore proposed to extend the study to nitrosobenzene, which only possesses a single N-O oscillator.
7.2 EXPERIMENTAL

Nitromethane (MeNO₂) was purified by fractional distillation over CaH₂. 2-Nitro-2-methyl propane (t-BuNO₂) and nitrosobenzene were commercially obtained and used directly. All infrared spectra were run on a Perkin-Elmer 580 spectrometer employing demountable cells with 25 μm teflon spacers between CaF₂ plates. Concentrations of the probe in solutions were maintained at a minimum.

7.3 RESULTS AND DISCUSSION

7.3.1 Pure Solvent Systems

Figure 7.1 presents a typical spectra depicting bands attributed to the asymmetric (N-O) (ν₃) and symmetric (N-O) (ν₁) vibrations⁶,⁹,¹³,¹⁴ (band X being due to a methyl bending mode) for a dilute solution of MeNO₂ in carbon tetrachloride. The spectral shifts for MeNO₂ in a range of solvents are displayed in Figure 7.2, where the shift in the symmetric frequency (ν₁) is plotted as a function of the corresponding asymmetric frequency (ν₃). Such plots appear not to have much significance when applied to pure solvents except being probably a useful aid in presenting data. The lines merely represent the limiting trends, apart from the point for the very small spectral response of the bands to solvent changes. This presumably arises from the very small polarity of the N-O linkage. The (N-O) ν₃ frequency is clearly less solvent sensitive compared to the corresponding ν₁ frequency and, therefore, a less reliable monitor.

Trends in ν₃ frequency are mainly dominated by the dipolar aprotic bases such as hexamethylphosphoric triamide (HMPA) and dimethylsulphoxide (DMSO), the latter displaying the larger perturbation. The shifts amongst the protic solvents can best be interpreted as a general scatter.
FIGURE 7.1
Infrared spectrum for dilute solution of nitromethane in carbon tetrachloride.
FIGURE 7.2
Plot of $\nu_3$ frequency versus $\nu_1$ frequency for MeNO$_2$ in various solvents.
This behaviour is generally also reflected in the trends for the $v_1$ frequency although anomalous high frequency shifts are indicated for water and fluorooalcohol solvents. The position in MeCN is notably curious on this plot. Similar trends are generally also displayed in the spectra for 2-nitro-2-methyl propane (t-BuNO$_2$) (Figure 7.3) although the correlation amongst the protic solvents is slightly improved. This probe, however, suffers from a reduced solvent sensitivity when compared with nitromethane. These results of solvent effects can be rationalised in terms of a weak protic solvent interaction, such that the dipolar aprotic bases dominate the shifts. There is plenty of evidence to show that RNO$_2$ compounds are indeed very weakly basic.

Figure 7.4 depicts the $v_3$ frequency for the compounds plotted as a function of acceptor numbers$^{15}$ (AN). A wide scatter is displayed for solutions of MeNO$_2$ in hydrogen bonding solvents which is generally also true for the aprotic solvents although rough trends are just discernible. This is in contrast to the behaviour of t-BuNO$_2$ where the AN correlation is quite encouraging for the more limited range of solvents. The anomalous result for fluoroalcohol, which is far removed from the other protic solvents probably also involves a steric factor. These results further reinforce the apparent dominance of the dipolar aprotic bases over protic solvents.

A significant difference between these probes is the basic character of their nitro functions, t-BuNO$_2$ being relatively a stronger base than MeNO$_2$$^{16}$ (Table 7.1). It is probable that this is a decisive factor in the AN correlations. AN is a measure of electrophilic properties$^{15}$ of solvents and is based on the strong basic character of triethylphosphine oxide (Et$_3$PO). Thus, one important implication of this discussion is that acceptor number is a valid solvent scale for relatively strong
FIGURE 7.3
Plot of $\nu_3$ frequency versus $\nu_1$ frequency for t-BuNO$_2$ in various solvents.
[Key as for Figure 7.2]
FIGURE 7.4(a)
Plot of Acceptor Number versus $v_3$ frequency for MeNO$_2$
in various solvents.
[Key as for Figure 7.2]
FIGURE 7.4(b)
Plot of Acceptor Number versus $\nu_3$ frequency for t-BuNO$_2$ in various solvents.
[Key as for Figure 7.2]
TABLE 7.1

Effect of solutes on the shift ($\Delta \nu$) of monomeric MeOH in CCl$_4$.

<table>
<thead>
<tr>
<th>Solute</th>
<th>($\Delta \nu$) MeOH (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeNO$_2$</td>
<td>26</td>
</tr>
<tr>
<td>t-BuNO$_2$</td>
<td>30</td>
</tr>
<tr>
<td>Et$_3$PO</td>
<td>280</td>
</tr>
</tbody>
</table>

bases only.

Evidence for the weak basic character (electron donicity) of these compounds is also indicated by Arnett$^{17}$ who showed that the nitro group remained virtually unprotonated even in sulphuric acid solutions. It is thought most probable that this weak basic nature of the nitro function is also responsible for the poor sensitivity of these probes to protic solvents. This does not necessarily imply that no hydrogen bonds are involved. Hydrogen bonds formed are definite but weak. That this is the case is evident from the effects of nitro group on the overtone regions of water.$^{18}$

The relatively strong dipolar aprotic influence is also reflected in the $^1\text{H}$ magnetic resonance shifts (Table 7.2) for MeNO$_2$ in various solvents.

TABLE 7.2

Solvent Effects on $^1\text{H}$ resonance shifts of nitromethane

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$^1\text{H}$ (ppm)</th>
<th>Solvent</th>
<th>$^1\text{H}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrachloromethane</td>
<td>+7.10</td>
<td>Diethylether</td>
<td>+3.91</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>+3.79</td>
<td>Dichloromethane</td>
<td>+3.21</td>
</tr>
<tr>
<td>Acetone</td>
<td>+0.77</td>
<td>Acetonitrile</td>
<td>+0.20</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>-0.69</td>
<td>Dimethylsulphoxide</td>
<td>-2.01</td>
</tr>
</tbody>
</table>

Gutmann's donor number (DN)$^{19}$ is a measure of solvent nucleophilic
characteristics and is known to correlate remarkably well with good
electron acceptors such as cations.\textsuperscript{20} The weakly basic nature of nitro
compounds suggests that DN might probably provide a better insight into
the infrared results. These are depicted in Figure 7.5 where the solvent
shifts for the $v_3$ frequency for the probes are compared. There does
seem to be a significant trend as indicated, with the exceptions of
HMPA and Et$_3$N. Steric factors may be responsible for the behaviour of
the latter two bases. The DN plots therefore suggest that the nitro
group may be behaving as an electron acceptor to some extent. However,
it remains possible that changes in the $v_3/v_1$ coupling may be obscuring
trends for the isolated N=O oscillators. Comparison of the behaviour
exhibited by these nitro derivatives with that for a single nitro
oscillator may provide useful information regarding the relevance of such
coupling. The shifts induced for (N=O) $\nu$ stretch frequency for nitroso­
benzene are therefore displayed against solvent acceptor number and
donor number respectively in Figure 7.6. It is again sufficient to note
the rather strong dominance displayed by the dipolar aprotic solvents
over their protic counterparts. The scatter is just as bad, so changes
in coupling are not thought responsible for the poor correlation and
conclude sensitivity too small to be useful.

7.3.2 Mixed Solvent Systems

A set of spectra depicting the changes in the asymmetric stretch
frequency for MeNO$_2$ in D$_2$O/DMSO mixed systems are presented (Figure 7.7).
Corresponding trends for the symmetric vibration are not displayed since
it lacked sensitivity.

Trends in the DMSO-rich regions could be interpreted as arising from
desolvation of the 'dipolar influence' by water through hydrogen bonding.
In the water-rich regions, an overall shift of band envelope may be
FIGURE 7.5(a)
Plot of Donor Number versus $\nu_3$ frequency for MeNO$_2$ in various solvents.
[Key as for Figure 7.2]
FIGURE 7.5(b)
Plot of Donor Number versus $v_3$ frequency for t-BuNO$_2$ in various solvents.
[Key as for Figure 7.2]
FIGURE 7.6(a)
Plot of Acceptor Number versus (N-O) stretch frequency for nitrosobenzene in various solvents.
[Key as for Figure 7.2]
FIGURE 7.6(b)
Plot of Donor Number versus (N-O) stretch frequency for nitrosobenzene in various solvents.
[Key as for Figure 7.2]
FIGURE 7.7
Infrared spectra in the $\nu_3$ stretch regions for dilute solutions of MeNO$_2$ in D$_2$O/DMSO systems.
noted. The fact that no distinct hydrogen bonded features are detected in these regions is not surprising for this very weak base; this observation further discourages any serious attempts to employ this hitherto powerful technique to deduce solvation numbers of these compounds.

7.4 CONCLUSIONS

Gutmann's acceptor number is a valid solvent scale for relatively strong bases only. Its failure when applied to weak bases suggests the corresponding donor number may be a better scale. The nitro function comprised of only electronegative atoms is virtually an electron-demanding rather than electron-donating function. Because of the weak basic character of the nitro group, a weaker hydrogen bonding interaction is indicated so that the dipolar aprotic solvents dominate the infrared shifts. Mixed solvent techniques involving protic media as one of the cosolvents can be a powerful probe of solvation. It is, however, unreliable for weak bases in the fundamental infrared.
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CHAPTER 8

Solvation of Dimethylsulphone
8.1 INTRODUCTION

This work relates to the investigation of the solvation of dimethylsulphone (Me₂SO₂), a typical system chosen to represent the sulphone group in biological systems. The chemistry of the sulphonyl group is of considerable interest both in the biological and industrial spheres. In the discussion, a lot of reference is made to the sulphoxide linkage of dimethylsulphoxide (DMSO) (the latter being used extensively in the study so far).

Me₂SO₂ which may be regarded as an oxidation product of DMSO is of natural occurrence in animals. Most previous work on sulphones has been directed towards the study of substituent effects. Several authors have concluded that substituent mass and coupling are insignificant in influencing the sulphonyl vibrations although the importance of substituent inductive effects has been indicated. Gillespie and Robinson have correlated the S-O stretch frequency and O=S for a series of sulphur-oxygen derivatives. The structure of methylsulphone is a distorted tetrahedron as deduced from microwave, X-ray and electron diffraction techniques. DMSO in contrast is pyramidal. This, in conjunction with the high polarity of the S-O bond, is believed to be responsible for the self association properties of DMSO. On grounds of symmetry, however, such complexities can virtually be disregarded for methylsulphone. The nature of the sulphur-oxygen linkage in these compounds is a subject of long-standing controversy. Most investigators are in favour of either single or double bond character of the S-O linkage. This view arose primarily as a result of comparisons of physical properties such as S-O distances, stretch frequencies, force constants and chemical properties. An extensive but non-committal review on the sulphone has been provided.
In the ensuing discussion, the sulphonyl linkage is depicted as S-O for simplicity.

8.2 EXPERIMENTAL

Me₂SO₂ was commercially obtained and crystallised from ethanol. Solutions were prepared by weights in fixed volumes. All infrared spectra were run on a Perkin-Elmer 580 infrared spectrometer using a demountable cell with 25 μm spacers between CaF₂ plates. Spectra were resolved with the aid of a computer program.

8.3 RESULTS AND DISCUSSION

8.3.1 Pure Solvent Systems

Methylsulphone is assigned in the fundamental infrared,¹⁵,¹⁶ being characterised by strong absorptions around ca. 1290 cm⁻¹ and ca. 1130 cm⁻¹ respectively, due to the asymmetric (ν₃) and symmetric (ν₁) S-O stretch vibrations. Infrared spectra in the S-O stretch regions for solutions of methylsulphone in water and tetrahydrofuran (THF) are depicted in Figure 8.1. In the ν₃ (S-O) stretch regions, although the spectrum in THF solutions is narrow, that in aqueous solutions is broad and asymmetric suggestive of mixed solvation for this probe in water. The bands at ca. 1336 cm⁻¹ and 1320 cm⁻¹ in the spectrum for aqueous solutions have been assigned to C-H bending modes.¹⁶ The comparison with the spectrum in THF suggests that these bands are solvent sensitive.

The results of spectral shifts for Me₂SO₂ in a range of protic and aprotic solvents are presented in Figure 8.2. It is noteworthy that the solvent sensitivity of the symmetric (ν₁) vibration is much smaller than that for the corresponding asymmetric (ν₃) vibration. A similar observation was also reported in the case of nitro compounds (Chapter 7) and is known for sulphur dioxide.¹⁷ One plausible explanation for this
FIGURE 8.1
Infrared spectra for solutions of dimethylsulphone in a water and b tetrahydrofuran in the S=O stretch regions.
FIGURE 8.2
Plot of $\nu_3$ (S-O) stretch frequency versus $\nu_1$ (S-O) stretch frequency for solutions of dimethylsulphone in various solvents.
underlying trend may be the relatively small dipole change accompanying a symmetric vibration. The latter, therefore, would be less responsive to solvent polarity. Proton donors such as water and ethylene glycol induce a marked low frequency shift for the bands. This for a particular vibration (in the absence of any appreciable coupling between the sulphonyl stretch modes), can be understood in terms of bond weakening, caused as a consequence of solvent interaction at the oxygen site(s).

The solvent induced shifts for the \( v_3 \) frequency as a function of solvent acceptor numbers\(^{18} \) (AN) are displayed in Figure 8.3. The best fit for the protic solvent data requires a mixture of di (+tri) solvates in water, mostly di-solvation in ethane-diol, mono (+di) solvation in methanol (and ethanol), and a mono-solvation in cases of iso-propanol, chloroform and methylene chloride (\( \text{CH}_2\text{Cl}_2 \)). Relative to the shifts induced by the aprotic solvents, those for the protic solvents are rather small. Thus, for example, the shift induced by MeOH is less than that induced by DMSO. This reflects the fact that sulphones are relatively weak bases. However, they are comparable in base strength with the esters (Chapter 5) which do not show this behaviour.

8.3.2 Water + Aprotic Mixed Systems

The trends in the \( v_3 \) and \( v_1 \) stretch frequencies in water + THF systems are presented in Figures 8.4 and 8.5 respectively.

\( v_3 \) Frequency

The apparent rapid loss of oscillator strength during initial additions of water in the THF-rich end, although unusual, can be understood in terms of simultaneous movements of the C-H band. Spectral resolution rejects any possible growth of a band in the vicinity of \( \text{ca.} \ 1306 \ \text{cm}^{-1} \). The presence of isosbestic points around \( \text{ca.} \ 1300 \ \text{cm}^{-1} \) and \( \text{ca.} \ 1295 \ \text{cm}^{-1} \) suggests the possible involvement of three distinct hydrogen-bonded
FIGURE 8.3
Plot of solvent acceptor number versus $\nu_3$ (S-O) stretch frequency for dimethylsulphone, with protic solvents adjusted to suitable solvated state acceptor number values.
[Key as for Figure 8.2]
FIGURE 8.4
Infrared spectra for solutions of dimethylsulphone (0.0258 g/ml) in the $v_3$ (S-O) stretch regions in water + THF systems.
FIGURE 8.5
Infrared spectra for solutions of dimethylsulphone (0.0258 g/ml) in the $\nu_1$ (S=O) stretch regions in water + THF systems. [Key as for Figure 8.4]
states (a), (b) and (c); these are due to the 'free', mono- and di-
hydrate species respectively. The equivalent structure (d) for the
di-hydrate is unlikely from structural and statistical points of view.

A growth and subsequent loss in peak intensity at ca. 0.899 water mole
fraction (mf) also suggests a possible trace of a tri-hydrate (e)
species in pure water.

\( \nu_1 \) Frequency

Analogous trends are observed for the symmetric vibration (Figure
8.5) although this is much less solvent sensitive. A feature due to the
mono-hydrate is proposed in the ca. 1142 cm\(^{-1}\) regions. Towards the rich
water regions, the changes however are less definitive. Up to this
point in the discussion, the coupling between the \( \nu_3/\nu_1 \) modes has been
ignored. Such coupling may be a significantly contributing factor, but
the extent to which this is so is difficult to evaluate.

The lower solvation number in water per (S-O) bond for the sulphone
when compared to DMSO\(^{19}\) should be interpreted in terms of its lower base
strength (Table 8.1).
TABLE 8.1
Effect of compounds on the shift ($\Delta \upsilon$) of monomeric MeOH in carbon tetrachloride

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta \upsilon$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_2$SO$_2$</td>
<td>90</td>
</tr>
<tr>
<td>Me$_2$SO</td>
<td>215</td>
</tr>
</tbody>
</table>

8.3.3 Alcohols + Other Solvents

A typical set of spectra for the $\upsilon_3$ vibration for Me$_2$SO$_2$ in MeOH + CH$_2$Cl$_2$ solutions is depicted in Figure 8.6. The observed trends in the methylenechloride-rich regions are characterised by loss in intensity and shifts to low frequency. As the MeOH mf increases, the observed shifts to low frequency is thought to arise from the "co-operativity" effects of methanol chain formation. The apparent isosbestic point around ca. 1304 cm$^{-1}$ is thought to be spurious as the solvation of the probe molecule is considered to be similar in both CH$_2$Cl$_2$ and MeOH. The asymmetry at lower frequency, observed in the pure MeOH spectrum would nonetheless seem to indicate the presence of more than one solvate species, i.e. mono with a trace of di. The $\upsilon_1$ frequency was, however, much less informative displaying hardly any significant shift. Trends for EtOH + CH$_2$Cl$_2$ systems were quite similar to those for methanolic systems and thus not displayed.

MeOH + DMSO mixed systems (Figure 8.7) display a most interesting behaviour with DMSO exhibiting a much stronger perturbation. That this property of DMSO is not unique to the sulphone was indicated in the work relating to esters (Chapter 5). Examination of the sulphone band in DMSO suggests the presence of at least two distinct features at ca. 1295 cm$^{-1}$ and ca. 1289 cm$^{-1}$ respectively.

One obvious cause for the features would be water impurity. The
FIGURE 8.6
Infrared spectra for solutions of dimethylsulphone (0.0225 g/ml) in the $v_3$ (S=O) stretch regions in MeOH + CH$_2$Cl$_2$ systems.
FIGURE 8.7
Infrared spectra for solutions of dimethylsulphone (0.0142 g/ml) in the ν₃ (S-O) stretch regions in MeOH + DMSO systems.
latter, however, can be rejected on grounds that stringent drying procedures were employed. A proposition that needs consideration is the 'reinforced' dipolar interaction (f) for the band at ca. 1289 cm\(^{-1}\) with the ca. 1295 cm\(^{-1}\) feature assigned to the 'free' sulphone. This, however, is inconceivable since the shift for the 'free' sulphone is much farther removed. On the same token, the species at ca. 1289 cm\(^{-1}\)

\[
\begin{align*}
(f) & \quad (g) & \quad (h)
\end{align*}
\]

could be attributed to a 'reinforced' dipolar interaction (g) and that at ca. 1296 cm\(^{-1}\) to (f) respectively. This argument appears reasonable. In particular, it is noted that structures such as (g) are sterically less favourable. That this is true is clearly indicated from the relatively lower concentrations of this feature in the pure solvent spectrum. The equivalent assertion that the species such as (h) may be involved cannot be discounted but its existence is highly unlikely because of the very weak acidity of methyl protons.

On these assignments, trends in the \(v_3\) frequency (Figure 8.7) can be understood by the loss in the di-solvate structure (ca. 1286 cm\(^{-1}\)) in MeOH-rich regions, with concomitant growth in the mono-solvate (at ca. 1302 cm\(^{-1}\)), attaining a maximum at ca. 0.501 methanol mf. The latter is subsequently lost to produce the features due to the 'dipolar interaction' in pure DMSO. The isosbestic point at ca. 1298 cm\(^{-1}\) is noteworthy which is suggestive of a 'specific' nature of this interaction.
8.4 CONCLUSIONS

Mixed solvent systems have indicated a mixture of di (+tri) solvation in water and a lower solvation (mono + di) in methanolic solutions. For the sulphone, this when compared to DMSO solvation seems dictated by base strength. Methylsulphone is more strongly perturbed in an environment of DMSO than the sulphone in alcoholic media.
REFERENCES TO CHAPTER 8

Appendix A
THEORY OF NMR CHEMICAL SHIFTS

When an atom (or molecule) is subject to a magnetic field, the field induces motion of the electron cloud so that a counter magnetic field is set up that opposes the applied field. The net field experienced by the nucleus is thereby diminished (by the counter field which screens [shields] it). This concept is introduced into equation (1), relating the applied field \( H_0 \) and the screening constant \( \sigma \) (also called the diamagnetic screening constant).

\[ \nu \propto H_0 \left( 1 - \sigma \right) \quad \ldots \quad (1) \]

\( \sigma \) is a dimensionless quantity and is usually recorded in parts per million (ppm).

The magnitude of such screening is a maximum for a free atom where the electrons can circulate freely. In a molecule, however, the free circulation around a particular nucleus is hindered by bonding (and by the presence of other positive centres), so that this screening is reduced and the nucleus resonates at a higher frequency (lower fields). In fact, there are two major contributions to \( \sigma \) (equation 2), the diamagnetic term \( \sigma_d \) (known also as the Lamb term) and the paramagnetic term \( \sigma_p \) (known also as the Ramsey term).

\[ \sigma = \sigma_d + \sigma_p \quad \ldots \quad (2) \]

The paramagnetic term (or Ramsey term) (equation 3) varies inversely as the energy separation \( \Delta E \) between ground and all excited electronic states of the molecule which are magnetically coupled to the ground state.

\[ \sigma_p \propto \frac{1}{\sum_{\Delta E}} \quad \ldots \quad (3) \]

This means that correlations are found between screening constants and the frequency of absorption lines in the visible and ultra-violet.\(^3,\,4,\,5\)
For most atoms, variations in this term provides the main contribution to chemical shifts. The resonance is at low fields (deshielding) when $\Delta E$ is small (i.e. longer wavelengths). The principle exception is hydrogen, for which there are only a few electrons to contribute to the screening and for which $\Delta E$ is large so that contributions to the total shielding from $\sigma_p$ are only minor.
REFERENCES TO APPENDIX A

1. J. A. POPLE, 

2. N. F. RAMSEY, 

3. J. MASON, 
   *Chemical Rev.*, 1981, 81, 211.

4. A. J. JONES, D. M. GRANT, J. G. RUSSELL, G. FRAENKEL, 

5. J. W. AKITT, 
Appendix B
The measurement of absolute positions of nuclear resonances are difficult to determine and so some reference signal is used and signals measured relative to those of the references. For $^1$H NMR work, the most commonly used reference signal is that from protons of tetramethylsilane (TMS). This compound is chosen because the protons of its methyl groups are more shielded than those of most other common compounds, its resonance arbitrarily set to 0 ppm. However, for other nuclei, other suitable reference materials may be used - these are mentioned under relevant Chapters.

Two types of referencing are used in NMR: internal and external; each having its merits and shortfalls.

a  **Internal Reference**

An internal reference is a compound, usually giving a sharp NMR line, that is dissolved directly and dispersed uniformly in the sample solution under study. The magnetic field acts equally on the sample and reference. Provided the reference compound does not react chemically with the sample, the only serious drawback to an internal reference is the possibility that intermolecular interaction will influence the resonance frequency of the reference. However, by careful choice of relatively inert compounds, this effect could be minimised. TMS is a good example of internal referencing in proton magnetic resonance studies.

b  **External Reference**

An external reference is a compound placed in a separate container from the sample. Usually an external reference is placed either in a small sealed capillary tube or in the thin annulus formed by two coaxial tubes. An external reference is advantageous in eliminating the possibility of intermolecular or chemical interaction with the sample
under observation. Also, there are no problems with solubility of the reference in the sample solution. However, there is a serious difficulty raised which is related to the different magnetic fields experienced by the reference and sample. A correction factor thus needs to be applied to the experimental shift ($\delta_{\text{obs}}$) which is indicated in equation (1)

$$\delta_{\text{true}} = \delta_{\text{obs}} + \frac{2\pi}{3} (\chi_{\text{ref}} - \chi_{\text{sample}}) \quad \ldots \quad (1)$$

where $\chi$ is the volume susceptibility whose value for most solvents is well-documented.\textsuperscript{2-4} Equation (1) assumes a cylindrical tube arrangement with length $\gg$ diameter.
REFERENCES TO APPENDIX B

Appendix C
CURVE DECONVOLUTION TECHNIQUES

In order to investigate an absorption spectrum, it is necessary to determine accurately the position, height and width of band components. Many methods are available which are universally applicable. Some of these are:

a. Visual inspection
b. Analogue curve fitting
c. Digital curve fitting
d. Numerical methods

a. Visual Inspection

This technique is a useful approach only if the profile is uncomplicated, since it effectively involves guess-work. Indeed, with experience and intuition, quite reasonable estimates of band parameters can be obtained.

b. Analogue Method

This is used in the 'Dupont Curve Resolver' (Figure C.1).

The spectrum to be resolved is placed on the bench of the apparatus and is presented to the operator as a laterally correct image by double reflection. A high intensity cathode ray tube projects a synthesised spectrum through the second (semi-transparent) mirror such that it is directly superimposed upon the image of the original spectrum. The synthesised profile is the sum of individual band shapes, each obtained from a central shape generator. This unit comprises a set of channels that generate a band shape function whose position, height and width may be varied. It is also possible to introduce an element of 'skewness' to the band profile. Further features include an integrating meter which can give the percentage area of each band (relative to the whole profile) and also an X-Y plotter that can plot the overall profile, the individual
component bands and the baseline.

One major disadvantage of the technique is the inability of checking the validity of the 'fit' between experimental and synthetic curves. Further, it can lead to erroneous results if viewing position is altered. However, used with care and discretion, the Dupont system provides a powerful tool for the resolution of overlapping absorption bands.

c Digital Method

A similar method, but in a digital form, is to generate band shape functions on a graphical visual display computer terminal on which the experimental spectrum is displayed. The fit is achieved by trial and error.

The VIDCA (Visual Displayed Curve Analysis) program has extensively
been used to analyse overlapping absorption bands. This is a digital curve fitting technique.

The absorption profile, usually in the form of a pen trace on a sheet of chart paper, is turned into a digital form using a computer-controlled digitising table - Ferranti 'Freescan'. The digitised curve can be called by the VIDCA program with axes and defined baseline which is displayed on a graphics screen. Band functions are then defined by the operator according to requirements by means of band height, width at half-height, position on abscissa and % band composition (Lorentzian or Gaussian). The required fit can be achieved by a process of trial and error. The VIDCA program further incorporates various 'error' procedures which enables the operator to facilitate the 'fit'. When a suitable fit has been achieved, the various bands with their respective parameters and overall envelope can be plotted onto a sheet of paper for inspection. The plotter used in this work was a CALCOMP 1012 fast drum plotter in four colours. A typical curve analysed spectrum is presented in Figure C.2.

For good curve fitting, several factors need to be observed:

a Use the minimum number of bands possible.
b The bands used must be dictated by chemistry.

One notes that although most of the disadvantage of the analogue technique is eliminated, a certain amount of operator subjectivity is still apparent.

d Numerical Methods

In general, the curve to be analysed is fitted to some polynomial function which is then reconstructed using sum or product of various band functions. Although these eliminate operator subjectivity, it could lead to serious errors of too many or too few bands. The application of these
DIMETHYL METHYL PHOSPHONATE IN METHANOL

WAVE NUMBERS 1/CM

ABSorbance

COLOUR KEY
BLACK - OBSERVED SPECTRUM
RED - COMPONENT BANDS
GREEN - TOTAL ORDNATE
BLUE - BASELINE/HEADINGS/GRATICULE

BASELINE - LHS 0.120
- RHS 0.070
# USER:- KIRAN PATEL

FIGURE C.2
methods has been described by Pitha and Jones.\textsuperscript{4}

Finally, computer analyses are aids to our knowledge of chemical systems and should always be treated with healthy scepticism and discretion.
REFERENCES TO APPENDIX C

1. B. E. BARKER, M. F. FOX,  

2. INSTRUCTION MANUAL 310 CURVE RESOLVER,  

3. N. G. M. PAY,  

4. J. PITHA, R. N. JONES,  
Studies of Solvation by Spectroscopic Methods

Kirankumar B. Patel

ABSTRACT

The work described in this thesis is concerned with the use of relatively simple compounds in dilute solution to study solvation phenomena. Spectroscopic techniques such as infrared and NMR have been used to follow the environment of the 'probe' throughout various mixed and pure solvent states.

The potential of NMR spectroscopy to solvation has been explored. Solvent effects on the $^3$P resonance show that the sensitivity decreases in the order phosphine oxides — phosphonates — phosphates. This trend is also seen amongst carbonyl compounds where the $^{13}$C NMR sensitivity decreases in the order ketones — acetates — carbonates. It is thought that the paramagnetic contribution to the chemical shift may be important in dictating these shifts.

Based on the evidence of previous work, it was always accepted that water formed the hydrate with maximum solvation number. The results from the ester study are important since it may be a mistake to assume such fixed solvation.

The fundamental infrared work incorporates a study that investigates the relevance of coupling in systems such as phosphate mono-anions, carboxylate anions and others. The results for the phosphate mono-anions show that the coupling between the P-O modes is sensitive to solvent perturbations. This trend is also partly seen amongst the carboxylate anions.

Finally, the validity of Gutmann's Acceptor Number is examined. It is concluded that this solvent scale is only applicable to solvated states that are identical with those for triethylphosphine oxide.