Spectroscopic Studies of Solvation in Aqueous and Alcoholic Media

A Thesis submitted by
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STATEMENT

The experimental work described in this thesis was carried out by the author, except where otherwise stated in the text, in the Department of Chemistry of the University of Leicester during the period between September 1981 and November 1984.

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.

DECEMBER 1984 Signed: ..........................
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"TRUTH HITS EVERYBODY"

Sting (Outlandos D'Amour)
Dedicated to my Mother and Father, without whose unremitting love, support and encouragement, this work may never have been completed.

Thank You
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CHAPTER 1

Introduction
1.1 PREVIEW

This work investigates the hydrogen bonding properties of water and alcohol systems. This Chapter discusses existing structural models for liquid water and aqueous solutions. Methanol with its difunctionality and two dimensional structure presents a simpler picture than does water for interpretation of solvation phenomenon, hence methanolic solvation is considered to aid the understanding of aqueous solvation. Many physical methods have been used to study hydrogen bonding (H-bonding) including X-ray diffraction, thermodynamic techniques, dielectric constant studies and spectroscopic techniques. In the present work we have used Near-Infrared, Infrared and NMR spectroscopy. Liquid water consists of a disturbed network of hydrogen bonded molecules with defects of non-H-bonded so called 'free' OH groups. Throughout this work, pure or extensively H-bonded water or alcohol is referred to as (H2O)bulk or (ROH)bulk. Non-bonded hydroxyl protons are termed (OH)free, non-bonded lone-pairs of electrons (LP)free, and unassociated molecules are referred to as monomeric species. It has long been realised that relatively narrow features detected in OH stretching overtones of water must relate to 'free' or weakly bound OH groups. One of the best features to study is in the first overtone region (7690-6060 cm⁻¹) for HOD in D₂O [1] (Figure 1.1). This work examines the first overtone stretching region for methanol, t-BuOH, 2,2,2-trifluoroethanol and hexafluoroisopropanol and the second overtone stretching region for water which shows the presence of '(OH)free' groups even more clearly.

With its di-difunctionality, water can form a tetrahedral structure (Figure 1.2). The strict ice-like structure remains only temporarily in the liquid on melting due to the constant distortion, breaking and making of bonds which results in cyclic aggregates predominating, haphazardly
FIGURE 1.1
Absorption spectrum in the $2\nu_{OH}$ region for HOD in D$_2$O as a function of temperature. The narrow band at ca. 1416 nm (7052 cm$^{-1}$) is assigned to OH groups (a) 65°C, (b) 55°C, (c) 45°C, (d) 35°C, (e) 25°C.

FIGURE 1.2
Tetrahedral structure of water molecule.
strung together [2,3], with no ordered ice-like regions in the liquid. Models which are most successful in relating the structure of water to its properties are due to Forslid [4] and Frank et al. [5]. The degree of association of water has been the subject of much speculation, evidence has been cited for both a mixture model and a continuum model [6]. These two major categories are discussed further after first examining the 'hydrogen bond' and the development of its definition.

1.2 THE HYDROGEN BOND

Latimer and Rodebush [7] in 1920 postulated intermolecular association in liquid water by the formation of a weak bond between a hydrogen atom and a lone pair of electrons on an oxygen atom in a different water molecule. This weak bond became known as the hydrogen bond. Werner [8] suggested the existence of a bond whereby an H-atom was shared between two electronegative atoms, in the initial stages of ammonium chloride formation, from ammonia and hydrogen chloride. It has since been realised that hydrogen bonding is important in an extensive range of molecular interactions. Wood [9] defines hydrogen bonding as "an attractive interaction between two molecules or between two parts of the same molecule, which requires the specific presence of a hydrogen atom in the vicinity".

Simple valence theory permits a hydrogen atom to form only one chemical bond. In many cases, however, hydrogen is formally two valent. It is when hydrogen is in this state that the additional bond is called a hydrogen bond. Many workers believe the hydrogen bond to be purely electrostatic in nature (A-H\(^+\) --- B\(^-\)), however this type of interaction does not explain all the properties related to the phenomenon [10], i.e. Et\(_3\)N (μ = 0.70), forms stronger H-bonds than MeCN (μ = 3.440) to hydroxylc
compounds. Also for bonds of the type OH---O a decrease in the H-bond length is accompanied by an increase in covalent character of the bond [11]. Coulson et al. [11] considered the H-bond as a resonance hybrid of three structures:

\[ \begin{align*} &\text{(a)} & &\text{(b)} & &\text{(c)} \\
&\text{O—H} & &\text{O}^- & &\text{H}^+ \\
&\text{O}^- & &\text{H}^- & &\text{O} \\
&\text{O} & &\text{H}^- & &\text{O}^+ \\
\end{align*} \]

The contribution of (c) was thought to be small for long H-bonds but more important in short hydrogen bonds.

Empirical calculations using quantum mechanics were developed, some of which helped in understanding hydrogen bonding but fell down in other respects. For instance, Pimentel's molecular orbital approach [12] failed to differentiate between hydrogen bonding in water and the different type of H-bond in FHF\(^+\). Other theories were postulated such as those by Hofacker [13] using localised orbitals and Paolini [14] using a three centre, four electron, molecular wave function, which postulated that p-orbitals on hydrogen might play a vital rôle in H-bonding, but this p-orbital effect was shown to be small if not non-existent in latter studies [15]. Figure 1.3 shows the electron density maps for water; a showing the total density change clearly showing the global features of the electron distribution due to hydrogen bond formation and b shows the electron density change due to charge transfer or delocalisation interaction and demonstrates the charge migration from the proton acceptor to the proton donor. Morokuma et al. [16] concludes "that the increase in density around the mid-point of the O---H unit in a is mainly due to the delocalisation of electrons for a covalent formation aided by the polarisation of the proton acceptor". Figure 1.4 shows a molecular orbital diagram for the hydrogen bond, showing that quantum mechanics can easily be adapted to explain such phenomenon.
FIGURE 1.3
Electron density maps of water (dimer).
FIGURE 1.4
Shows a qualitative molecular orbital diagram for the hydrogen using sp³ hybridised orbitals, thus minimising the lack of orthogonality in the orbitals described; (a) represents H₂O sp³ hybrid, (b) the interaction of sp³ on H₂O with the s orbital on an incoming hydrogen. The dotted electrons represent the electron density on this hydrogen forming the 'σ*' antibonding orbital and 'σ the bonding orbital, (c) represents the formation and position of the nodal planes in 'σ*' and 'σ.'
Water and alcohols have proton donating and accepting groups, hence show extensive self-association which has a significant effect on their physical properties. Other molecules may only possess one or other of these groups. These are not H-bonded in the pure state, but readily associate via H-bonds with other bases or acids. Hydrogen bond energies result in self-associated molecules having relatively high melting and boiling points and low vapour pressures. Self-association also results in a high dielectric constant and change in dipole moment. Gutmann [17] and Taft et al. [18,19] classified the relative acidity or basicity for hydrogen bond acceptors and donors. X-ray diffraction [20] has shown the oxygen to oxygen distance in O-H...O interactions to be between 0.24 and 0.33 nm with the bond angle, $\theta$, between 140° and 180°.

Pure electrostatic attraction would not have such directional and nuclear-separation limits.

1.3 THE STRUCTURE OF WATER

The structure of liquid water can be encompassed by two broad categories; the 'mixture' model and the 'continuum' model. Quantum mechanical calculations [21-24] offer a good description of the structure and properties of water.

The polarity of the OH bonds make the OH protons slightly acidic. The oxygen can behave as a dibase due to the availability of the two lone
pairs of electrons. Tusi et al. [25], using IR data from matrix isolation techniques, support the idea of the water dimer being 'linear'. It is important to note that two H-bonds to the oxygen are expected to lie close to the tetrahedral direction, however one H-bond to oxygen need not lie along the Td direction. The Ice 1h structure is that of a perfect H-bonded network. Elevating the temperature results in melting, i.e. a phase change occurs which alters the symmetry. The H-bonds, either distort or break, it is debatable as to which predominates which leads on to the two main categories for models describing the structure of liquid water.

1.3.1 The Mixture Model

Mixture models envisage equilibria between distinct hydrogen bonded species and, in some cases, monomers that are distinguishable in an instantaneous picture. There are two limiting cases; (i) bonds break to a large extent, thus each water molecule may be involved at any instant in 4, 3, 2, 1 or 0 bonds and (ii) structure models, i.e. flickering clusters, interstitial models. The simplest mixture models are those in which only two species are required, i.e. a dense phase and an ice-like phase. The most important mixture model is that proposed by Frank and Wen [26,27]. They envisaged cooperatively bonded water existing in clusters of ice-like material surrounded by, and alternating roles with, disordered fluid, which made up the rest of the system, and called it the "flickering cluster" model. The lifetime of the cluster was estimated at $10^{-10}$-$10^{-11}$ seconds from dielectric relaxation experiments. Figure 1.5 shows a water cluster model based on the "flickering cluster". The "flickering cluster" idea is a useful one for explaining some of the properties of water that are physically unreasonable.

Eyring et al. [29] assumed two species of solid-like molecules existed
**FIGURE 1.5**

Water cluster model of Nemethy and Scheraga [28], based on the "flickering cluster".
in equilibrium. The first structure was a cage-like cluster of approximately 46 molecules with a density of Ice I, dispersed in an Ice III-like structure with an equilibrium established between both species. On melting, most of the Ice I structure reformed into the denser Ice III structure, the former having almost disappeared by 4°C. Wada [30] wrote that water equilibrated between two states, \((\text{H}_2\text{O})_{\text{icy}}\) with a lower density and \((\text{H}_2\text{O})_{\text{packed}}\) with a higher density. The equilibrium shifted towards the latter species as temperature increased. Some workers thought that ice-like lattices persist into the liquid state [31] with monomeric water molecules in the interstitial cavities of the lattices [4,32]. Nemethy and Scheraga [28] suggested that the average cluster size decreases from 91 to 25 in the 0-70°C temperature range, using a semi-quantitative analysis. However, Lentz et al. [33] suggested that clusters are small containing about 7 or less \(\text{H}_2\text{O}\) molecules. Another model related to the mixture model was proposed by Pauling [34,35]. He suggested that water formed clathrate cages and that monomeric \(\text{H}_2\text{O}\) molecules occupy the guest sites. Figure 1.6 shows a possible framework of hydrogen bonded water molecules, adopting Pauling's model and Figure 1.7 shows an example of a water clathrate 'cage' structure.

1.3.2 The Continuum Model

Continuum models are single state models with each molecule considered to be in a similar structural position to all others, which may vary with temperature as bonds break or lengthen and distort [36,37]. Morgan et al. [31], using X-ray diffraction, described water as being a partially four-coordinated tetrahedral structure with continuously changing neighbours trying to achieve full bonding. Pople [37] claimed the majority of hydrogen bonds were distorted rather than broken. He used statistical mechanics to obtain satisfactory quantitative comparisons with various
FIGURE 1.6
Possible framework of hydrogen bonded water molecules - Pauling [34].

FIGURE 1.7
An example of a water clathrate 'cage' structure. The water molecules are hydrogen-bonded in such a way that the framework produces a cavity or 'hole' in which the cation (in this example R-N⁺) where R is an alkyl group) can 'sit'.
properties, e.g. radial distribution function, density changes in the Ice-Water transition and dielectric constants. Naberukhin et al. [38] reported that their calculations suggested the existence in water of a continuous distribution of hydrogen bonds with respect to energy (over a temperature range of 0-400°C) hence supporting the continuum model. Substantiating evidence for a continuous model for liquid water is provided by Khukovskii [39]. Infra-red spectral data supports the proposition on the presence in liquid H₂O of a continuous statistical distribution with respect to energy and geometrical parameters of H-bonds.

1.4 COMPUTER EXPERIMENTS

The behaviour of an assembly of water molecules was analysed by Rahman and Stillinger [40], by means of a molecular dynamics simulation. The approach used is fundamentally different from the models discussed previously. An ensemble of 216 molecules was treated in a fixed volume corresponding to the density of 1g/cm³. The motion of the molecules is calculated using classical dynamics. The static structure is described in terms of various radial and angular pair correlation functions, which provide a description of the system. A strong tendency towards tetrahedral coordination is seen. The correlations become weaker and the number of nearest neighbours increases with temperature, as expected. Second neighbours are also strongly correlated which confirms the persistence of a H-bonded lattice in the liquid, with strong distortions as indicated by large angular deviations from the ideal H-bonding directions. However, there are also contacts between pairs of molecules which do not form a hydrogen bond. Analysis of the distribution of pair interaction energies indicates that 3-bonded molecules are most frequent. Some molecules have more than 4 neighbours. The calculations reveal a
picture of a "random, defective, and highly strained network of hydrogen bonds that fills space rather uniformly". Stereoscopic pictures of the molecular configurations indicate no long-range correlations, strong local tetrahedral coordination and the presence of non-bonded OH groups. No evidence was seen for a partitioning of molecules into two classes, i.e. bonded and unbonded, as postulated in two-state theories, nor for the presence of definite clusters with anomalous densities or with ice I-like structure, nor for interstitial molecules and clathrate-like structures, nor for interpenetrating H-bonded networks. Hence computer experiment results favour a non-structured "continuum" and would appear to eliminate structure models, i.e. flickering clusters. Most models are limited in scope because they treat only some of the observed features of water. They give partial descriptions of what water may be like [41].

1.5 THE (OH)\text{free}/(LP)\text{free} CONCEPT

Because of a close link between the narrow feature at ca. 1416 nm in the first overtone spectrum of water and the gas phase monomer band, it was originally assumed this band was due to monomers and so supporting the flickering cluster model [26]. However, recently, Symons et al. [42] state that, in view of the scavenging ability of water, monomeric molecules have undetectably low concentrations at ambient temperatures [43]. Careful study of the water spectrum in this region supported this contention [44]. The existence of significant concentrations of non-H-bonded or monomeric water molecules in liquid water has been claimed and disclaimed on many occasions. Although many models for liquid water do not require the presence of significant concentrations of monomer, a few do depend upon the presence of appreciable monomer concentration. These all stem from Pauling's suggestion [35] that water can be pictured in terms of 'gas
hydrate' voids largely occupied by monomeric water molecules'. This idea has been extended by Frank and Quist [5] and others [26,28] and, in some ways, comparable to the vacant lattice point model of Forslind [4].

Infrared and Raman spectroscopy are the most productive techniques for producing evidence of non-bonded OH groups. Many published results indicate the presence of (OH)$_{\text{free}}$ groups in considerable concentration, i.e. molecules having three or fewer H-bonds to neighbours with one proton not involved in H-bonding. However the number of residual H-bonds is unspecified. Hence some workers assume that bands assigned to (OH)$_{\text{free}}$ groups are for units having three H-bonds [45]. Walrafen [46] uses the term 'Free OH groups' without further specification. Bonner and Woolsey [47] assume the data relates to monomeric water, while McCabe et al. [48] interpret results in 'single H-bonded' terms. Kleiss, Strobel and Symons [44] re-define (OH)$_{\text{free}}$ groups as describing water molecules that have one proton H-bonded and the other not so bonded.

There are many theories on the structure of liquid water based on conflicting results and differing interpretations. A recent theory is presented by Symons [42] who envisages water as a three-dimensional network involving units linked together with 4, 5, 6 and 7 ring systems, distinguishable but not of any particular significance since they must be quite haphazardly stuck together [2]. Due to the continuous rapid motion of these molecules, H-bonds are subject to constant strain, thus they bend, stretch, and occasionally break. Symons says their ability to move is enhanced by exchange processes involving bifurcated H-bonds (Figure 1.8). These are thought to be weak interactions with very short lifetimes in the continuously moving system.

A consequence of (OH)$_{\text{free}}$ groups being assigned in the structure of water is that lone-pair free groups must exist in equivalent amounts [42].
FIGURE 1.8
Mechanism for exchange of (OH)_free and (LP)_free groups via bifurcated bonds.
As yet, no method has been found of detecting the presence of (LP)\text{free} groups in water, although they have been characterised by Symons et al. [49] in the IR $v_{\text{OH}}$ stretch region for methanol and triethylamine systems (1.9) and also in the overtone region [50]. Further, they suggest that (OH)\text{free} and (LP)\text{free} groups are present at about 8% concentration in liquid water at room temperature. They postulate a simple equilibrium to account for the presence of (OH)\text{free} groups, i.e. a simple mass law description:

$$(\text{H}_2\text{O})_{\text{bulk}} \rightleftharpoons (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}}$$

When an electrolyte is dissolved in water, cations scavenge (LP)\text{free} groups and anions scavenge (OH)\text{free} groups [51];

$$M^+ + [(\text{LP})_{\text{free}}]_n \rightarrow M^+ - - (\text{LP})_n$$

$$A^- + [(\text{OH})_{\text{free}}]_n \rightarrow A^- - - (\text{HO})_n$$

The net effect is a gain or loss of [(OH)\text{free}] groups as measured by vibrational spectroscopy.

1.6 AQUEOUS SOLVATION

1.6.1 Non-Electrolytes

These can be classified into two main categories: (i) those not interacting specifically with solvent and (ii) those interacting with solvent.

(i) Non-Interacting Solutes

These solutes cannot integrate into the three dimensional structure of water, hence are largely rejected and have low solubilities. Water tries to form clathrate-type cages around the solutes, but entropy opposes this and clustering and phase-separation result.

(ii) Interacting Non-Electrolytes

Non-electrolytes containing an acidic or basic functional group can form H-bonds to the basic oxygen or acidic proton of water, thus producing
FIGURE 1.9
Infrared spectrum in the O-H stretch region for MeOH and Et$_3$N systems: 0.7 MF MeOH showing features assigned to $I$, (LP)$_{\text{free}}$ groups, II, Et$_3$N-HOMe---units and bulk MeOH (central band).
1.6.2 Electrolytes

When an electrolyte dissolves, the solvation energy must be sufficient to overcome the high lattice energy. The solvation energy is the energy difference between the gas phase and hydrated species. In ideal electrolyte solutions, i.e. with negligible ion-ion interactions, the solute can be considered as having unit activity. This is valid only for dilute solutions. The solvent is assumed to be a dielectric continuum. The Born equation [52] can then be used to calculate the free energy of solvation:

\[ \Delta G^\circ = -N \frac{(Ze)^2}{2r} \cdot (1-1/\varepsilon) \]

where:
- \( \Delta G^\circ \) = Partial molar free energy
- \( N \) = Avogadro's number
- \( Z \) = Ionic charge
- \( e \) = Electronic charge
- \( r \) = Ionic radius
- \( \varepsilon \) = Dielectric constant of the medium

Also:
\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]

where:
- \( \Delta H^\circ \) = change in molar enthalpy
- \( T \) = temperature of the system
- \( \Delta S^\circ \) = change in molar entropy

Thus enthalpy and entropy changes of solvation are also related to the ionic radius and dielectric constant of the medium. However, applying theoretical treatments to aqueous solutions presents problems, since Walden's rules for ionic mobilities are not obeyed in water, indicating that the solvent cannot be considered as a dielectric continuum [53].
Also, an 'effective ionic radius' is used, which has an incremental addition to the measured radius in order to obtain agreement between calculated and observed results. Changes have been made to the Born equation to include solvation numbers and dipole moments to explain aqueous solvation [11,54].

A commonly used model for ionic solvation was put forward by Frank and Wen [26] which defines three regions of molecules around an ion in aqueous solution:

A simple model for the structure modification produced by a small ion.

In region A, water molecules are electrostricted due to the alignment of their dipoles under the influence of the ion. Region B consists of several molecule layers of unstructured disordered solvent and region C is bulk solvent unperturbed by the ion. The decrease in entropy with ionic volume for these schemes can be explained by the disordered zone decreasing and disappearing for small ions such as $F^-$. These ions are called "structure makers". It has been noted that larger cations and anions produce a decrease in order - these are called "structure breakers" [55].
Symons et al. [2] criticised the concept of structure making and breaking. He suggests that anions are hydrogen bonded to a number of water molecules corresponding to their solvation numbers, also these hydration sphere molecules are further hydrogen bonded to bulk water. This implies that the disordered water region invoked to explain entropy increase on solvation, is not present. Entropy changes described in terms of structure making and breaking are explained by the increase or decrease in H-bond strengths to the dissolved ion, rather than a net gain or loss of hydrogen bonds. In the case of tetraalkylammonium cations, $R_nN'^+X^-$, to a first approximation the relatively smaller anion undergoes solvation to a greater extent thus producing a loss of $(\text{OH})_{\text{free}}$ groups. The relatively larger cation is unable to form H-bonds, i.e. it is more a question of "no points of attachment" rather than mere size. Conversely, large anions, i.e. Na$^+\text{BPh}_4^-$ undergo negligible solvation relative to the smaller more active Na$^+$ cation, resulting in a loss of $(\text{LP})_{\text{free}}$ groups and a gain in $[(\text{OH})_{\text{free}}]$. 

\[ \text{i.e.} \quad \text{Na}^+ + (\text{LP})_{\text{free}} \rightarrow \text{Na}^+ - (\text{LP})_{\text{free}} \]

\[ \text{BPh}_4^- + (\text{OH})_{\text{free}} \leftrightarrow \text{Negligible solvation} \]

Figure 1.10 shows a pictorial model for ionic solvation [61].

1.6.3 Hydrophobic Interactions of Polar Molecules

Polar solute molecules which have large non-interacting regions are envisaged as being enclosed in a clathrate of tetrahedrally bonded water molecules [2, 56-58], with its polar region directly H-bonded to the solvent. A good example is found in the case of water/t-\text{BuOH} [59, 60] where a significant downfield shift is observed on monitoring the NMR hydroxyl resonance in the water rich region. Clathrate cage formation is only thought to occur at low concentrations of solute in water. As the
FIGURE 1.10
Model for Ionic Solvation.
(a) is the primary hydration shell,
(b) are Franck-Wen clusters,
(c) is broken water structure,
(d) is normal water.
solute concentration increases, there are insufficient water molecules to enclose the solute. This gives rise to the tendency of shared cages, thereby giving rise to the phenomenon of hydrophobic bonding.

1.7 THE STRUCTURE OF METHANOL AND ALCOHOLS

Studies of the crystal structure of solid methanol show a "linear" arrangement of methanol molecules [62,63].

\[
\text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\
\quad \longrightarrow \text{O-H} \quad \longrightarrow \text{O-H} \quad \longrightarrow \text{O-H} \quad \longrightarrow \text{O-H} \\
\]

Methanol can be considered as a derivative of water but with one proton replaced by a methyl group. Methanol molecules are tri-functional, offering two basic sites for bonding, although generally only one is used, thus displaying only minor cross-linking. Methanol has a two-dimensional structure compared to water which is three-dimensional, consequently methanol studies are simplified compared to those for water.

It has been suggested that unrestrained cyclic rings or chains of 4-7 molecules may represent the majority of species in liquid methanol at room temperature. Choppin [64] calculated that methanol is about 80% H-bonded at 25°C, however unlike water, the methanol overtone spectrum only shows a small shoulder at ca. 1410 nm, which may be attributable to (OH)$_2$ free groups [64,65]. The HOD overtone spectrum shows a much stronger absorbance in this region, assigned to (OH)$_2$ free groups thought to be present at about 8% concentration, and also very weakly H-bonded species. Symons [42] postulates that the absence of detectable (OH)$_2$ free groups is due to weak bonding between (OH)$_2$ free groups and the second available lone-pair of electrons on oxygen.
Simple aliphatic alcohols and water have similar proton donating abilities [17-19,66,67]. It is thought that solvation of both anions and non-electrolytes by methanol occurs via H-bonds in a manner similar to that shown for water.

It is considered generally that most alcohols have a similar structure to methanol. However, those containing large alkyl groups, i.e. t-BuOH, have a larger concentration of terminal groups. Spectroscopic evidence can be seen in the form of large narrow features in the overtone region of t-BuOH at ca. 1416 nm, and also for ¹PrOH although to a lesser extent and EtOH even less. Fluoroalcohols also show strong narrow features in the overtone indicating a high concentration of (OH)\text{free}, particularly in the case of hexafluoroisopropanol (see Chapter 7), where two 'free' conformers give rise to about 23% (OH)\text{free} and very little strong H-bonding is observed, there being a small absorbance in the bulk region at ca. 1575 nm.

1.8 HYDROGEN BOND STUDIES USING THE INFRARED TECHNIQUE

The theoretical basis of infrared spectroscopy is well documented, hence only its application to H-bond studies is mentioned here. When a molecule forms a H-bond, i.e. A-H---B, the A-H bond is weakened and lengthened resulting in a decrease in its vibration energy. Hence a shift to lower frequency is observed. The resulting band is usually broad, enveloping all the absorptions from the many H-bonded species in solution.
In general, only the transitions from the ground state are seen in the fundamental region. The low resolution means it is difficult to determine concentrations of individual or unique species in the fundamental region [68]. The first overtone region is more useful for H-bond studies since it aids resolution, i.e. the decrease in sensitivity is greater for the "bulk" bands than for the (OH)_{free} band. In the first overtone region the separation of the "bulk" and (OH)_{free} bands is almost doubled and enhanced, allowing the (OH)_{free} peak to be seen much more easily [64,69]. In the second overtone region, intensities are very weak and require longer pathlengths. Figure 1.11 shows the change in band shape for the spectrum of HOD in D_{2}O, on going from the fundamental IR region (3700-3000 cm^{-1}) through the first overtone region (7690-6060 cm^{-1}) and into the second overtone region (12500-9090 cm^{-1}). The band shapes clearly show how (OH)_{free} and very weakly bonded species absorb more intensely in the overtone regions, the 3\nu_{OH} band more so than the 2\nu_{OH} band, compared to the fundamental which favoured 'bulk' H-bonds.

![Diagram of band shapes](image)

**FIGURE 1.11**
The fundamental, first and second overtone bands of HOD in D_{2}O at room temperature.
1.9 THE USE OF NUCLEAR MAGNETIC RESONANCE

NMR studies of H-bonding are numerous and the subject has been extensively reviewed [10, 60, 70]. The nuclear magnetic resonance technique is used in this work to complement infrared spectroscopy. The most useful parameter obtained from proton NMR studies of hydrogen bonding is the chemical shift. Hydrogen bonded proton magnetic resonance shifts are to lower field relative to the unassociated state. The shift is proportional to the energy of the H-bond to the proton observed. NMR spectra for H-bonding protons are often single peaks resulting from several time averaged absorptions over the relatively large NMR time scale of about $10^{-2}$ s. For example, water shows one peak which is the weighted average of bulk H-bonds, (LP)$_{\text{free}}$ and (OH)$_{\text{free}}$ groups:

The (OH)$_{\text{free}}$ groups present in water are the main upfield contribution to the observed $\delta$(H$_2$O) resonance and bulk H-bonds are the major downfield contribution. Adding base to water results in a loss of (OH)$_{\text{free}}$ but a gain in (LP)$_{\text{free}}$ and B$^-$--HO species which occur close to the $\delta$(H$_2$O) position. Thus the net result is usually a negligible shift or a small upfield one. In electrolyte solvation studies, attempts have been made to isolate individual ion contributions to the overall shift of the observed hydroxyl resonance [71-73]. This can be achieved by constructing an IR/NMR correlation plot to enable NMR shifts to be estimated for
species whose IR shift is known but for which no NMR shift is known. By
determining the NMR shifts of H-bonded species, i.e. A$^-$$^\ldots$HO, B$^-$$^\ldots$HO,
it is possible to explain solution shifts by using a model which accounts
for anion and cation hydration and changes in \([\text{OH}]_{\text{free}}\) and \([\text{LP}]_{\text{free}}\). Such a correlation has already been constructed for methanol [74] which
ultimately leads to the calculation of anion and base solvation numbers
in MeOH. Chapter 9 in this thesis describes the construction of a novel
IR/NMR correlation plot for water which is used to convert IR parameters
into previously unknown NMR parameters for H-bonded species, i.e.
B$^-$$^\ldots$HO, A$^-$$^\ldots$HO, and ultimately is used to calculate aqueous solvation
numbers by using a model designed to account for hydration species and
changes in \([\text{OH}]_{\text{free}}\), \([\text{LP}]_{\text{free}}\). The latter terms play an important
rôle in explaining the observed solution shifts.
REFERENCES FOR CHAPTER 1

REFERENCES FOR CHAPTER 1 (Continued)

REFERENCES FOR CHAPTER 1 (Continued)


CHAPTER 2

Instrumentation and Experimental
2.1 INTRODUCTION

Fundamental Infrared spectra in the OH and C=O stretch regions were recorded on a Perkin-Elmer 580 spectrometer. First and Second Overtone spectra were run on a Perkin-Elmer 340 UV/VIS/NIR spectrometer. All NMR spectra were obtained from a Jeol PS 100 NMR spectrometer.

2.2 INSTRUMENTATION

2.2.1 Perkin-Elmer 580 Spectrometer

The Perkin-Elmer 580 spectrometer [1] is a double beam, ratio recording instrument using a four-grating spectral splitting system through its frequency range of 4000 to 200 wavenumbers, with a "live" zero and single beam facility. It has a dual chopping system, exposing the sample to the source for one quarter of the time and eliminating the measured re-radiation from the sample or reference.

It has a Grating Littrow type monochromator with an accuracy of 0.4 % T over the 4000-700 cm\(^{-1}\) region. It has a self-igniting, self-regulating 4.5 mm Opperman source. The detector is a vacuum thermo-couple with a Caesium Iodide lens. Precise measurements were obtained by using the variable abscissa and ordinate expansions together with wavenumber markers displayed every 100 cm\(^{-1}\) from 4000-2000 cm\(^{-1}\) and every 50 cm\(^{-1}\) from 2000-180 cm\(^{-1}\). The accuracy of the marker can be checked using an absorbance band from a polystyrene film sample.

All scan speeds, slit widths and noise filtering are integrated into one control. The instrument has a recirculating air-drier which purges the sample compartment during use. Demountable Beckman RIIC FH-01 cells with teflon spacers, stainless steel vented screw plugs and silica and calcium fluoride windows were used for most of the fundamental work. Matched windows were used in the reference beam. For pathlengths greater or equal to 1 mm, a matched pair of Hellma silica fixed path-
length cells were used.

Variable temperature studies in the fundamental IR region were obtained using a Specac 20.000 variable temperature unit, for use with the Beckman demountable cell. [It covers the range 450 K to 83K.]

Figure 2.1 shows a diagram of the variable temperature unit. The cell is locked into a stainless steel cell holder and refrigerant vessel (Figure 2.1a), which has facilities for connecting a vacuum pump (1), heaters (2) and thermocouple lead (3). The copper-constantan junction thermocouple is placed directly into the access hole in the cell (4) for accurate temperature measurement.

The variable temperature unit is then sealed in a chrome-plated nickel outer jacket (Figure 2.1b) with sodium chloride windows heated to ambient temperatures to prevent atmospheric condensation. It is aligned in the spectrometer cell compartment by using the back-plate (5). A vacuum pump is connected to the outlet pipe (1) on the top plate and the unit evacuated to 0.1 mmHg pressure. For low temperature work, liquid nitrogen is used in the refrigerant chamber. A Specac 20,100 temperature controller with a range between 83 K and 523 K to an accuracy of ±1 K is used to thermostat control the temperature.

2.2.2 Perkin-Elmer 340 UV/VIS/NIR Spectrophotometer

This is a microprocessor-controlled recording spectrophotometer [2], with a 16 bit microcomputer which monitors all instrumental functions, such as transmittance, absorbance, baseline corrections and all other control functions, i.e. wavelength scanning and slit width control. It incorporates a two-stage monochromator, the first being a quartz prism Littrow monochromator after which the source energy passes through a dual grating monochromator. A lead sulphide cell is used as the detector in the NIR with a tungsten lamp as the light source. In the
FIGURE 2.1
SPDCAC 20.000 variable temperature unit a - inner refrigerant vessel, b - outer jacket.
UV/visible region detection is via a photomultiplier.

Figure 2.2 shows the functional block diagram for the P.E. 340. The instrument has a wavelength range of 190-2600 nm, which encompasses the Near-Infrared region (800-2600 nm) and the UV/VIS region (190-850 nm). The wavelength accuracy is to within ±1 nm at 20º ± 5ºC and the wavelength reproducibility better than 0.5 nm. The photometric scale is accurate to ±0.3% T with the reproducibility better than 0.15% T. The baseline flatness is to within ±0.002 A with a stability of 0.0004 A/hr after a 3 hr warm up period. The operator can select any one of the nine different scan speeds and also any intermediate multiples of ordinate expansion between 0.00 to 9.99. Upon switching the P.E. 340 on, the computer surveys the complete spectral range, storing any noise and atmospheric absorptions in its memory, thus producing a flat baseline. Quartz/glass cells can be used in the NIR region with little or no absorbance, although any signals from the cells can be incorporated into the baseline correction by the computer.

Required temperatures can be set manually on the temperature control unit. The cells are housed in a copper block which contains the heater and thermocouple. Heating is accomplished by a heating coil around the copper block, whilst cooling is achieved by adding Drikold refrigerant to a copper shroud covering the block. Temperatures accurate to ±0.1ºC can be thermostatically obtained over the -100 to +100ºC range of the system.

2.2.3 Jeol PS 100 Spectrometer

A simple diagram of the instrument is shown in Figure 2.3 [3]. The Jeol 100 MHz NMR spectrometer [4] consists basically of four parts, the spectrometer, excitation power supply, a variable temperature NMR probe and the electromagnet.
FIGURE 2.2
Functional Block Diagram of the Perkin-Elmer 340 UV/VIS/NIR Spectrometer [2].
FIGURE 2.3
Simplified diagram of a NMR spectrometer [3].
The radio frequency oscillator, the receiver and an external oscilloscope allowing a visual display of the spectra, are contained in the spectrometer. Also contained here is the supastabilizer, which detects and controls internal or external variations in the magnetic field occurring in the pole gap, the NMR control which compensates long-range stability with the external or internal lock systems, the resolution control used to compensate the field uniformity of the sample position, the integrator and the spin de-coupler which allows calibration of chemical shifts to be made.

The probe contains a cross coil type indicator incorporating two mechanisms. One rotates the sample on the Y-axis, the other a variable temperature control mechanism. Variable temperature work is achieved by using a JNM-VT-3C type controller attached to the probe [5]. It has a temperature range of -170° to +200°C and a stability of ±0.5°C. Low temperatures are achieved by using nitrogen gas evaporated from liquid nitrogen stored in a metal Dewar. Air from an air compressor, passed through a heat blasting pipe is used to achieve high temperatures. The temperature is automatically controlled.

The uniform field necessary for high resolution NMR work is provided by a low-impedance type electromagnet. The excitation power supply provides the stable electromagnetic exciting current.

Samples with a nuclei of spin $\frac{1}{2}$, when placed in the external magnetic field, can be aligned with or against the field. When the nuclei are aligned with the field, this is more stable, hence the corresponding energy level is more populated. If the nuclei absorbs radio frequency energy, then those aligned with the field become opposed to the field. The energy needed to "flip" the nuclei depends on the strength of the external field, i.e. the stronger the field, the greater the energy.
needed. Hence by keeping the radio frequency energy constant and varying the magnetic field at some value of field strength the energy needed to flip the proton matches the energy of radiation, thus absorption occurs, giving a signal. The frequency at which the proton absorbs, i.e. effective field, depends on its electronic environment.  

2.2.4 Purification of Materials

All materials used were of the highest grade obtainable and, where thought necessary, were purified further. This usually involved fractional distillation over CaH₂ and drying over CaH₂ or molecular sieves. Deuterated materials were purchased from the Aldrich Chemical Co. Ltd. or Merck Sharp & Dohme with an isotopic purity of 99%+. They were used without further purification. Water was purified by deionisation followed by passage through a millipore "Milli-Q" system. Preparation of solutions is explained in each chapter. Volumes were measured using Hamilton 2.5 ml gas-tight (series 1002), S.G.E. 10 microlitre and Eppendorf variable syringes. Salts were purchased from Aldrich Chemical Co. Ltd. and Fluorochem Ltd., in most cases at >98% purity. They were dried at an appropriate temperature, in vacuo for 48 hours before use and stored in a dessicator over silica gel or P₂O₅.

2.2.5 Use of Computers

Various programs written in FORTRAN and BASIC were used in this work. They were run on a CDC Cyber 73 mainframe computer incorporating a NOS operating system. The programs were used for calculating mole-fractions, molalities, least-squares analysis and graph plotting routines which used GHOST files. Graph plots were drawn on a CALCOMP 936 plotter. Deconvolution of spectra was achieved using a V.I.D.C.A. program (Visually Displayed Curve Analysis) [6], which was run on a DEC PDP 11/45 computer incorporating a RSX-11M operating system.
Spectra were digitised using a Ferranti-freescan cursor controlled
digitiser. A DEC GT 42 refresh display unit was used for visual
analysis and a DEC PDP 11/10 was the control unit linking with the
PDP 11/45. A CALCOMP 1012 plotter was used for plotting. The
deconvolution procedure is described in detail in Chapter 4.
REFERENCES FOR CHAPTER 2


[5] JNM-VT-3C, JEOL (Japan Electron Optics Laboratory Co. Ltd.).

CHAPTER 3

A Near-Infrared Study of Aqueous Electrolyte Systems
3.1 INTRODUCTION

This work comprises an investigation into salt effects on the Near-Infrared spectrum of HOD in D$_2$O in the Second Overtone region (1100-800 nm), (12500-9090 cm$^{-1}$). Infra-red fundamental and overtone regions show large differences over the hydroxyl stretching vibration for water or HOD, because signals from weakly hydrogen-bonded OH groups are more intense in the overtone regions, relative to the bulk water bands. The ratio of the intensities is inverse in the fundamental region. The difference is understood by selection rules governing overtone bands, if the anharmonicity (degree of allowedness) is greater for (OH)$_{free}$ groups, which accounts for the difficulty in obtaining evidence for a band associated with (OH)$_{free}$ groups in the fundamental region. This is shown by Luck [1] and Verrall [2] to be due to the width and intensity of the bulk water band. The fundamental thus favours strongly bonded species, while the overtone region favours weakly bound oscillators, (Fig. 3.1). A band assignable to (OH)$_{free}$ groups is found in the first overtone region at 1418 nm and in the second overtone at 960 nm [3]. Apart from the obvious advantage of detecting the presence of (OH)$_{free}$ groups, it is also possible to measure quantitatively more accurately in the overtone region. The photometric accuracy of the equipment is higher and the layer thicknesses which can be used in the absorption cells for investigating solutions lie in a more favourable range (1-10 nm) resulting in higher accuracy and reproducibility.

3.2 PREVIOUS WORK

Suhmann and Breyer [4] reported in 1933 that Near-Infrared bands of water are characteristically changed by the presence of dissolved electrolytes. Since then this technique has been used to obtain infor-
FIGURE 3.1(a)
Plot of optical density vs. frequency for the IR absorption of HOD at ~2500 cm⁻¹ for various temperatures [2].

FIGURE 3.1(b)
Absorbance vs. wavelength (microns) of a 6.0 molar solution of HOD in D₂O as a function of temperature [20].
FIGURE 3.1(c)
Change in the peak intensity of the water O-H stretch in 10% H2O/D2O with temperature.
mation about the structure of water in electrolyte solutions [5-10]. Many possible combination bands and overtones overlap in almost any portion of the water spectrum [11]. Hence absolute assignments of frequencies and intensities are difficult to accomplish. Study is confined to the investigations of relative spectral changes, such as those produced by changing the temperature or adding a solute.

3.2.1 Interpretation of Water Peaks

Regarding band assignments, Herzberg [12] claimed to have accurately established the positions of the fundamental and overtone bands of water vapour. In the first overtone region, Toth and Margolis [13] obtained the vapour phase spectrum of water showing five peaks, which are called various combination bands of \( \nu_1, \nu_2 \) and \( \nu_3 \) transitions, from the fundamental. McCabe et al. [14] studied the temperature effect on liquid water and found two bands present, one for water molecules with two 'OH' hydrogen bonds and the other for water with one 'OH' hydrogen bond at higher energy. Choppin et al. [15,16] identified three bands for pure water and water in inert solvents while investigating the \( \nu_1 + \nu_3 \) peak in the 7200-6500 cm\(^{-1}\), (1390-1540 nm) region and the \( \nu_1 + \nu_2 + \nu_3 \) peak in the 8700-8000 cm\(^{-1}\) (1150-1250 nm) range, naming these as water molecules with two, one and no hydrogen bonds. Bonner et al. [17,18] also identified three bands in the 8700-8000 cm\(^{-1}\) region. They interpreted the higher and lower energy bands as corresponding to the non-bonded and bonded hydroxyl groups of the 1:1 complex respectively, whilst the middle band was called the bonded hydroxyl groups of the 1:2 complex. Luck and Schiöberg [19] found three bands for HOD/D\(_2\)O in the first overtone region, describing them as corresponding to non-bonded hydroxyl groups at higher frequency and weakly bonded at lower frequencies.
Overtone work has led to much debate concerning the 1418 nm peak observed by Worley and Klotz [20], as to whether it is that of the water monomer or (OH)$_{\text{free}}$ species. Bonner and Woolsey [21] claimed from Second Overtone studies that this peak is due to the monomer. Luck and Ditter [22] claim the peak was due to (OH)$_{\text{free}}$ species as well as very weak hydrogen bonded 'OH' groups, while Kleiss, Strobel and Symons [23], concluded that the concentration of water monomer is negligible in water, based on Second Overtone studies.

3.2.2 Estimates for % (OH)$_{\text{free}}$ in Water

Investigations have been made on the temperature dependence of Infrared Overtone spectra of water by Luck [19]. Bonner [21] using a differential method for studying the temperature effect on water gives a value of approximately 6% for the concentration on non-bonded water at 25°C or approximately 12% (OH)$_{\text{free}}$. Bonner showed that hydrogen bonding increases in water on lowering the temperature. Similarly, Waggener [24] noted that the bands become sharper and shift to higher energy as temperature increases. Luck [25] estimates a value of 8-16% broken H-bonds in a HOD/D$_2$O mixture at 25°C from Near-Infrared work. Walrafen gives a value of approximately 10% [26], broken H-bonds from Raman studies, whilst Pauling [27] estimates 15% from a heat of melting study. A value of 8% broken H-bonds is given by Haggis [28] from dielectric constant work. All these values lead to an overall average value of approximately 8% broken H-bonds which is used in the analysis of the work in this chapter. As will be seen later in this work, this value of 8% gives the best fit between experimental and a theory developed herein.

3.2.3 Structural Temperature

Following Bernal and Fowler [29], Bunzl [8] describes the structural
temperature of a solution as the temperature at which pure water has the same degree of association. Jolicoeur [30] illustrated the qualitative similarity between the effects of the tetraalkylammonium ion and that of a reduction in temperature on the spectrum of water. Ideas concerning the formation of a more ordered water structure around the hydrophobic surfaces of these ions have been largely developed by Frank [31]. Within the series of tetraalkylammonium ions, the order of structural temperatures obtained by Jolicoeur is consistent with other workers results, notably Bunzl [8] and Walrafen [32]. Jolicoeur decided that the influence of cations on the water spectrum was small, but for anions it was found to be large. He assigned anions bonded to bulk water to be the cause.

3.2.4 Effect of added solutes on the (OH)_free band

The effects of tetrabutylammonium bromide and sodium tetraphenylboride have been compared by Jackson and Symons [33]. A decrease in (OH)_free group concentration is noted for the tetraalkylammonium salt and an increase for the sodium salt. He assigned the drop in (OH)_free to scavenging by the bromide ion only and an increase in (OH)_free from the sodium ion scavenging lone-pair groups, the tetraphenylboride ion being largely unsolvated. These results compliment those by Luck [34,35] in the first overtone and of Jolicoeur [36] and Bunzl [8].

Symons [37] argued recently that changes induced by added solutes in the (OH)_free band in the first overtone region can be understood in terms of a simple equilibrium:

\[(H_2O)_{\text{bulk}} \rightleftharpoons (OH)_{\text{free}} + (\text{LP})_{\text{free}}\]

He noted that to a first approximation, all basic aprotic solvents induce the same loss of (OH)_free groups. Rastogi [38] recently concluded that in general R₄N⁺ ions are not solvated due to their large size and
low surface charge density. However, there is a suggestion that large
tetraalkylammonium cations invoke cage formation in the water structure,
which would shift the equilibrium back towards bulk, hence this has to
be considered, although it is assumed $R_nN^+$ cations undergo negligible
solvation relative to the anions.

3.2.5 Solvation studies using Diffraction Techniques

Comparisons of results for hydration numbers can be made with other
areas of chemistry. Symons' result for the chloride ion is in good
agreement with recent results from neutron scattering studies by
Enderby [39]. Narten [40] has also shown the chloride ion to have a
hydration number of six. Recent neutron diffraction work by Newsome
et al. [41] showed that the solvation number of Li$^+$ varies with
concentration in D$_2$O. They conclude that the hydration number is
significantly less than four at high concentrations, (10M), but
increases to 5.5±0.3 at lower concentrations, (3.6M). This latter
number is consistent with the molecular dynamics study made by Vogel
[42] but does not support the tetrahedral model proposed by Michaelian
and Moskovits [43]. Narten et al. [40] found the coordination around
Li$^+$ to be tetrahedral for water. Newsome [41] also adds that Li$^+$
orientates water in a similar way to Ca$^{2+}$ and Ni$^{2+}$ at low concentrations
and has found evidence for a further shell of weakly coordinated water
molecules at 4.5 Å which contrasts with the situation for Cl$^-$, where no
such effect exists. Investigations by Hewish et al. [44] using neutron
scattering techniques, indicate that the number of D$_2$O molecules which
coordinate to Ca$^{2+}$ are strongly concentration dependent. Results
indicate the Ca$^{2+}$ solvation number increases from six to ten as the
molality decreased from 4.5 to 1 and also that the Ca$^{2+}$ ions are weakly
hydrating in solution. Thus the concentration dependence of the Ca$^{2+}$
solvation number ties in with that for Li⁺ as observed by Newsome [41]. As a consequence of this it is important to monitor only the initial change in the water second overtone spectrum on adding electrolytes. Hence this work concentrates on salt effects at low salt concentration on the 3νOH water spectrum measuring only the initial drop or gain in (OH)\text{free} concentration.

3.2.6 (OH)\text{free} and (LP)\text{free} scavenging vs structure making and breaking

An interesting effect on the spectrum of liquid water is found in perchlorate studies. Symons and Waddington [45] calculated a hydration number of four for aqueous perchlorate ions using a high frequency peak previously studied by others. They assigned the high frequency component to the O-D stretching mode of HOD water molecules hydrogen bonded to perchlorate ions. Walrafen [46] carried out Raman work on perchlorate salts in H₂O, D₂O and HOD solutions and claimed that the perchlorate anion was a structure breaker since a band appeared at the monomer side of the main water peak as perchlorate is added.

A review by Symons [33] disclaimed the use of structure breaking and making concepts. He put forward an alternative explanation for results, showing trends for various structure makers and breakers produced by McCabe and Bonner [47,48].

\[
\begin{align*}
\text{Li}^+ & > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ & \text{structure makers} \\
\text{ClO}_4^- & > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^- & \text{structure breakers}
\end{align*}
\]

Symons [49,50] claims that scavenging of (OH)\text{free} groups by anions or bases and (LP)\text{free} groups by cations or acids to give water-solute H-bonds are responsible for the changes in the water peaks. He has also stated that weak hydrogen bonding between (OH)\text{free} groups and anions or bases can cause the growth of a band close to the (OH)\text{free} band, resulting in the apparent increase in the (OH)\text{free} peak and so an
incorrect assumption of structure breaking. Generally the concept of 

(\text{OH})_\text{free} \text{ and (LP)}_\text{free} \text{ scavenging appears to give a more accurate explanation of results obtained, rather than the concept of structure making and breaking.}

3.2.7 The Use of HOD rather than H$_2$O

HOD solutions are used rather than H$_2$O, as is used by other workers in overtone studies. For water \(v_1 + v_3\) are coupled vibrations and since the extent of coupling varies with hydrogen bonding, it is best to remove the coupling using HOD. In the first overtone for H$_2$O, the $2v_2$ bend overlaps with $v_1$ producing an enhanced Fermi resonance peak. This problem is also removed by using isotopically dilute solutions of HOD in D$_2$O. In the HOD molecule, the three vibrational modes appear in separate regions of the spectrum and are not coupled together, thereby greatly simplifying spectral interpretation.

3.3 EXPERIMENTAL

All spectra were recorded on a Perkin-Elmer 340 UV/VIS/NIR spectro-photometer. In the second overtone study [3\(\nu\)(OH)$_\text{free}$ = 960 nm], a stock solution of 20% H$_2$O/D$_2$O \%v was used since the second overtone peak intensity is much less than in the first overtone region [2\(\nu\)(OH)$_\text{free}$ = 1405 nm]. Solutions recorded in the first overtone region contained 3% H$_2$O/D$_2$O \%v.

Second overtone solutions were made up using a constant volume of HOD stock - 2.5 mls in the sample solutions, adding a known volume of salt/D$_2$O solution, then making up to 5 mls with a weighed amount of D$_2$O. Salt/D$_2$O stock solutions were made up of fixed concentrations. Hence by adding increasing volumes of salt/D$_2$O to each sample, the molefraction of salt could be calculated accurately. The reference solutions were made up using a known volume of salt/D$_2$O solution and making up to 5 mls
with D$_2$O, the volumes of salt/D$_2$O solutions being equal in sample and reference solutions. First overtone solutions were made up the same way except that 2 mls of HOD stock were used in each sample solution. It is useful to keep the concentration of OH oscillators constant in each sample so that effects on the spectra are due to the salt and not to an imbalance of OH oscillators. All spectra were recorded at 25°C ± 0.1°C. H$_2$O was purified using a 'Milli-Q' system and D$_2$O (99.8%) was used without further purification. Salts used were dried for 48 hours under vacuum at elevated temperatures, except for tetraalkylammonium salts which melt at moderate temperatures. All salts were stored under vacuum in a dessicator over silica gel, and samples prepared in a dry box under a nitrogen atmosphere. All second overtone spectra were recorded using a photometric scale of 0-0.02 absorbance units and an expansion of ×5, over the 1100-800 nm range, using quartz cells with a pathlength of 1 cm. First overtone spectra were recorded over the 1650-1300 nm region with a photometric scale of 0-0.8 using cells with a 2 mm pathlength and an expansion of ×5. A scan time of 3 minutes was used to record all spectra. Before each series of runs, any absorbance by the cells was added into the baseline correction.

3.4 RESULTS

The effect of electrolytes on the first and second overtone spectra of HOD in D$_2$O at 5°, 25° and 50°C are shown in Figures 3.4 (i)-(vi). The spectra obtained were superimposed on each other to see the effect of added salt over a molefraction range. The solubility of the salts in HOD determined the range used, although only the initial 0-0.015 salt molefraction is actually measured. Examples of overlayed spectra are shown in Figures 3.4 (vii)-(x). The results at 5° and 50°C show similar trends to those observed at 25°C.
FIGURE 3.4(i)
Change in the 3νOH peak intensity measured relative to pure HOD (20% H2O/D2O) in D2O, on addition of various salts.
Temperature = 25°C ± 0.1
FIGURE 3.4 (II)
Change in the 3νOH peak intensity measured relative to pure HOD (20% H$_2$O/D$_2$O) in D$_2$O, on addition of various salts.
Temperature = 25°C ± 0.1
Change in the 3vOH peak intensity measured relative to pure HOD (20% H2O/D2O) in D2O, on addition of various salts.

Temperature = 25°C ± 0.1
FIGURE 3.4(iv)
Change in the $3\nu_{OH}$ peak intensity measured relative to pure HOD (20% H$_2$O/D$_2$O%v) in D$_2$O, on addition of various salts.
Temperature = 50°C ± 0.1
FIGURE 3.4(v)
Change in the 3υOH peak intensity measured relative to pure HOD (20% H2O/D2O) in D2O, on addition of various salts.
Temperature = 5°C ± 0.1
FIGURE 3.4(vi)
Change in the 2νOH peak intensity measured relative to pure HOD (3% H₂O/D₂O) in D₂O, on addition of various salts.
Temperature = 25°C ± 0.1
FIGURE 3.4(vii)
Change in the 3νOH peak of HOD (20% H₂O/D₂O) on addition of NaClO₄.
Temperature = 25°C ± 0.1
FIGURE 3.4(vii)
Change in the 3\(\nu\)OH peak of HOD (20\% H\(\text{O}\)/D\(\text{O}\)/0\%) on addition of BeCl\(_2\).

Temperature = 25\(^\circ\)C ± 0.1

Molefraction BeCl\(_2\)
1. 0
2. 0.0140
3. 0.0220
4. 0.0290

Absorbance

Nanometers (nm)
FIGURE 3.4(ix)
Change in the 3\nuOH peak of HOD (20% H2O/D2O\%v) on addition of Bu\textsuperscript{+4}NBr.
Temperature = 25°C ± 0.1
FIGURE 3.4(x)

Change in the 2νOH peak of HOD (3% H₂O/D₂O%) on addition of NaI.
Temperature = 25°C ± 0.1
The acidic nature of (OH)\text{free} generated in equilibrium (1) enables it to solvate anions (2), whilst lone-pair groups solvate cations (3),

\begin{align*}
\text{(H}_2\text{O})\text{bound} &= (\text{OH})\text{free} + (\text{LP})\text{free} \\
\text{A}^- + (\text{OH})\text{free} &= \text{A}^- \cdots \text{H}_2\text{O} \\
\text{M}^+ + (\text{LP})\text{free} &= \text{M}^+ \cdots \text{O}^- 
\end{align*}

when a salt is added to HOD. Hence changes observed in the overtone spectra are assigned to these effects. It is difficult to interpret the nature of individual ion effects without assuming that either the anion or cation for a particular salt undergoes negligible solvation. For this purpose tetraalkylammonium salts are studied to gain insight into the extent of anion solvation, by assuming that large bulky \text{R}_n\text{N}^+ cations undergo negligible solvation [37,38]. Recent diffraction studies mentioned in Section 3.2.5 indicate that the chloride ion has a solvation number of six in water at 25°C. This is accepted as being a good number, hence the extent to which tetraalkylammonium chloride salts scavenge (OH)\text{free} groups is a measure of the effect of an anion having a solvation number of six. Using the results for \text{Bu}^+_n\text{NCl} and \text{Et}_n\text{NCl} in HOD at 25°C in the second overtone region as a reference point, it is possible to assign solvation numbers to cations, for salts where the anion is Cl\text{−}, such as \text{NaCl}, \text{LiCl}, \text{KCl}, \text{CsCl}. If chloride has a solvation number of six, then since \text{NaCl} in HOD shows a gain in (OH)\text{free}, this would indicate \text{Na}^+ scavenges more (LP)\text{free} groups than Cl\text{−} scavenges (OH)\text{free} groups. Hence a solvation number slightly larger than six appears reasonable for \text{Na}^+ at this qualitative stage. A similar number for \text{K}^+, i.e. 6 or 7, looks acceptable while \text{Li}^+ appears to be less than 6 since LiCl shows a decrease in (OH)\text{free} absorbance. It is possible to use sodium tetraphenylboron salt in HOD to get a measure of the extent to which \text{Na}^+ scavenges (LP)\text{free} groups, thus
generating (OH)_free due to a buffering effect in equilibrium (1), assuming that BPh_4^- anions undergo negligible solvation. However this salt is sparingly soluble in water, hence there is a large error in this particular result. Having established that Na^+ and K^+ have solvation numbers greater than that for chloride ions, it is possible to estimate solvation numbers for other anions such as CH_3COO^-, CF_3COO^-, SCN^-, CNO^-, CN^-.

Results suggest that the other halide anions, Br^- and I^- have solvation numbers less than 6, probably ca. 5, while F^- is similar to Cl^-.

An estimate for the ClO_4^- anion cannot be made at this stage since the change in the second and first overtone water spectra is not thought to be simply a measure of (OH)_free groups, but to have a contribution from weak bonds between ClO_4^- and water which appear to be close to the (OH)_free band.

Trends observed from graphs 3.4(i)-(iii) for salts in HOD at 25°C show solvation numbers for the halides are in the order F^- > Cl^- > Br^- > I^- and for monovalent cations in the order Cs^+ > Na^+ > K^+ > Li^+. On going down group 7 the electronegativity decreases and the anion size increases. Thus the charge density decreases and this appears to reduce the solvation number on going from F^- to I^-.

In contrast for the group I cations, the solvation number trend shows an increase on proceeding down the group. The small decrease in electropositivity is outweighed by the increase in cation size resulting in a larger solvation number (i.e. the larger the cation, the more lone-pair groups can fit around it).

We suggest that tetraalkylammonium cations undergo negligible solvation by lone-pair groups. However, the results indicate that the small Me_4N^+ cations undergo solvation to a greater extent than the large Bu_4N^+ cations, which have a lower charge density relative to Me_4N^+.
\( \text{Me}_4\text{N}^+ > \text{Et}_4\text{N}^+ \approx \text{Bu}^+\text{N}^+ \)

Possibly some of the protons of the methyl groups of \( \text{Me}_4\text{N}^+ \) can form weak H-bonds to \((\text{LP})_{\text{free}}\) groups. Group II cations show a similar trend to group I in that the solvation number increases proceeding down the group in the order:

\[ \text{Be}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+} \]

Results also indicate \( \text{NCO}^- \) and \( \text{NCS}^- \) have similar solvation numbers and \( \text{CN}^- \) to have a relatively lower one:

\[ \text{NCO}^- \approx \text{NCS}^- > \text{CN}^- \]

The result for \( \text{Et}_3\text{PO} \) is an important one since it is considered to be a tri-base in water. Hence it provides a useful internal reference [51,52] along with the \( \text{Bu}^+\text{NCl} \) result for obtaining a qualitative view on solvation numbers, for anions and cations within the extensive series of salts studied.

When a salt is added to water, as \((\text{OH})_{\text{free}}\) groups are scavenged, reaction (I) re-equilibrates to offset this loss;

\[
(\text{H}_2\text{O})_{\text{bulk}} \rightarrow (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}} \quad (I)
\]

thus increasing the number of \((\text{LP})_{\text{free}}\) groups present. As yet there is no evidence from either first or second overtone studies for an increase in absorbance of any water peaks corresponding to \((\text{LP})_{\text{free}}\) groups.

This absence of any specific "\((\text{LP})_{\text{free}}\)" band for water is in contrast with Symons' results for methanol [55]. He suggests that these groups are less well defined in water, there being several modified OH groups, all of which will contribute small changes to the spectrum. Thus:

\[
\begin{align*}
\text{(H}_2\text{O})_{\text{bound}} & \quad b < a \\
\text{(LP)}_{\text{free}} & \quad d > c
\end{align*}
\]
H-bonds to (LP)\textsubscript{free} molecules are weaker than in bulk water (b<a), however, the remaining lone-pair hydrogen bond is stronger than normal (d>c). The weakening effect on the two normal H-bonds (c) is distributed, hence H-bonds (b) are not sufficiently weakened for them to absorb in the second overtone region. In the first overtone, (LP)\textsubscript{free} groups are expected to absorb at higher wavenumbers than bulk, although still closer to bulk H-bonds rather than (OH)\textsubscript{free}. In view of this complexity it is not surprising that a specific O-H stretch frequency due to (LP)\textsubscript{free} units is not detected. Strong water-anion H-bonds are not seen within the observed second overtone band. However, weak water-anion bands do contribute as in the case of ClO\textsubscript{4}\textsuperscript{-} ion which produces a much greater increase in absorbance, because of two contributing factors, than would otherwise be seen. The anion is scavenging (OH)\textsubscript{free} groups but the weak ClO\textsubscript{4}\textsuperscript{-}---HO interaction allied with the cation scavenging (LP)\textsubscript{free} groups produces a false picture regarding generation of (OH)\textsubscript{free} groups. Contributions from weak interactions such as these have to be taken into account when trying to quantify the results, as will be discussed in Chapter 4, using curve analysis techniques. Cation solvates generally absorb close to the bulk band and so are not observed in the second overtone region, due to the relatively strong M\textsuperscript{+}---HO H-bonds. When discussing cation solvation, it is important to note that they can solvate via one or both lone-pairs on water;

\[
\begin{align*}
M^+ & \cdots \text{O} \\
H & \cdots \text{O} \\
\text{H} & \\
\text{O} & \\
\text{M}^+ & \cdots \text{O} \\
\text{H} & \cdots \text{H} \\
\text{H} & \\
\text{H} &
\end{align*}
\]

or, more precisely, cation binding may cause the loss of one or two
bonds to other water molecules. A recent molecular dynamic study on the orientation of water molecules [53] in the hydration shell of the ions in a MgCl₂ solution suggests Mg²⁺ uses one or two lone-pairs on water molecules. Without knowing whether a cation is solvated via one or both (LP)free groups, it is difficult to establish fixed solvation numbers. It appears reasonable to assume they are solvated via a combination of one and two (LP)free groups. This will be discussed further in the next chapter after further analysis.

Example:

\[
\text{Mg}^{2+} \overset{\text{H}}{\text{O}} \\
\text{H} \quad \text{or} \quad \text{Mg}^{2+} \overset{\text{H}}{\text{O}} \\
\text{H} 
\]

3.5 CONCLUDING REMARKS

The results recorded in the first overtone region show trends similar to those obtained in the second overtone. However, the main study of salt effects on water structure was carried out in the 3v OH region since it favours more weakly H-bonded species, hence changes on the (OH)free group concentrations are magnified. Since (OH)free groups are scavenged preferentially by anions, due to their relatively acidic nature, monitoring them provides the best indication of solvation numbers. By solvation number is meant the number of water molecules in direct contact with the ion.

The temperature effect on the pure HOD peak [54] shows a loss of (OH)free groups as the temperature decreases. However, the peak is still pronounced at 2°C showing a significant contribution from very weakly hydrogen bonded species as well as (OH)free groups. Consequently, changes in the weakly bound species on adding salt to water have to be
accounted for, since changes in the $3\nu_{\text{OH}}$ spectra are not solely due to (OH)$_{\text{free}}$ groups. This is attempted in the next chapter where the results are quantified by curve analysing the spectra, i.e. dividing up into separate component bands, accounting for weakly bound contributions to observed spectral changes and comparing experimental results with those calculated by simple theory.
REFERENCES FOR CHAPTER 3

REFERENCES FOR CHAPTER 3 (Continued)

REFERENCES FOR CHAPTER 3 (Continued)


CHAPTER 4

Analysis of HOD results using Curve Analysis and Simple Theory
4.1 INTRODUCTION

This work concerns analysing the experimental data obtained in Chapter 3 by quantifying results using curve analysis techniques and comparing the deconvoluted effect of added salts on (OH)$_{free}$ with theoretical results. The theoretical results are obtained from a Law of Mass Action approach.

4.2 EXPERIMENTAL

The Second Overtone HOD spectra were deconvoluted using computer graphics. This procedure involves several stages, initially a Ferranti Freescan cursor controlled digitiser is used to digitise the spectra. The data coordinates are stored in files on a DEC PDP 11/45 computer. The experimentally obtained spectra were recorded using a nanometer energy scale, on a Perkin-Elmer 340 UV/VIS/NIR spectrophotometer. Hence the digitised files had to be converted to wavenumbers so as to remove any skew effect the nanometer scale might have on the peaks. The linear relationship between energy and wavenumbers means that this is the more fundamental unit, so this conversion is advisable.

The converted files were visually analysed on a DEC GP42 refresh display which provided interactive graphics. The observed spectra envelope can be simulated by placing a minimum of three bands under the overall Second Overtone band. This is done using a V.I.D.C.A. Program (Visually Displayed Curve Analysis) [1]. This enabled the individual band parameters: peak height, position, half-band width at half-height and percentage Gaussian, to be altered until a good fit with the experimental band was obtained. Copies of the final deconvoluted spectra were obtained using a CALCOMP 1012 plotter. This procedure was undertaken for each Second Overtone system studied at 25°C.
4.3 RESULTS

The deconvoluted spectra of HOD in D₂O at 5°C, 25°C and 50°C are shown in Figs. 4.1, 4.2 and 4.3 as examples, showing the pure HOD band simulated using three bands. Band I at 10460 cm⁻¹ represents (OH) free groups and very weak H-bonds, which have to be accounted for, as will be described later in this chapter. Band I parameters are fixed, i.e. the position remains unaltered in every curve analysed spectra as does the half-band width at half-height. The pure energy distribution function of (OH) free in isolation is 100% Gaussian. Bands II and III are allowed small changes in position, in order to obtain a good spectral fit, over the temperature range studied. At 25°C, band II occurs at 10,290 cm⁻¹ and band III at 10,000 cm⁻¹. However, on cooling to 5°C bands II and III get broader, whilst at 50°C their half-band width at half-height gets narrower as expected for hydrogen bonded oscillators. Thus bands II and III represent weakly hydrogen bonded species. These two bands combined produce a skew band, relating to these species. Skew bands cannot be simulated graphically, hence it is necessary to use two bands but we do not attach physical significance in the sense of two discrete species. A sloping baseline is used on all deconvoluted spectra to allow for absorption from peaks at lower wavenumbers.

All the Second Overtone systems studied were deconvoluted using three bands. However, added salts such as NaClO₄ cause a larger increase in absorbance than expected. This is assigned to water weakly hydrogen bonded to ClO₄⁻ ions. This band occurs close to the (OH) free band, hence band II absorbance is greater than would otherwise be the case, due to this ClO₄⁻--HOD contribution. Strictly, we should introduce a fourth band for this weak oscillator, however, it is best to use the minimum number of bands and since there is no evidence for a distinct
FIGURE 4.1
The deconvolution of the OH band of HOD in D$_2$O at 5°C.
FIGURE 4.2
The deconvolution of the OH band of HOD in D$_2$O at 25°C.
FIGURE 4.3

The deconvolution of the OH band of HOD in D₂O at 50°C.
ClO₄⁻ -- HOD band growing up, there is no need to use more than 3 bands. The spectra are well simulated using 3 bands, so it is sufficient to say that any contribution from the ClO₄⁻ anion is accounted for by the relative increase in band II absorbance.

Figure 4.4 illustrates the changes in the simulated bands with increasing NaClO₄ concentration in HOD at 25°C. Band II shows a greater increase than band I because of the ClO₄⁻ contribution. Band III also shows a significant increase, suggesting that ClO₄⁻ -- HO⁻ units contribute to the whole of this region. Basic salts when added to HOD cause a loss of (OH)free groups and some of the weakly hydrogen bonded species (band II). Acidic salts in HOD show a gain of (OH)free groups together with weakly hydrogen bonded species (band II). Figure 4.5 shows the changes in the simulated bands for a typical tetraalkylamonium salt in HDD at 25°C. A decrease in band I is observed due to the anion scavenging the relatively acidic (OH)free groups. The cation undergoes negligible solvation relative to the anion, hence a large decrease is observed. Band II representing weakly hydrogen bonded species also shows a decrease in absorbance. Band III, which also represents weakly hydrogen-bonded species, on the low energy side of the experimental band shows no change in absorbance. Generally in the HOD/salt systems studied, there are no peaks found corresponding to anion-water complexes. The absorbance of these species is at lower energy than the intense HOD bands, except in the case of ClO₄⁻, as mentioned earlier.

The change in percentage band I concentration, on adding various salts to HOD, is shown for all the systems studied in Figs. 4.6-4.8. The tetraalkylammonium halide salts show the largest decrease in absorbance, notably the chloride more so than bromide salts, iodide being
FIGURE 4.4
Change in the deconvoluted peaks of HOD in D$_2$O in the Second Overtone region on addition of NaClO$_4$.
Temperature = 25°C ± 0.1

Band I = (OH)$_{free}$ + very weak H-bonds
Band II = Weak H-bonds
Band III = Weak H-bonds
FIGURE 4.5
Change in the deconvoluted peaks of HOD in D₂O in the Second Overtone region on addition of Bu₄NCl.
Temperature = 25°C ± 0.1

Band I = (OH)free + very weak H-bonds
Band II = Weak H-bonds
Band III = Weak H-bonds
FIGURE 4.6
Change in the deconvoluted Band 1 of HOD in D_2O on addition of various salts in the Second Overtone region.
Temperature = 25°C ± 0.1
FIGURE 4.7
Change in the deconvoluted Band 1 of HOD in D₂O on addition of various salts, in the Second Overtone region. Temperature = 25°C ± 0.1
FIGURE 4.8
Change in the deconvoluted Band 1 of HOD in D$_2$O on addition of various salts in the Second Overtone region.
Temperature = 25°C ± 0.1
insoluble. Salts containing divalent cations also exhibit marked
decreases in the (OH)$_{\text{free}}$ absorbance, notably BeCl$_2$, MgCl$_2$ and CaCl$_2$.
The anion charge is twice as effective at scavenging (OH)$_{\text{free}}$ groups
as monovalent cation salts because there are twice as many anions as
cations. Hence divalent cation salts show trends comparable to the
tetraalkylammonium salts. Divalent anion salts such as Na$_2$CO$_3$ and
Na$_2$SO$_4$ show a large increase in (OH)$_{\text{free}}$ absorbance because there are
twice as many cations as anions.

To observe the change in the pure (OH)$_{\text{free}}$ absorbance it is necessary
to separate the very weakly bound contribution from band I, which is
estimated to be about a 50:50 mixture of (OH)$_{\text{free}}$ and very weakly
hydrogen bonded species. This estimate is based on base titration work
[2] in which the fall in band I is never found to be greater than 50% of
the pure HOD peak intensity, even up to a cosolvent molefraction of
0.2 for strong bases, i.e. DMSO, DMA, by which time nearly all the
(OH)$_{\text{free}}$ groups are expected to have been scavenged. We postulate that
change in the very weakly bound contribution to band I is in a
parallel sense to a change in band II absorbance with increasing solute
concentration.

A computer program [2] incorporating this postulate and the 50:50
estimate for band I is used to separate the very weakly bound contribu­
tion from band I. By inputting the deconvoluted data for bands I and
II, the program calculates 50% of band I absorbance, due to (OH)$_{\text{free}}$ and
50% due to weakly bound. It then calculates the change in band I
absorbance for each molefraction of solute, which is attributable to a
change in both (OH)$_{\text{free}}$ and weakly bound. To separate out the weakly
bound contribution from this change in band I, it is necessary to know
the percentage change in weakly bound as a solute is added. This is
achieved by calculating the percentage change in band II, which is postulated to occur in a parallel sense to the weakly bound contribution in band I.

Hence the pure (OH)$_{\text{free}}$ change on adding a solute to HOD is represented by the following equations:

(i) for acids:

\[
\text{Pure (OH)}_{\text{free}} = \left( 50\% \text{ of pure HOD deconvoluted Band I absorbance units} \right) + \left( \frac{\text{change in Band I absorbance units}}{\text{units}} \right) - \left( \frac{\% \text{ change in Band I very weak hydrogen bonds}}{\text{units}} \right)
\]

(ii) for bases:

\[
\text{Pure (OH)}_{\text{free}} = \left( 50\% \text{ of pure HOD deconvoluted Band I absorbance units} \right) - \left( \frac{\text{change in Band I absorbance units}}{\text{units}} \right) + \left( \frac{\% \text{ change in Band I very weak hydrogen bonds}}{\text{units}} \right)
\]

Figures 4.9-4.11 show changes in the concentration of the pure (OH)$_{\text{free}}$ peak on addition of various salts, for a 50:50 ratio of (OH)$_{\text{free}}$ to weakly bound for band I. The natural log gradients of the pure (OH)$_{\text{free}}$ band for all systems studied are given in Table 1. In the case of a 40:60 ratio of (OH)$_{\text{free}}$ to weakly bound for band I, natural log gradients have also been calculated and on comparison with gradients based on a 50:50 ratio show little change, indicating acceptable results are obtained irrespective of the precise ratio used. Changes in the natural log concentration of the pure (OH)$_{\text{free}}$ peak, for a 50:50 ratio, are shown in Figures 4.12-4.14. Figure 4.15 shows the change in concentration of pure (OH)$_{\text{free}}$ peak for various salts, based on a 40:60 ratio of (OH)$_{\text{free}}$ to weakly bound for band I.

From the natural log graphs, trends follow the same pattern as found in the previous chapter, with the notable exception of NaClO$_4$. The gradient for NaClO$_4$ is now less because the increase in the weakly hydrogen bonded species has been accounted for. The ClO$_4$ anion gives
FIGURE 4.9
Change in the concentration of the pure (OH)\textsubscript{free} peak of HOD in D\textsubscript{2}O, in the Second Overtone region on addition of various salts, based on a 50:50 ratio of (OH)\textsubscript{free} to weakly bound for band I.
Temperature = 25°C ± 0.1
FIGURE 4.10
Change in the concentration of the pure (OH)$_{\text{free}}$ peak of HOD in D$_2$O, in the Second Overtone region, on addition of various salts, based on a 50:50 ratio of (OH)$_{\text{free}}$ to weakly bound for band I.
Temperature = 25°C ± 0.1
FIGURE 4.11
Change in the concentration of the pure (OH)$_{\text{free}}$ peak of HOD in D$_2$O, in the Second Overtone region, on addition of various salts, based on a 50:50 ratio of (OH)$_{\text{free}}$ to weakly bound for band I.
Temperature = 25°C ± 0.1
FIGURE 4.12
Change in the natural log concentration of the pure (OH)\_free peak of HOD in D\_2O in the Second Overtone region on addition of various salts, based on a 50:50 ratio of (OH)\_free to weakly bound for band I. Temperature = 25°C ± 0.1
FIGURE 4.13
Change in the natural log concentration of the pure (OH)$_{\text{free}}$ peak of HOD in D$_2$O in the Second Overtone region on addition of various salts, based on a 50:50 ratio of (OH)$_{\text{free}}$ to weakly bound for band I.
Temperature = 25°C ± 0.1
FIGURE 4.14
Change in the natural log concentration of the pure (OH)$_{\text{free}}$ peak of HOD in D$_2$O in the Second Overtone region on addition of various salts, based on a 50:50 ratio of (OH)$_{\text{free}}$ to weakly bound for band I.
Temperature = 25°C ± 0.1
FIGURE 4.15
Change in the concentration of the pure (OH)free peak of HOD in D$_2$O, in the Second Overtone region on addition of various salts, based on a 40:60 ratio of (OH)free to weakly bound for band I.
Temperature = 25°C ± 0.1

![Graph showing the effect of various salts on the concentration of HOD in D$_2$O]
TABLE 1

<table>
<thead>
<tr>
<th>Salt</th>
<th>50:50</th>
<th>40:60</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBPh₄</td>
<td>21.61</td>
<td>24.10</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>21.49</td>
<td>24.09</td>
</tr>
<tr>
<td>NaN</td>
<td>16.61</td>
<td>19.13</td>
</tr>
<tr>
<td>CF₃COONa</td>
<td>13.14</td>
<td>12.05</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>13.46</td>
<td>14.84</td>
</tr>
<tr>
<td>NaF</td>
<td>11.39</td>
<td>12.97</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>10.78</td>
<td>11.91</td>
</tr>
<tr>
<td>KBr</td>
<td>9.13</td>
<td>10.18</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>9.22</td>
<td>10.10</td>
</tr>
<tr>
<td>NaClO₄</td>
<td>10.63</td>
<td>10.95</td>
</tr>
<tr>
<td>NaN₂O₄</td>
<td>8.19</td>
<td>9.55</td>
</tr>
<tr>
<td>NaSCN</td>
<td>7.93</td>
<td>8.39</td>
</tr>
<tr>
<td>NaBr</td>
<td>7.95</td>
<td>9.04</td>
</tr>
<tr>
<td>CH₃COONa</td>
<td>7.18</td>
<td>8.13</td>
</tr>
<tr>
<td>CsCl</td>
<td>6.61</td>
<td>7.17</td>
</tr>
<tr>
<td>KCl</td>
<td>5.25</td>
<td>6.05</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.65</td>
<td>4.00</td>
</tr>
<tr>
<td>NaF</td>
<td>3.45</td>
<td>3.82</td>
</tr>
<tr>
<td>LiBr</td>
<td>0.23</td>
<td>0.29</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>1.20</td>
<td>1.03</td>
</tr>
<tr>
<td>LiCl</td>
<td>5.46</td>
<td>6.39</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>-17.14</td>
<td>-21.93</td>
</tr>
<tr>
<td>Me₄NCl</td>
<td>-14.04</td>
<td>-15.89</td>
</tr>
<tr>
<td>Et₄NBr</td>
<td>-17.03</td>
<td>-19.29</td>
</tr>
<tr>
<td>Me₄NBr</td>
<td>-16.39</td>
<td>-20.80</td>
</tr>
<tr>
<td>Et₃PO</td>
<td>-17.27</td>
<td>-21.69</td>
</tr>
<tr>
<td>Bu₄NBr</td>
<td>-18.14</td>
<td>-21.29</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>-19.55</td>
<td>-22.50</td>
</tr>
<tr>
<td>BeCl₂</td>
<td>-23.30</td>
<td>-25.50</td>
</tr>
<tr>
<td>Bu₄NCl</td>
<td>-29.35</td>
<td>-35.75</td>
</tr>
<tr>
<td>Et₄NCl</td>
<td>-36.85</td>
<td>-39.42</td>
</tr>
</tbody>
</table>

rise to the greatest increase in weakly bound water, relative to the other salt systems. Hence compensation for weak hydrogen bonds will affect the NaClO₄ result more than other salts. The result for ClO₄⁻ is in keeping with other workers' results [3] who find ClO₄⁻ to have a solvation number of four in water. Tetraalkylammonium salts still show the greatest loss of (OH)₆free groups, chloride more so than bromide, while NaBPh₄ and Na₂CO₃ show the largest increase. The next stage is to quantify these results by comparison with theoretical gradients for bases and acids in water.

-88-
A theoretical approach using the Law of Mass Action was considered by G. P. Smith [2] for bases in water at 25°C, the results of which are shown in Table 2. Two sets of results are shown because two slightly different approximations were proposed by Symons and Blandamer [2].

Symons assumes that, on addition of base to water, the total number of moles in the equilibrium mixture is given by:

\[ M = [(H_2O)_{\text{free}}] + [(OH)_{\text{free}}] + [(LP)_{\text{free}}] + [B] + [OH--B] \]

where \( M \) = total number of moles

\([B]\) = moles of base

\([OH--B]\) = number of moles of water bound to base, i.e. dependent on the basicity of the base.

Blandamer's alternative assumption, in which he considers the number of hydrogen bonds in the system, is that the total number of moles in the equilibrium mixture equals:

\[ M = [(H_2O)_{\text{free}}] + [(OH)_{\text{free}}] + [(LP)_{\text{free}}] + [B(OH)] \]

where \([B(OH)]\) = number of moles of base bound to water, i.e. independent of the basicity of the base.

**TABLE 2**

<table>
<thead>
<tr>
<th>Theoretical Gradients</th>
<th>Symons</th>
<th>Blandamer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monobase</td>
<td>- 7.79</td>
<td>- 7.00</td>
</tr>
<tr>
<td>Tri-base</td>
<td>-22.63</td>
<td>-19.03</td>
</tr>
<tr>
<td>Tetra-base</td>
<td>-29.96</td>
<td>-24.30</td>
</tr>
<tr>
<td>Penta-base</td>
<td>-37.33</td>
<td>-29.12</td>
</tr>
<tr>
<td>Hexa-base</td>
<td>-45.03</td>
<td>-33.54</td>
</tr>
</tbody>
</table>

These two different assumptions lead to the derivation of different equations, for a base scavenging \((OH)_{\text{free}}\) in water, from the Law of Mass Action Theory. The derivations for a base in water are not discussed here since this work has been done by Smith [2]. However, the derivations for acids in water are discussed in Appendix B. The two different treatments for acids and bases lead to similar equations being derived which
are put into quadratic form. A computer program was written [2] using the quadratic equations to give theoretical gradients for acids and bases in water. The results for acids are given in Table 3.

<table>
<thead>
<tr>
<th></th>
<th>Symons</th>
<th>Blandamer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoacid</td>
<td>5.30</td>
<td>5.71</td>
</tr>
<tr>
<td>Di-acid</td>
<td>10.87</td>
<td>11.43</td>
</tr>
<tr>
<td>Tri-acid</td>
<td>15.89</td>
<td>16.42</td>
</tr>
<tr>
<td>Tetra-acid</td>
<td>20.23</td>
<td>20.68</td>
</tr>
<tr>
<td>Penta-acid</td>
<td>23.95</td>
<td>24.29</td>
</tr>
<tr>
<td>Hexa-acid</td>
<td>27.13</td>
<td>27.36</td>
</tr>
<tr>
<td>Hepta-acid</td>
<td>29.84</td>
<td>29.98</td>
</tr>
<tr>
<td>Octa-acid</td>
<td>32.18</td>
<td>32.23</td>
</tr>
</tbody>
</table>

The derived equations are valid only whilst the equilibrium between bulk water and (OH)$\text{free}$, (LP)$\text{free}$ groups remains constant, i.e. at low concentrations of acid and base. It is possible to calculate $\alpha$ by fixing a value for $k$ (equilibrium constant) for different solute concentrations. The basicity and acidity of the base and acid can be altered to produce theoretical results for mono, di, tri, etc., acids and bases. The equilibrium constant is determined by assuming the initial (OH)$\text{free}$ concentration to be 8% in pure water at 25°C. Figure 4.16 shows the theoretical change in the natural log (OH)$\text{free}$ concentration on addition of acid to HOD at 25°C for both the Symons and Blandamer approach. By comparison of the two sets of gradients, it is seen that Symons' data produces steeper gradients for bases but Blandamer's gives slightly steeper gradients for acids.

If Et$_3$PO is a tri-base in water, then the gradient for Et$_3$PO, -17.27, fits in best with the Blandamer theoretical result, -19.03, for a tri-base, compared to Symons' result of -22.63. The chloride anion is regarded as being a hexa-base in water. Hence the gradient for Et$_4$NCl,
FIGURE 4.16
Theoretical changes in the natural log \((\text{OH})_{\text{free}}\) concentration on addition of acidic salts, assuming 8% \((\text{OH})_{\text{free}}\) at 25°C.

- Blandamer Theory
- Symons Theory

1. Monoacid
2. Diacid
3. Triacid
4. Tetraacid
5. Pentaacid
6. Hexaacid
7. Heptaacid
8. Octaacid
-36.85, also fits best with the Blandamer theoretical result of -33.54 for a hexa-base. Symons result for a hexa-base, -45.03, is too high for Cl\(^-\) to have a solvation number of six. On the Symons scale of theoretical gradients, the chloride anion would be a penta-base. Hence the Blandamer set of gradients appear to fit best with the experimental set of results obtained.

By assuming the Cl\(^-\) anion to have a solvation number of six in water, then since the NaCl result is that of a monoacid, this would indicate Na\(^+\) scavenges 7 (LP)\(^{\text{free}}\) groups to Cl\(^-\) scavenging 6 (OH)\(^{\text{free}}\) groups. The solvation numbers of other anions can be determined by comparing the gradient of each sodium salt with the theoretical gradients, to determine the net acidity, then subtracting the Na\(^+\) contribution of 6 or 7 (LP)\(^{\text{free}}\) groups, leaving the number of (OH)\(^{\text{free}}\) groups scavenged by the anion. Once anion solvation numbers have been determined in this way from sodium salts, the number of (LP)\(^{\text{free}}\) groups scavenged by other cations can be determined similarly. Table 4 lists the solvation numbers for the various anions and number of (LP)\(^{\text{free}}\) groups scavenged by cations studied in HOD at 25°C.

The results compare well with literature values for ion solvation numbers in water. Enderby et al. [4] have shown that chloride ions have 6 water molecules directly bonded via one OH-unit and that sodium ions also have a solvation number of six, using neutron diffraction. A computer simulation study by Mezei and Beveridge [5] also shows Na\(^+\) to have 6 water molecules directly bonded to it. Other important cation solvation numbers in the literature include 6 for potassium [6] and 5 for Li\(^+\) [7]. It is important to note that findings from neutron and X-ray diffraction studies show that cation solvation numbers are maximised at low salt concentration but decrease and level off at higher
TABLE 4

<table>
<thead>
<tr>
<th>Anion Solvation Numbers</th>
<th>Number of (LP)free groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻</td>
<td>6</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>6</td>
</tr>
<tr>
<td>Br⁻</td>
<td>4/5</td>
</tr>
<tr>
<td>I⁻</td>
<td>4/5</td>
</tr>
<tr>
<td>ClO₄²⁻</td>
<td>4</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>4</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>4</td>
</tr>
<tr>
<td>NCO⁻</td>
<td>4</td>
</tr>
<tr>
<td>CH₃COO⁻</td>
<td>4</td>
</tr>
<tr>
<td>CF₃COO⁺</td>
<td>3</td>
</tr>
<tr>
<td>CN⁻</td>
<td>3</td>
</tr>
<tr>
<td>BF₄⁻</td>
<td>0/1</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>10</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>8</td>
</tr>
<tr>
<td>Et₃PO</td>
<td>3</td>
</tr>
<tr>
<td>Li⁺</td>
<td>4/5</td>
</tr>
<tr>
<td>Na⁺</td>
<td>6/7</td>
</tr>
<tr>
<td>K⁺</td>
<td>6/7</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>7</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>4</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>9</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>9/10</td>
</tr>
<tr>
<td>Me₄N⁺</td>
<td>2/3</td>
</tr>
<tr>
<td>Et₄N⁺</td>
<td>0/1</td>
</tr>
<tr>
<td>Bu₄N⁺</td>
<td>0/1</td>
</tr>
</tbody>
</table>

salt concentrations. This was found in recent work on Li⁺ and Ca²⁺ by Enderby. The results for Ca²⁺ [8], as mentioned in the previous chapter, suggest that its solvation number varies between 6 and 10, depending on salt concentration. Bubak et al. [9] noted that the water structure on addition of LiCl, stabilizes at high salt concentration, i.e. 10 molal onwards, which correlates with Newsome's findings [7]. A solvation number of 7 was attributed to Mg²⁺ by Allam et al. [10]. However, a recent molecular dynamics study [11] suggests Mg²⁺ can use both lone-pairs on water. It is reasonable to think in terms of cation solvation occurring via a balance between one and both (LP)free groups on water molecules, making it impossible to assign cation solvation numbers based on this overtone study which measures relative scavenging of (OH)free and (LP)free groups.

Regarding anion solvation numbers in the literature, diffraction work [12,13] indicates Br⁻ and I⁻ to be octahedrally bonded to water. This result ties in with the halides all being octahedrally bonded, however
this second overtone study differentiates between Cl\(^-\), Br\(^-\) and I\(^-\) ions. Chloride forms relatively strong H-bonds with water, whereas Br\(^-\) and I\(^-\) form weaker H-bonds which may occur under the 3\(\nu\)OH envelope, thus giving a slightly greater increase in absorbance, in the case of acidic salts such as NaBr, NaI, than would otherwise be the case which, in turn, would point towards Br\(^-\) and I\(^-\) having a lower solvation number than Cl\(^-\). Work done on the nitrate ion \([14]\) calculates a solvation number of 1.3\(\pm\)0.2 with water molecules coordinated axially to the NO\(_3\)\(^-\) ion. This result is considerably less than the value of 4 determined in this work. A recent UV/ESR study \([15]\) indicates Ag\(^+\) to have a primary solvation sphere of four water molecules arranged tetrahedrally, in good agreement with the Ag\(^+\) result in this work.

4.4 CONCLUDING REMARKS

Recent theory regarding how a cation solvates in water, i.e. via one or both (LP)\(_{\text{free}}\) groups, makes it difficult to fix cation solvation numbers since the numbers produced relate to the number of (LP)\(_{\text{free}}\) groups scavenged by the cation and not necessarily the number of water molecules, unless the assumption is made that cations bond only via one lone-pair on water which is probably not the case. The good tie-up between established solvation numbers, i.e. 6 for Cl\(^-\) and 3 for Et\(_3\)PO, makes the overall approach look reasonably healthy. It is difficult to separate very weak H-bonds from band I on curve analysed spectra and a value has to be fixed on the percentage of (OH)\(_{\text{free}}\) groups in water but a good scale for ion solvation numbers has been established.
REFERENCES FOR CHAPTER 4

CHAPTER 5

Methanol with Salts and Bases in the First Overtone Region
5.1 INTRODUCTION

This work considers the solvation of various anions and bases in methanol at 25°C. This is achieved by monitoring the growth of lone-pair groups as a consequence of bases and anions scavenging OH groups, represented by equilibrium (I).

\[
\text{Base} + (\text{MeOH})_{\text{bulk}} \rightleftharpoons \text{Base}--\text{HO-Me} + (\text{LP})_{\text{free}} \quad \quad \ldots \quad \ldots \quad (I)
\]

We cannot rule out the possibility of equilibrium (II), involving weakly bound OH groups, although we favour (I) in which base attacks any OH groups, not necessarily weakly bound.

\[
(\text{OH})_{\text{weakly bound}} + (\text{LP})_{\text{free}} \rightleftharpoons (\text{MeOH})_{\text{bulk}} \quad \quad \ldots \quad \ldots \quad (II)
\]

\[
\text{Base} + (\text{OH})_{\text{weakly bound}} \rightleftharpoons \text{Base}--\text{HO-Me} + (\text{LP})_{\text{free}}
\]

[The "solvation number" of anion or aprotic molecule is defined, regarding this work, as the number of solvent molecules interacting directly therewith.]

Band maxima assigned to (LP)_{\text{free}} groups occur at 3440 cm\(^{-1}\) in the fundamental and 6790 cm\(^{-1}\) in the first overtone region [1]. The second overtone methanol spectrum is complicated by C-H stretch contributions, hence the first overtone region (1650-1300 nm, 7690-6060 cm\(^{-1}\)) is used in this work. Although methanol is trifunctional, it normally behaves as if it were difunctional compared to water which normally uses all four functional groups. As a consequence of this, methanol studies are less complicated than water, hence spectroscopic studies are more informative.

A sharp band at 7050 cm\(^{-1}\) has been assigned to (OH)_{\text{free}} groups present in water, however (LP)_{\text{free}} groups present in equal amounts in water have not yet been detected even in aqueous solutions of aprotic bases which should be rich in (LP)_{\text{free}}. This is thought to be due to the greater complexity of the (LP)_{\text{free}} unit in water, as discussed above.
However, for methanolic solutions the number of specific structures is reduced since the molecule forms only two hydrogen bonds and not four.

The overtone region shows that the concentration of (OH)$_{\text{free}}$ groups present in methanol must be small compared with that for water.

5.2 PREVIOUS WORK

Symons et al. [1] identified (IP)$_{\text{free}}$ groups in the first overtone spectrum of methanol, at 6790 cm$^{-1}$, i.e. at a higher frequency than that for bulk methanol, indicating the hydrogen bonding to be weakened in this unit, as expected. They suggest that strongly basic cosolvents bound to methanol should absorb close to the bulk band. Such a band has been detected for MeOH + Et$_3$N systems in the fundamental region [1].

(i) Ionic Studies

Strauss and Symons [2] investigated the solvation of ions in MeOH at low temperatures using the fundamental region, since at low temperatures the OH stretch for MeOH narrows revealing better resolution of the band components when electrolytes are added. The broad band for MeOH narrows when ROH molecules are present as dilute solutions in ROH, because of decoupling, but the bands remain broad at room temperature. With the exception of perchlorate and tetrafluoroborate salts, when electrolytes are dissolved in MeOH, the room temperature fundamental spectra remain relatively uninformative. When perchlorate salts are added a new high frequency band appears, as is found in the first overtone region at a higher frequency than the (IP)$_{\text{free}}$ band. Walrafen [3] favoured the concept of the ClO$_4^-$ anions not being solvated but acting as "structure breakers" and that this new feature is due to (OH)$_{\text{free}}$ groups. Symons et al. [4,5] prefer the concept that this band is due to OH groups relatively weakly bonded to ClO$_4^-$ anions. The other major component is assigned to bulk solvent and solvent bonded to the cations.
When NaBPh₄ is added to MeOH [2], OH groups prefer to remain bonded to solvent rather than form very weak and ill-defined hydrogen bonds to the phenyl groups of the BPh₄⁻ anions. The Na⁺ cation is solvated via (LP)free groups by forming weak bonds, hence there should be an excess of (OH)free groups. However, these can form weak hydrogen bonds to the second set of lone-pairs not usually involved in such bonding in bulk MeOH. Symons has postulated that since (OH)free groups are not detected in cold methanol cross-linking structures are formed:

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

The OH groups responsible for the high frequency band, ca. 1410 nm, in the first overtone region are those marked α. Low temperature work [2] on methanol shows the order of ion interaction on the νOH stretch for anion solvates to be almost equal for Cl⁻, Br⁻, I⁻ and NO₃⁻. In the case of ClO₄⁻, it is very weakly hydrogen bonded because the negative charge is evenly dispersed throughout the ion. Hence the perchlorate solvate occurs at higher frequency. The nitrate ion is clearly asymmetrically solvated in methanol [6], which is explained in terms of its high polarisability with one or two strongly hydrogen bonded oxygen ligand(s). Thus the hydrogen bonds formed are much stronger than those formed by ClO₄⁻ anions. Symons et al. [7] studied halide solvation in MeOH using the fundamental region. The concentration of free and H-bonded MeOH in CCl₄ solutions of tetraalkylammonium halides was investigated.

There have been recent investigations on cation solvation in MeOH using NMR [8], notably Na⁺ solvation in MeOH. Monte Carlo statistical
mechanics simulations [9] have also recently predicted a solvation number of 6 for Na\(^+\) in MeOH. In particular, analysis of the hydrogen bonding does not show evidence for significant structure broken regions in these solutions. Rather the ions plus their first solvent shells interface readily into the bulk solvent. An interesting prediction is that the first two solvent shells around Na\(^+\) contain the same number of methanol molecules. Although this contrasts with conventional ideas about solvation, it is a consequence of the substantial compression of the first solvent shell. Recent theoretical studies on solvation have produced results which correlate well with experimental data.

Jorgensen et al. [10] carried out Monte Carlo statistical mechanics simulations on dilute solutions of Na\(^+\) in water. They found that, in agreement with X-ray data, the coordination of Na\(^+\) in water is 6, identical to the value obtained for Na\(^+\) in MeOH [9].

(ii) Assignment of Methanol Bands

Bourderon and Sandorfy [11] examined the problem of assigning the first overtone of the OH stretching vibration of hydrogen bonded alcohols for methanol and tertiary butanol. They identified the first O-H overtones even though they were overlapped by CH and OH combination bands. The comparison between methanol and t-BuOH is interesting because of the appreciable steric hindrance in t-BuOH and because there are three methyl groups in the molecule but no hydrogens on the carbon which carries the hydroxyl group. Asselin and Sandorfy [12] have also contributed to the extensive literature on methanol systems and t-BuOH. They studied self-associated alcohols down to liquid nitrogen temperatures and observed the "free" band for t-BuOH at room temperature but below -60°C only one OH stretching band remains. They observed that in the spectrum of t-BuOD, the contribution of CH absorption is less important
than for MeOH. Bourderon et al. [13] studied the fundamental first and second overtones of MeOH and attempted to demonstrate the presence of oligomers and monomers in liquid MeOH.

They found no evidence for the presence of monomers in the fundamental. In the first overtone region they assigned the 6340 cm\(^{-1}\) band to bulk methanol - they argue that the other 3 sub-bands are due to oligomers and monomer. They add that the contribution of "free" OH groups to the 7100 cm\(^{-1}\) monomer sub-band is unknown due to C-H and C-D absorptions in this region. They state that the 6340 cm\(^{-1}\) bulk band is definitely due to the polymer as was noted by Sandorfy et al. [14], in contrast to Luck and Ditter [15] who claimed it was due to a combination of the OH + CH\(_3\) type. Sandorfy et al. [13] noted that the second overtone region showed strong oligomer contribution to the spectrum with a shoulder on the high frequency side of the broad band, accountable to the "free" species.

5.3 EXPERIMENTAL

All the first overtone methanol spectra, (1650-1300 nm), were recorded on a Perkin-Elmer 340 UV/VIS/NIR spectrophotometer. Spectra were recorded at 25°C±0.1 and 50°C±0.1, on a photometric scale of 0 - 0.2, a \(\lambda\) expansion of \(\times 5\) and a 3-minute scan time. All salts used were of Analar grade, and were dried under vacuum and stored in a dessicator over silica gel before use. Cosolvents, of the best available grades, were purified by distillation over CaH\(_2\) and dried over CaH\(_2\). Methyl alcohol-d, 99.5%, was used without further purification. Each sample contained 20% MeOH by volume, a known volume of cosolvent or salt/MeOD solution was added and, finally, MeOD added to make up to the 5 ml mark. The reference contained the same volume of cosolvent or salt/MeOD solution; then MeOD was added to make up to the 5 ml mark.
Stock solutions of MeOD + salt were prepared by weight so that the mole fraction of salt was established.

It is useful to keep the concentration of OH oscillators constant in the sample solutions so that spectral changes are only a result of salt or base effects on the solvent and not due to an imbalance of [OH] groups throughout the systems studied. Glass cells with a 2 mm pathlength were used in this work. Absorbance due to the cells was recorded into the baseline correction before each system studied.

5.4 RESULTS

(i) Anion and Base Solvation

The Near-Infrared spectra were superimposed on each other for each system studied. Examples of these overlays are shown in Figures 5(a-e), showing the effect on the methanol spectrum caused by temperature change and the addition of Et₄NCl, NaClO₄, NaBPh₄ and DMA which represent four different types of solute studied in this work. Figure 5.1(a) shows the change in absorbance of the weak hydrogen bond entities and "(LP)free" band as a function of temperature. The bands representing weak H-bonds are seen to grow up about twice as rapidly as the (LP)free band with increasing temperature. Figure 5.1(b) shows the change in absorbance of weak H-bonds and "(LP)free" band for CD₃OH in CD₃OD. A trend is observed which is similar to that found for MeOH in MeOD, except the observed change in absorbance is less. Figures 5.1(c) and 5.1(d) show the change in the weak H-bond bands and "(LP)free" band as a function of temperature for CD₃OH/OD and MeOH/OD respectively, after curve analysis. The curve analysis procedure is discussed in Section 5.4(ii). Both systems show similar trends regarding growth in the weak H-bond entities with increasing temperature. The deconvoluted spectra for MeOH/OD and CD₃OH/OD are shown in Figures 5.8 and 5.8(b) respectively.
FIGURE 5a(i)
Effect of temperature on the first overtone spectrum of methanol (20% v/v) in MeOD.

Temperature
1. 25 °C
2. 30 °C
3. 35 °C
4. 40 °C
5. 45 °C
6. 50 °C
7. 55 °C

Absorbance

Temperature

1. 25 °C
2. 30 °C
3. 35 °C
4. 40 °C
5. 45 °C
6. 50 °C
7. 55 °C
**FIGURE 5a(ii)**

Temperature effect on CD$_3$OH/OD (10% v/v) vs CD$_3$OD.

Isosbestic point c.a. 1495 nm
FIGURE 5b
Effect of Et$_4$NCl on the first overture spectrum of methanol
50% v/v in MeSO at 25°C.

Molefraction of Et$_4$NCl
1.0.00
2.0.042
3.0.083
4.0.125
5.0.17

Absorbance

Nanometers
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0

Loss of bulk methanol
Growth in (H2)free
Loss of weak H-bonds
1500 nm
FIGURE 5d
Effect of NaBPh₄ on the first overtone spectrum of methanol (20% v/v) in MeOD at 25°C.

Molefraction of NaBPh₄
1. 0.00
2. 0.008
3. 0.016
4. 0.024
5. 0.032

Absorbance

1472 nm

Loss of \((LP)_{\text{free}}\)

Growth in \(\text{OH}\) weakly bound

Nanometers
Effect of DMA on the first overtone spectrum of methanol (10% v/v) in MeOD at 25°C.

FIGURE 5e
FIGURE 5.1a
Temperature effect on 2vOH of MeOH/OD (20% MeOH in MeOD V/V)

- Weak H-bonds
  - (1410 nm, 7092 cm⁻¹)
  - Gradient = 0.57 x 10⁻³

- Weak H-bonds
  - (1435 nm, 6969 cm⁻¹)
  - Gradient = 0.42 x 10⁻³

- (LP) free band
  - (1473 nm, 6790 cm⁻¹)
  - Gradient = 0.23 x 10⁻³
FIGURE 5.1b
Temperature effect on $2\nu \text{OH}$ of CD$_3$OH/OD (10% CD$_3$OH in CD$_3$OD $v/v$)

- Weak H-bonds
  - $1410 \text{ nm}$
  - $7092 \text{ cm}^{-1}$
  - Gradient = $0.18 \times 10^{-3}$

- Weak H-bonds
  - $1435 \text{ nm}$
  - $6969 \text{ cm}^{-1}$
  - Gradient = $0.15 \times 10^{-3}$

- (LP)$_{\text{free band}}$
  - $1473 \text{ nm}$
  - $6790 \text{ cm}^{-1}$
  - Gradient = $0.066 \times 10^{-3}$
FIGURE 5.1c
Temperature effect on $2\nu$OH of CD$_3$OH/OD (10% CD$_3$OH in CD$_3$OD v/v) after deconvolution.

FIGURE 5.1d
Temperature effect on $2\nu$OH of MeOH/OD (20% MeOH in MeOD v/v) after deconvolution.
The deconvoluted bands for CD$_3$OH show a greater shift to higher wavenumber than MeOH with increasing temperature. The "(LP)$_{free}$" band for CD$_3$OH shifts 36 cm$^{-1}$, 10 nm, going from 25$^\circ$ to 50$^\circ$C while for MeOH a 25 cm$^{-1}$, 5 nm, shift is observed. Also the weak H-bond entities shift 23 cm$^{-1}$, 4.3 nm, for CD$_3$OH over the range 25$^\circ$ to 50$^\circ$C while for MeOH a 9 cm$^{-1}$, 1 nm, shift is observed.

The change in the (LP)$_{free}$ methanol band due to added tetraalkylammonium salts is shown in Figures 5.2 and 5.3. All halide salts show about the same effect on the spectrum regarding (LP)$_{free}$ growth. This accords with the view that the large $R_4N^+$ cations undergo negligible solvation relative to the anions [16]. To check this postulate, tetramethylsilane was added to MeOH in MeOH. Spectral changes are small compared with those induced by $R_4N^+X^-$ salts, hence changes in the spectra are assigned to anion solvation only.

The strongly basic acetate ion produces a result comparable to the halides, indicating Cl$^-$, Br$^-$, I$^-$ and CH$_3$COO$^-$ have the same solvation number in methanol at 25$^\circ$C. The results for CN$^-$, OCN$^-$ and NO$_3^-$ indicate that these anions have solvation numbers about half those for the halide ions (Figures 5.2, 5.3 and Table 1). The perchlorate anion is considered later since curve analysis is required to deduce the effect on the (LP)$_{free}$ band.

**TABLE 1**

Gradients (Arbitrary Units)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu$_4$NCl</td>
<td>1.16</td>
</tr>
<tr>
<td>Et$_4$NCl</td>
<td>1.17</td>
</tr>
<tr>
<td>Me$_4$NCl</td>
<td>1.10</td>
</tr>
<tr>
<td>Bu$_4$NBr</td>
<td>1.12</td>
</tr>
<tr>
<td>Et$_4$NBr</td>
<td>1.04</td>
</tr>
<tr>
<td>Bu$_4$NI</td>
<td>1.04</td>
</tr>
<tr>
<td>Bu$_4$NCH$_3$CO$_2$</td>
<td>1.01</td>
</tr>
<tr>
<td>Et$_4$NCO$_2$</td>
<td>0.62</td>
</tr>
<tr>
<td>Et$_4$NOCN</td>
<td>0.63</td>
</tr>
<tr>
<td>Bu$_4$NNO$_3$</td>
<td>0.61</td>
</tr>
</tbody>
</table>
FIGURE 5.2
Change in the (LP) free band of MeOH/OD (20% MeOH in MeOD %v/v) on addition of tetraalkylammonium salts, 1st. overtone region.
Temperature = 25°C ± 0.1
FIGURE 5.3
Change in the (LP)\textsubscript{free} band of MeOH/OD (20\% MeOH in MeOD v/v) on addition of tetraalkylammonium salts in the first overtone region.
Temperature = 25° C ± 0.1
The large absorbance due to weak ClO$_4^-$--HOMe hydrogen bonds masks the true effect on the (LP)$_{\text{free}}$ band on the observed spectrum. Several perchlorate salts were studied, NaClO$_4$, producing a large absorbance at 1435 nm, 6969 cm$^{-1}$, Figure 5(c), due to Na$^+$ scavenging 6 lone-pair groups to ClO$_4^-$ scavenging 2 OH groups. Hence the net result is a loss of (LP)$_{\text{free}}$ groups, a gain in OH weakly bound and a gain in ClO$_4^-$--HOMe, with an isobestic point occurring at 1471 nm. The rate of growth for ClO$_4^-$--HOMe weak interactions is approximately twice as much for Mg(ClO$_4$)$_2$ as for the 1:1 electrolytes, LiClO$_4$, NaClO$_4$ and Bu$_4$NClO$_4$ as expected.

Cation solvates occur close to the bulk band in methanol [2] which shows a maximum at 6350 cm$^{-1}$, 1575 nm. Hence cation effects on the spectra are relatively small, the small monovalent cations forming slightly weaker bonds and small divalent cations forming slightly stronger bonds with the methanolic oxygen lone-pair of electrons than bulk methanol [18]. All the perchlorate salts studied show a substantial loss of absorbance in the bulk methanol region, see Figure 5(c). The tetraalkylammonium salts also show a reduction in bulk absorbance. The most dramatic loss of bulk is shown for Bu$_4$NCl, Et$_4$NCl [Figure 5(b)], and Bu$_4$NNO$_3$, however Me$_4$NCl [Figure 5(h)], does not produce such a dramatic loss of bulk absorbance. This anomalous behaviour for Bu$_4$NCl, Et$_4$NCl and Bu$_4$NNO$_3$, compared to how other salts affect the bulk band is not clearly understood. Figure 5.4 shows the change in the bulk band for the salts studied. The change in the bulk methanol band on addition of bases is shown in Figure 5.7. DMSO-$d_6$, [Figure 5(i)], and CD$_3$CN, [Figure 5(g)], produce the greatest loss of bulk absorbance compared to the other bases. This can be understood in terms of an intermolecular CH$_3$ + OH coupling contribution to the
FIGURE 5.4
Change in the bulk methanol band on addition of various salts, 1st. overtone region.
Temperature = 25°C ± 0.1
bulk band absorbance [15]. When deuterated bases are added to methanol, 
(CD$_3$)$_2$SO-–HOMe hydrogen bonds replace methanol to methanol hydrogen 
bonds, likewise for CD$_3$CN, hence the CH$_3$+OH intermolecular coupling 
is diminished, thus a greater loss in bulk absorbance is observed. 
Indeed, Figure 5(a)(ii), showing the effect of temperature on the 
CD$_3$OH/OD spectrum, shows a change in band shape compared to methanol's 
spectrum, notably in the bulk region. This indicates that the broad 
"bulk" band ca. 1575 nm in methanol is due to a CH$_3$+OH intermolecular 
coupling band, which is not present in CD$_3$OH/OD. 
The observed change in (IP)$_{\text{free}}$ absorbance due to added base is 
shown in Figure 5.5. The measured gradients from the slopes would 
indicate the same relative basicity for DMSO, DMSO-d$_6$, THF and DMA, 
while Et$_3$PO produced a steeper gradient. HMPA appears to be between 
Et$_3$PO and the other bases. Table 2 lists the gradients for the (IP)$_{\text{free}}$ 
growth due to added base in methanol at 25°C.

<table>
<thead>
<tr>
<th></th>
<th>Gradients (Arbitrary Units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_3$PO</td>
<td>0.63</td>
</tr>
<tr>
<td>HMPA</td>
<td>0.48</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.38</td>
</tr>
<tr>
<td>DMSO-d$_6$</td>
<td>0.36</td>
</tr>
<tr>
<td>THF</td>
<td>0.35</td>
</tr>
<tr>
<td>DMA</td>
<td>0.34</td>
</tr>
</tbody>
</table>

The result for CD$_3$CN, [Figure 5(g)], shows a large absorbance in the 
weakly bound region, ca. 1450 nm. This may be due in part to weak 
CD$_3$CN-–HOMe interactions which act to obscure the true effect on the 
(IP)$_{\text{free}}$ growth. Curve analysis is required to deduce the position of 
the CD$_3$CN-–HOMe solvate and, by allowing for this weak interaction, 
deduce the solvation number of CD$_3$CN in methanol. This will be discussed 
later in the curve analysis section [5.4(ii)].
FIGURE 5.5
Change in the (LP)$_{free}$ band of MeOH/OD (20% MeOH in MeOD Vv) on addition of bases in the first overtone region.
Temperature = 25°C ± 0.1
On a qualitative scale it is possible to deduce solvation numbers for the anions and bases studied in methanol, if Et₃PO is used as an internal reference point. It has been shown that Et₃PO is a di-base in methanol [19], hence by direct comparison of all gradients for salts and bases with the Et₃PO result, the relative basicities of other salt anions and bases can be determined. These are listed in Table 3.

**TABLE 3**

<table>
<thead>
<tr>
<th>Solvation number in Methanol at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₄NCl</td>
</tr>
<tr>
<td>Et₄NCl</td>
</tr>
<tr>
<td>Bu₄NCl</td>
</tr>
<tr>
<td>Bu₄NEtBr</td>
</tr>
<tr>
<td>Et₄NEtBr</td>
</tr>
<tr>
<td>Bu₄NI</td>
</tr>
<tr>
<td>Bu₄NCH₃CO₂</td>
</tr>
<tr>
<td>Et₄OCN</td>
</tr>
<tr>
<td>Et₄NCN</td>
</tr>
<tr>
<td>Bu₄NNO₃</td>
</tr>
<tr>
<td>Et₃PO</td>
</tr>
<tr>
<td>HMPA</td>
</tr>
<tr>
<td>DMSO</td>
</tr>
<tr>
<td>DMSO-d₆</td>
</tr>
<tr>
<td>THF</td>
</tr>
<tr>
<td>DMA</td>
</tr>
</tbody>
</table>

These solvation numbers look reasonable values for anions and bases in methanol. All the halides have the same number, i.e. 4, in keeping with other workers' results [17]. In aqueous solutions it has been shown [20] that Cl⁻ has a solvation number of 6 and Et₃PO one of 3 [19]. The decrease in going from 6 to 4 for Cl⁻ is in line with the fall from 3 to 2 for Et₃PO. It is expected that anions and bases have lower solvation numbers in methanol since water brings out a maximum solvation number due to the significantly large (OH)₉ free group concentration. The acetate ion is also found to have a solvation number of four, with presumably each oxygen forming two hydrogen bonds. Linear ions CN⁻ and NCO⁻ have solvation numbers of two, these bonds may also be linear:
The more weakly basic nitrate ion also has a solvation number of two. The NO$_3^-$ ion has a high polarisability, so possibly solvation at two oxygens pulls the $\delta$-ve charge away from the third oxygen. This result accords well with the nitrate ion undergoing asymmetric solvation [6], in dilute methanolic solution, in the absence of significant ion-pairing.

Work done on the solvation of bases in water [21], in the Second Overtone region, indicates DMSO, DMA to be dibasic and HMPA tribasic or higher. Hence a result for DMSO, DMA indicating them to be monobasic in methanol and THF mono/dibasic, fits in with the expected drop in solvation number on going from water to methanol.

The change in the (LP)$_{\text{free}}$ band of methanol at 50°C due to the addition of various solutes is shown in Figure 5.6. The same relative trends are found as occur at 25°C, indicating the scavenging of OH groups in methanol by anions and bases to be unaffected by temperature.

An interesting system looked at in the first overtone region of methanol was NaBPh$_4^-$, Figure 5(d). In this system the Na$^+$ cation scavenges (LP)$_{\text{free}}$ groups, thus generating a growth in OH weakly bound ca. 1440 nm. An isosbestic point occurs at ca. 1472 nm, very close to the (LP)$_{\text{free}}$ position. This system was deconvoluted, the results of which are discussed later in this Chapter. Figure 5(f) shows the change on the methanol spectrum when NaBPh$_4^-$ has been added to generate OH weakly bound, then a base added to scavenge OH weakly bound. The NaBPh$_4^-$ concentration is kept constant in each methanol sample as base is titrated in. An isosbestic point appears at ca. 1460 nm, accompanying observed growth in the (LP)$_{\text{free}}$ and bulk regions as base is added to the system. The
Molefraction of DMSO-\textsubscript{d\textsubscript{6}}

1. 0
2. 0.05
3. 0.1
4. 0.2

FIGURE 5f

Methanol/OD (MeOH in MeOD 20\% \textsubscript{v/v})
at 25°C containing NaBP\textsubscript{4}
(0.033 molefraction) with added DMSO-\textsubscript{d\textsubscript{6}}.

Absorbance

Growth in bulk MeOH

Loss of OH weakly bound

Growth in (LP)\textsubscript{free}

Nanometers
FIGURE 51
Effect of DMSO-\textsubscript{d\textsubscript{6}} on the first overtone spectrum of methanol (20\% v/v) in MeOD at 25°C.

1. 0.00
2. 0.02
3. 0.05
4. 0.10
5. 0.16

Absorptance

Mole fraction of DMSO-\textsubscript{d\textsubscript{6}}

Loss of bulk methanol
Isosbestic at 1500 nm
Growth in (EP) free

Nanometers

1300
1400
1500
1600
FIGURE 5.6
Change in the (LP)_{free} band of MeOH/OD (20% MeOH in MeOD \( \nu/\nu \)) on addition of various salts in the first overtone region.
Temperature = 50°C ± 0.1
FIGURE 5.7
Change in the bulk methanol band on addition of various bases in the first overtone region.
Temperature = 25°C ± 0.1
addition of CHCl₃ to methanol at 25°C results in a growth of OH weakly bound at ca. 1405 nm, 7117 cm⁻¹ and a loss in the bulk region.

(ii) Curve Analysis

The curve analysis technique outlined in Chapter 4 for Second Overtone aqueous systems was applied to several methanol systems. It was of particular importance for deducing the ClO₄⁻ and CD₃CN solvation numbers, showing where the growth of OH weakly bound occurs in methanol when NaBPh₄ is added and for showing that the same trends occur for a tetra-base: Et₃NCl, dibase: Et₃PO and mono-base: DMSO-d₆ before and after curve analysis.

Figures 5.8 and 5.8(b) show the deconvolutions of MeOH/OD and CD₃OH/OD respectively at 25°C, using a minimum of 4 bands, which represent a range of OH oscillators going from strongly hydrogen bonded methanol to very weakly bonded. The effect of a tetraalkylammonium salt on the methanol spectrum at 25°C is highlighted in the case of Et₃NCl, Figure 5.9. The overall band shape is significantly changed with a large drop in bulk methanol and OH weakly bound, accompanied by a large growth in the band at 6738 cm⁻¹ under which (LP)⁺ groups are present. Figure 5.10 clearly shows a loss in absorbance in the (LP)⁺ region on adding NaBPh₄, due to Na⁺ scavenging. The bulky BPh₄⁻ is thought to undergo negligible solvation relative to the smaller, more active cation. The curve analysis indicates a large growth in OH weakly bound at ca. 6934 cm⁻¹.

The effect of adding perchlorate salts to methanol is shown in Figures 5.11 and 5.12 for Bu₄NClO₄ and Mg(ClO₄)₂ respectively. In the former case, the cation is thought to play no major rôle in the overall change, hence Bu₄NClO₄ is a true measure of the anion effect. The spectrum shows a lack of resolution due to the inclusion of (LP)⁺.
FIGURE 5.8

The deconvolution of the OH band of MeOH in MeOD at 25°C.
FIGURE 5.8b
The deconvolution of the OH band of CD$_3$OH in CD$_3$OD at 25°C.
FIGURE 5.9
The deconvolution of the OH band of MeOH in Et₄NCl/MeOD at 25°C.
[M.F. Et₄NCl = 0.17]
FIGURE 5.10

The deconvolution of the OH band of MeOH in NaBPh₄/MeOD at 25°C. [M.F. NaBPh₄ = 0.032]
FIGURE 5.11

The deconvolution of the OH band of MeOH in Bu\textsubscript{4}NCIO\textsubscript{4}/MeOD at 25°C.

[M.F. Bu\textsubscript{4}NCIO\textsubscript{4} = 0.054]

![Graph showing deconvolution of the OH band of MeOH in Bu\textsubscript{4}NCIO\textsubscript{4}/MeOD at 25°C.](image)
FIGURE 5.12
The deconvolution of the OH band of MeOH in Mg(ClO₄)₂/MeOD at 25°C.
[M.F. Mg(ClO₄)₂ = 0.041]
A drop in the OH weakly bound band ca. 1410 nm, 7097 cm⁻¹, is observed due to ClO₄⁻ scavenging, accompanied by a growth in the (LP)free band ca. 1487 nm, 6727 cm⁻¹. An additional 5th. band is required to obtain a good fit between experimental and simulated envelopes representing ClO₄⁻—HOME weak interactions. Figure 5.12 shows the extent to which Mg(ClO₄)₂ alters the methanol band shape. There is good resolution due to loss of (LP)free groups. Here there is a greater contribution from ClO₄⁻—HOME weak H-bonds and from the cation. If Mg²⁺ scavenges 6 lone-pair groups [17] and ClO₄⁻ scavenges 2 OH groups, the imbalance leads to a growth in OH weakly bound. Thus for Mg(ClO₄)₂, the spectral change is a result of loss of (LP)free groups, an increase in OH weakly bound and ClO₄⁻—HOME weak interactions.

The change in the deconvoluted bands of MeOH/OD on addition of Bu₄⁺ClO₄⁻ is shown in Figure 5.13. The diagram shows an increase in (LP)free, an increase in ClO₄⁻—HOME weak interactions and a decrease in OH weakly bound. Figure 5.14 shows the change in the methanol deconvoluted bands with added Et₄NCl. Here the growth of (LP)free groups is significantly larger than in the ClO₄⁻ case due to Cl⁻ having a larger solvation number, hence scavenging more OH groups. The effect of NaBPh₄ on the deconvoluted bands of methanol is shown in Figure 5.15. Here the reverse effect on the component bands is observed, compared to the results for added bases. The (LP)free band shows a decrease in absorbance due to Na⁺ scavenging while OH weakly bound shows a large increase in absorbance.

The curve analysis procedure applied to Bu₄⁺NI, Et₄NCl, Et₃PO, DMSO-d₆, Bu₄⁺ClO₄⁻ and CD₃CN enabled the ClO₄⁻ and CD₃CN solvation numbers to be determined. Figure 5.16 shows the change in the deconvoluted bands of methanol due to added CD₃CN. An additional fifth band ca. 6900
FIGURE 5.13
Change in the deconvoluted bands of MeOH/OD in the first overtone region on addition of Bu$_4$NCIO$_4$.
Temperature = 25°C ± 0.1
FIGURE 5.14
Change in the deconvoluted bands of MeOH/OD in the first overtone region on adding Et₄NCl.
Temperature = 25°C ± 0.1
FIGURE 5.15
Change in the deconvoluted bands of MeOH/OD in the first overtone region on adding NaBPh₄.
Temperature = 25°C ± 0.1
FIGURE 5.16
Change in the deconvoluted bands of MeOH/OD in the first overtone region on adding CD$_3$CN.
Temperature = 25°C ± 0.1
cm\(^{-1}\), 1449 nm, had to be used to obtain a good fit between experimental and simulated spectra. This band is assigned to relatively weak CD\(_3\)CN-HOMe interactions which gives rise to a larger increase in absorbance in the (LP)\(_{\text{free}}\) region than would otherwise be the case. Hence by allowing for these weak oscillators, the actual growth in the (LP)\(_{\text{free}}\) band due to CD\(_3\)CN scavenging OH groups can be deduced.

Figure 5.17 shows the relative effect on the (LP)\(_{\text{free}}\) band absorbance for added solutes after curve analysis. The result shows the same trend for the solutes as observed earlier in this study. The gradients are given below:

<table>
<thead>
<tr>
<th>Solute</th>
<th>Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu(^{+})N(<em>{\text{ClO}})(</em>{4})</td>
<td>0.182</td>
</tr>
<tr>
<td>Et(_{3})NCl</td>
<td>0.186</td>
</tr>
<tr>
<td>Et(_{3})PO</td>
<td>0.094</td>
</tr>
<tr>
<td>Bu(^{+})N(<em>{\text{ClO}})(</em>{4})</td>
<td>0.082</td>
</tr>
<tr>
<td>DMSO-d(_{6})</td>
<td>0.051</td>
</tr>
<tr>
<td>CD(_3)CN</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Bu\(^{+}\)N\(_{\text{ClO}}\)\(_{4}\) produces a gradient close to Et\(_{3}\)PO, which is known to be a di-base in methanol, hence ClO\(_{4}\)\(^-\) is assigned a solvation number of 2, in keeping with other workers' findings [17]. The extent to which the ClO\(_{4}\)\(^-\)---HOMe band grows up in the curve analysed methanol/ClO\(_{4}\)\(^-\) systems is based on the Bu\(^{+}\)N\(_{\text{ClO}}\)\(_{4}\) analysis. An additional fifth band is incorporated to account for ClO\(_{4}\)\(^-\)---HOMe weak bonds. The rate of ClO\(_{4}\)\(^-\)---HOMe band growth is then used in the deconvolutions of LiClO\(_{4}\), NaClO\(_{4}\), and Mg(ClO\(_{4}\))\(_{2}\). Only when a good fit is obtained for all the perchlorate systems, by using the same extent of ClO\(_{4}\)\(^-\)---HOMe growth, is the final actual increase in absorbance due to these weak interactions used. This systematic trial and error approach has to be adopted for what would otherwise be an arbitrary contribution from ClO\(_{4}\)\(^-\)---HOMe growth in these systems. Having obtained good "fits" for all the
FIGURE 5.17
Change in the deconvoluted band of MeOH/OD containing (LP)\textsubscript{free} groups in the first overtone region due to added solutes.
Temperature = 25°C ± 0.1
perchlorate systems, the \((LP)_{\text{free}}\) band absorbance is monitored, which by comparison with the \(\text{Et}_3\text{PO}\) result produces the \(\text{ClO}_4^-\) disolvate result. \(\text{CD}_3\text{CN}\) produces a curve analysed \((LP)_{\text{free}}\) gradient close to \(\text{DMSO-d}_6\), hence it is assigned a solvation number of 1.

Table 4 lists the "best" \(\text{cm}^{-1}/\text{nm}\) values for all the methanol deconvoluted bands at 25°C, averaged from the systems studied.

### Table 4

Infrared Parameters for deconvoluted band maxima in the \(2\nu\text{OH}\) region for methanol at 25°C

<table>
<thead>
<tr>
<th>Band Description</th>
<th>(\text{nm})</th>
<th>(\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Weak H-bonds</td>
<td>1408</td>
<td>7100</td>
</tr>
<tr>
<td>(2) Weak H-bonds</td>
<td>1442</td>
<td>6935</td>
</tr>
<tr>
<td>(3) &quot;((LP)_{\text{free}})&quot; band</td>
<td>1487</td>
<td>6725</td>
</tr>
<tr>
<td>(4) Bulk H-bonds</td>
<td>1579 (1554)²</td>
<td>6335</td>
</tr>
</tbody>
</table>

² Value for \(\text{CD}_3\text{OH}\) in \(\text{CD}_3\text{OD}\)

(iii) Cation Solvation

The effect of \(R_4\text{N}^+\) ions on the methanol spectra is assumed to be small, as in the case for tetramethylsilane. Hence the effects for these salts are assigned entirely to the anions. However, for salts containing metal cations, the following reaction should occur:

\[
\begin{align*}
\text{Me}^+ + (\text{MeOH}) & \rightarrow \text{Me}^+ - \text{O-H} - \text{O-H} - \\
& + \text{H-O} - \text{H-O} - \\
& \text{(OH)_{free}}
\end{align*}
\]

giving rise to a gain in [OH] weakly bound units. This was observed experimentally for \(\text{Na}^+\text{BPh}_4^-\). There was also a marked loss of absorption in the \((LP)_{\text{free}}\) region, illustrated after curve deconvolution (Figure 5.10). If the simple postulate is made that the initial, linear loss of
(LP)\text{free} is a measure of the sodium solvation number, assuming BPh$_4^-$ undergoes negligible solvation and using as before the data for Et$_3$PO as a reference, a solvation number of 5.7 for sodium in methanol is found. This result ties in with recent molecular dynamics computer simulation work [9] which predicts a solvation number of six for Na$^+$ in methanol. This result for Na$^+$ can be checked by studying results for NaClO$_4$, i.e. comparing the decrease in (LP)\text{free} band absorbance against the Et$_3$PO result, hence giving the Na$^+$ solvation number. These results would be less accurate, especially in view of the extra band assigned to ClO$_4^-$ solvates.

**(iv) Resolution Enhancement**

A resolution enhancement technique [22] was applied to methanol (CH$_3$OH or CH$_3$OD) in CH$_3$OD (or CD$_3$OD) at 25°C. Data coordinates were read directly into a Z80 microcomputer from the spectra. The resolution enhanced spectra was obtained by subtracting a fraction (k) of the second derivative spectrum from the original absorbance, i.e. Resolution enhanced spectra = Original absorbance - k (2nd. derivative)

The fraction (k) of the second derivative being changed until a good resolution enhanced spectrum is obtained.

The resolution enhanced spectrum of MeOH in MeOD showed a bulk methanol band at 6302.6 cm$^{-1}$, the OH weakly bound at 7097 cm$^{-1}$ and the (LP)\text{free} band at 6845 cm$^{-1}$, 1461 nm (Figure 5.18). The same technique was applied to CD$_3$OH in CD$_3$OD at 25°C. The bulk band was positioned at 6446 cm$^{-1}$ (Figure 5.19), a shift of 143.4 cm$^{-1}$ from the MeOH position. This result indicates that the broad methanol band assigned to bulk hydrogen bonds must have an intermolecular CH$_3$-OH coupling contribution, since a significant shift is observed on deuterating methanol accompanied by a loss of bulk absorbance. By removing CH$_3$-OH intermolecular
FIGURE 5.18

The resolution enhanced spectrum of methanol (208 \text{\%}) in KClO$_3$. Temperature = 25°C ± 0.1.

Original spectrum

Resolution enhanced spectrum

Wavenumber (cm$^{-1}$)

6302.6

6845

7097

7389
coupling, the CD$_3$OH spectrum is seen to change shape, showing a shift in bulk to higher frequency and loss of resolution in the (LP)$^\text{free}$, OH weakly bound regions, ca. 6845 cm$^{-1}$, 7097 cm$^{-1}$ respectively. The CD$_3$OH position for OH weakly bound, 7121 cm$^{-1}$, shows a 24 cm$^{-1}$ shift to higher frequency compared to the methanol position. However, the apparent (LP)$^\text{free}$ position, 6845 cm$^{-1}$, is identical for MeOH and CD$_3$OH.

Hence with the aid of computer controlled resolution enhancement, the exact positions of the envelope components can be fixed for (LP)$^\text{free}$, bulk and OH weakly bound methanol. This technique would lend itself to a more accurate method of monitoring change in (LP)$^\text{free}$ group concentration on adding a base because changes in the spectrum are magnified, hence more accurate results would be obtainable.

5.5 CONCLUDING REMARKS

This study has provided a useful method of determining anion and base solvation numbers in methanol by measuring changes in (LP)$^\text{free}$ concentration as opposed to (OH)$^\text{free}$ concentration normally associated with water + base systems. The results indicate lower solvation numbers for anions and bases in methanol compared to aqueous solvation numbers and correlate favourably with other workers' findings.
REFERENCES FOR CHAPTER 5

CHAPTER 6

A Near-Infrared Study of 2,2,2-Trifluoroethanol
6.1 INTRODUCTION

This work considers the effect on the $2\nu_{OH}$, (1650-1300 nm), spectra of 2,2,2-Trifluoroethanol when salts and bases are added. A less comprehensive study is also made in the fundamental region (3750-3000 cm$^{-1}$). 2,2,2-Trifluoroethanol exhibits a sharp peak at 7087 cm$^{-1}$, (1411 nm), assigned to (OH)$_{\text{free}}$ groups. The main concern of this work is the effect on the (OH)$_{\text{free}}$ band when solutes are added, which leads to a qualitative estimate of base and anion solvation numbers.

6.2 PREVIOUS WORK

6.2.1 Relative Acidities of Fluoroalcohols

A comprehensive literature exists regarding the increased acidity of fluoroalcohols relative to typical alcohols. Swarts [1], in 1929, pointed out that the introduction of fluorine increases the acidity of alcohols. Henne and Francis [2] found perfluorinated primary alcohols to be $10^6$ times more acidic than their unfluorinated analogues, based on the ionisation constant of alcohols perfluorinated in the a-position, to be of the order of magnitude of $K_i = 10^{-12}$. They report $4 \times 10^{-12}$ for CF$_3$CH$_2$OH. They also found that this increase in acidity is not doubled in secondary alcohols and not tripled in tertiary alcohols, again based on ionisation constants. The ionisation constants for primary, secondary and tertiary fluorinated alcohols studied were all of the order $4 \times 10^{-12}$. They stated that the bulk of the inductive effect is exercised by the first fluorinated group.

Dyatkeens et al. [3], measured the pK$_a$ of some fluoroalcohols and found the high electronegativity of the fluorine atom and a great $-I$ effect of perfluoroalkyl groups connected with it, facilitate protonisation of the neighbouring H atom and sharply increase acidic properties of fluoro-organic compounds as compared with the corresponding non-
fluorinated analogues. Middleton and Lindsey [4], synthesised secondary and tertiary fluoroalcohols and found them to be strong hydrogen bonding donors as evidenced by their solvent properties, complex formation, acidities and IR, NMR spectra, due to the cumulative inductive effect of the fluorine atoms present.

Ballinger et al. [5], showed the acid ionisation constant for 2,2,2-Trifluoroethanol to fit well with data for carboxylic acids and phenols. They studied substituent effects on the ionisation constant $pK_{HA}$ for a series of mono-substituted methanols. Strongly electron attracting groups like CF$_3$ lead to the strongest acids. Rao et al. [6], did an NMR study of hydrogen bonding in ethanol and 2,2,2-Trifluoroethanol. The chemical shift at infinite dilution in benzene is lower for the fluoroalcohol, because the more electronegative group should lessen the shielding of the hydroxyl proton. The greater acidity of the fluoroalcohol, compared to ethanol should result in a decreased shielding of the hydroxyl proton. They also say that steric effects are important in view of the decrease in chemical shift at infinite dilution with the increase in the bulk of the alkyl group. Their observation that 2,2,2-Trifluoroethanol is less associated than ethanol at low concentrations due to the electronegativity of the CF$_3$ group, is supported by IR and NMR studies on chloroethanols [7,8]. It was found that chloroethanols also show greater concentration of monomeric species compared to ethanol.

6.2.2 Effect on Electronic Transitions

2,2,2-Trifluoroethanol causes a greater shift to higher energy (lower wavelength) on the $n-\pi^*$ transition of the carbonyl group of acetone than ethanol [9], indicating that the fluoroalcohol is a better hydrogen bond donor than ethanol. Rao et al. [10], studied the effects of non-polar, polar and proton-donating solvents on the $n-\pi^*$ transitions of
C=O, C=S, NO_2 and N=N groups. Among the proton donating solvents studied, they found the shift to high energy in 2,2,2-Trifluoroethanol to be nearly equal to that in water, which produces the biggest shift. The high energy shifts in the alcohols studied, decreased in the order; 2,2,2-Trifluoroethanol, methanol, ethanol, isopropanol and t-butanol. This trend is exactly opposite to that for the self-association of alcohols. It is suggested that electron-withdrawing groups decrease the extent of self-association of alcohols and increase the ability to donate hydrogen bonds.

6.2.3 Band Assignments and Conformations of 2,2,2-Trifluoroethanol

Purcell and Wilson [11] determined IR stretching frequency shifts and proton chemical shifts for the hydroxyl group of 2,2,2-Trifluoroethanol hydrogen bonded to a variety of Lewis bases. They assigned the fundamental band at 3615 cm\(^{-1}\), the first overtone band at 7087 cm\(^{-1}\) and the second overtone OH band at 10,395 cm\(^{-1}\) for 2,2,2-Trifluoroethanol. According to Kruger's study [12] of halo-substituted ethanol, the OH band at 3615 cm\(^{-1}\) is due to the gauche or intramolecularly bonded form of trifluoroethanol. The trans or "free" OH vibration is estimated to occur at 3636 cm\(^{-1}\). Kruger studied various OH stretch bands of the fluoroalcohols; including 2,2,2-trifluoroethanol in CCl_4, which exhibits temperature dependent band asymmetry due to trans-gauche equilibria arising from rotation about the C-O bond, with relatively small populations in the trans forms. Results are discussed in terms of intramolecular OH-\(\cdots\)-X hydrogen bond interaction, inductive effects, non-bonded interactions, O-H bond polarisation, C-X bond polarisability and the size of the halogen atoms in a geometrically constrained system. Kruger expected that CF\(_3\)CH\(_2\)OH would be completely intramolecularly bonded. However, Cannon and Stace [13] reported a "free" OH stretching
band for 2,2,2-trifluoroethanol in CCl₄ solution (3617 cm⁻¹), which persisted even in pure liquid state (3628 cm⁻¹). Their interpretation did not support intramolecular OH---X bonding. Kruger [12] says a simple equilibrium is conceivable for 2,2,2-trihaloethanols, considering rotation about the C-C and C-O bond.

The OH group is always gauche to two halogen atoms. The hydroxyl proton can get away from the gauche halogen(s) only by rotation about the C-O bond. Oki and Iwamura [14] found an OH band for 2,2,2-trifluoroethanol in CCl₄ solution, which was asymmetric on the high frequency side and interpreted this in terms of an unresolved doublet due to trans-gauche isomerism because of restricted rotation about the C-O bond. From mathematical resolution of the doublet they concluded that 2,2,2-trifluoroethanol was predominantly in the intramolecularly bonded gauche form. Haszeldine [15] had earlier reported intramolecular OH---X hydrogen bonding in primary and secondary haloalcohols, but due to poorly resolved spectra, could not come to detailed conclusions on the "free" OH band.

6.3 EXPERIMENTAL

All first overtone spectra were recorded on a Perkin-Elmer 340 UV/VIS/NIR spectrophotometer. A time scan of 3 minutes and a λ exp = ×5, was used. All spectra were recorded at 25°C ±0.1, and a photometric scale of 0-0.5 was used. 2,2,2-Trifluoroethanol, used without further purification, was obtained from Aldrich Chemical Co. Ltd. at 99+ %
purity. Salts were dried under vacuum and stored over silica gel in a
dessicator before use. All solvents were purified by distillation over
CaH$_2$ and dried over CaH$_2$ before use. Deuterated fluoroalcohol was not
available, hence all systems studied were recorded using difference
spectra.

In the case of the salt systems, a stock solution of fluoroalcohol +
salt was made up by weight, to a known volume. Sample solutions were
prepared using a known volume of base or fluoroalcohol + salt solution
and making up to the 5 ml volume mark with fluoroalcohol. The systems
studied were checked for changes in volume on mixing. A maximum volume
change of ~2% was observed for bases added to fluoroalcohol, up to 0.25
molar fraction of base. A negligible volume change was found for salt/
fluoroalcohol solution added to fluoroalcohol. The spectra were
subsequently corrected for any change in volume on mixing. The reference
solutions consisted of the same volume of added solute as in the sample,
but were made up to the 5 ml mark with CCl$_4$. If the salts were insoluble
in CCl$_4$, MeOD was used instead.

Each difference spectrum has to be corrected for loss of OH oscillator
in the sample, since [OH] is not kept constant in the sample solutions.
This was achieved by calculating the % moles of fluoroalcohol in each
sample, which decreases as more solute is added, then increasing the
absorbance accordingly, normalising to 100% [OH].

All fundamental infrared spectra were recorded on a Perkin-Elmer 580
spectrometer. The solutions were made up in the same manner as previously
described for the first overtone study. All fundamental spectra were
recorded using demountable CaF$_2$ cells with a 12µm spacer, at a temperature
of 25°C. A variable vertical expansion and a horizontal expansion of x5
was used. Glass cells with a 2 mm pathlength were used in the first
overtone work.

6.4 RESULTS

6.4.1 Anions and Bases

The first overtone spectra were recorded in the 7690-6060 cm\(^{-1}\) region (1650-1300 nm). The effect of added bases and tetraalkylammonium salts on the (OH)\(_{\text{free}}\) band (ca. 7087 cm\(^{-1}\), 1411 nm) are shown in Figs. 6.1 and 6.2 respectively. The experimentally observed (OH)\(_{\text{free}}\) absorbances have been corrected for loss of [OH] as solute is added, since the [OH] oscillator concentration is not kept constant in the sample beam.

An early qualitative assessment showed that all the tetraalkylammonium salts produce a similar gradient for loss of (OH)\(_{\text{free}}\) groups, except \(\text{Bu}^+\text{NClO}_4\). The perchlorate anion is expected to form weak bonds close to the (OH)\(_{\text{free}}\) groups. The resulting growth of a weakly bound feature reduces the fall in (OH)\(_{\text{free}}\) absorbance to some extent. Strong bases such as DMA, DMSO, Et\(_3\)N and DMF, produced gradients for loss of (OH)\(_{\text{free}}\) groups similar to those for \(\text{R}_n\text{N}^+\text{X}^-\) salts, indicating that these solutes have approximately the same effect regarding the extent to which they scavenge (OH)\(_{\text{free}}\) groups.

Thus at this stage of analysis it seems that these strong bases and anions have similar solvation numbers in trifluoroethanol. Weaker bases such as acetone, CH\(_3\)NO\(_2\) and CD\(_3\)CN produce lower gradients. These bases form relatively weak hydrogen bonds compared to the stronger bases. Thus their related \(v_{\text{OH}}\) bands occur at higher frequencies, close to the very weakly bound region of trifluoroethanol. Hence these weak hydrogen bonded bases cause an increase in weakly bound absorbance which reduces the observed loss of (OH)\(_{\text{free}}\) to some extent. The stronger bases have related absorption bands which occur close to the bulk region (1575 nm), well removed from the weakly bound region.
FIGURE 6.1
Change in the $v_0\bar{H}$ "free" band of 2,2,2-Trifluoroethanol measured relative to pure 2,2,2-Trifluoroethanol on addition of Bases.
Temperature = 25°C
FIGURE 6.2
Change in the $2v_{OH}$ "free" band of 2,2,2-Trifluoroethanol measured relative to pure 2,2,2-Trifluoroethanol on addition of Tetraalkylammonium salts.

Temperature = $25^\circ C \pm 0.1$
Figure 6a shows the change in the first overtone spectrum of 2,2,2-trifluoroethanol as a function of temperature, showing a loss in the strongly hydrogen bonded region (1575 nm), and a growth in the weakly bound, (OH)\(_{\text{free}}\) region, as temperature increases from -6°C to 65°C. Figure 6.3 shows a linear change in "free" absorbance with temperature. The effect on the trifluoroethanol spectrum due to adding a strong base (i.e. DMSO) is shown in Figure 6b. The main feature is a significant drop in (OH)\(_{\text{free}}\) absorbance. There appears to be a growth in the bound region, ca. 1575 nm, as base is added which may be due to base bound to trifluoroethanol, giving a relatively intense band. In contrast, Figure 6c shows the effect of adding a weak base, CD\(_3\)CN, which also produces a loss of (OH)\(_{\text{free}}\) groups. However, the most noticeable feature is a large growth in the weakly bound region due to weak CD\(_3\)CN---HO- interactions. This increase in weakly bound species reduces the apparent loss of (OH)\(_{\text{free}}\). Curve analysis is required by using computer graphics, to separate the two conflicting features (i.e. loss of (OH)\(_{\text{free}}\) but a gain in weak CD\(_3\)CN---HO- interactions). Computer graphics can also be used to correct the difference spectra by normalising the absorbance of each spectrum to 100% [OH], simply by increasing the absorbance relative to the % moles [OH] in each sample. This is discussed later in this chapter, showing the true effect on the trifluoroethanol first overtone spectrum, due to added solutes.

Figure 6d shows an even larger growth in weakly bound species when CH\(_3\)NO\(_2\) is added. Hence CH\(_3\)NO\(_2\)---HO units absorb closer to (OH)\(_{\text{free}}\) than CD\(_3\)CN---HO- units, as expected, since CH\(_3\)NO\(_2\) is a weaker base than CD\(_3\)CN. An analogous situation for salts occurs only for Bu\(_4\)NClO\(_4\), which shows a large increase in weakly bound ClO\(_4^\text{-}\)---HO- species close to (OH)\(_{\text{free}}\) [Figure 6e].
FIGURE 6.3
Effect of temperature on the deconvoluted (OH) free band of 2,2,2-Trifluoroethanol.

Absorbance Units

Temperature °C
FIGURE 6b
Effect of DMSO on 2νOH of 2,2,2-Trifluoroethanol (Difference Spectrum).
Temperature = 25°C ± 0.1
FIGURE 6c
Effect of CD₃CN on 2νOH of 2,2,2-Trifluoroethanol (Difference Spectrum).
Temperature = 25°C ± 0.1

CD₃CN Molefraction
1. 0  
2. 0.072  
3. 0.14  
4. 0.206  
5. 0.269

Absorbance

Nanometers (nm)

Growth due to CD₃CN---HOCH₂CF₃

loss of (OH) free
Figure 63
Effect of CH$_3$NO$_2$ on 2000 of 2,2,2-trifluoroethanol (difference spectrum). Temperature = 25°C ± 0.1
FIGURE 6e
Effect of $\text{Bu}^+\text{NCLO}_4$ on $2\nu_{\text{OH}}$ of 2,2,2-Trifluoroethanol (Difference Spectrum).
Temperature = 25°C ± 0.1
The effect of addition of a typical tetraalkylammonium salt, Bu⁺NCl, to 2,2,2-trifluoroethanol is shown in Figure 6f. A significant loss of (OH)\text{free} absorbance is observed and there is no apparent growth in the weakly bound region.

To analyse the results further, curve analysis is required, adopting the same approach described in Chapters 4 and 5. Each first overtone spectrum is put onto a digitised file on a PDP 11/45 computer, then converted from a wavelength scale to a wavenumber scale, as explained in the aforementioned chapters. Figure 6g shows that the trifluoroethanol spectra can be simulated using 4 bands which represent a range of OH oscillators from strongly hydrogen bonded to (OH)\text{free}. We do not suggest that the 4 bands have any precise significance, i.e. we do not imply there to be 4 distinct species present under the overall spectral envelope.

The extent to which dilution might play a role in controlling the concentration of (OH)\text{free} when a solute is added, was examined. CH₂Cl₂ was added to 2,2,2-trifluoroethanol and hexafluoroisopropanol. [OCl⁻ was found to be immiscible in both fluoroalcohols, hence could not be used.] The results are shown in Figure 6.4, where for 2,2,2-trifluoroethanol a 6% increase in (OH)\text{free} absorbance is measured at 0.25 CH₂Cl₂ molefraction. This relatively small dilution effect is accounted for in Figure 6.5, which shows the effect of bases on the (OH)\text{free} band after deconvolution. Figure 6.6 shows how tetraalkylammonium salts affect the (OH)\text{free} band, after deconvolution.

TMS and Bu⁺Sn being inert solutes, were thought ideal to see if there is any increase in (OH)\text{free} absorbance, purely due to a large bulky cation (R₄N⁺) being present. However, both were immiscible in trifluoroethanol. Hence no allowance can be made for a cation dilution effect. Figure 6.6
FIGURE 6E
Effect of Bu₄NCl on νOH of 2,2,2-Trifluoroethanol (Difference Spectrum). Temperature = 25°C ± 0.1
FIGURE 6q
The deconvolution of the OH band of CF₃CH₂OH at 25°C.
FIGURE 6.4
Effect of CH$_2$Cl$_2$ on the deconvoluted "free" bands of 2,2,2-Trifluoroethanol and Hexafluoroisopropanol, measured relative to pure fluoroalcohol.
Temperature = 25°C ± 0.1
FIGURE 6.5

Effect of Bases on the (OH)\textsubscript{free} band of 2,2,2-Trifluoroethanol, after deconvolution and after dilution correction, measured relative to pure fluoroalcohol.

Temperature = 25°C ± 0.1
FIGURE 6.6
Effect of tetraalkylammonium salts on the (OH)\textsubscript{free} band of 2,2,2-Trifluoroethanol, after deconvolution, measured relative to pure fluoroalcohol.
Temperature = 25°C ± 0.1
shows that all the salts studied appear to scavenge (OH)$_{\text{free}}$ groups to the same extent. The LN-% (OH)$_{\text{free}}$ slopes for added bases and salts are shown in Figures 6.7 and 6.8 respectively, the gradients are listed in Table 1.

**TABLE 1**

<table>
<thead>
<tr>
<th>IN-% (OH)$_{\text{free}}$ Gradients</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NO$_2$</td>
</tr>
<tr>
<td>CD$_3$CN</td>
</tr>
<tr>
<td>Acetone</td>
</tr>
<tr>
<td>Et$_3$N</td>
</tr>
<tr>
<td>DMSO</td>
</tr>
<tr>
<td>DMF</td>
</tr>
<tr>
<td>DMA</td>
</tr>
<tr>
<td>But$_4$NI</td>
</tr>
<tr>
<td>But$_4$NBr</td>
</tr>
<tr>
<td>Me$_4$NCl</td>
</tr>
<tr>
<td>But$_4$NCl</td>
</tr>
<tr>
<td>But$_4$NNO$_3$</td>
</tr>
<tr>
<td>But$_4$NClO$_4$</td>
</tr>
</tbody>
</table>

The stronger bases, i.e. DMA, DMF, Et$_3$N and DMSO bring the (OH)$_{\text{free}}$ band down about twice as fast as the relatively weaker bases. The (OH)$_{\text{free}}$ falls to approximately 20-25% of the initial concentration up to a base molefraction of 0.17 for strong bases. These curves show signs of levelling off but are still falling rapidly indicating that all the (OH)$_{\text{free}}$ may disappear at a base molefraction of about 0.3.

The tetraalkylammonium salts reduce the (OH)$_{\text{free}}$ about 25% more rapidly than the strong bases. Results indicate that Cl$^-$, Br$^-$, I$^-$, NO$_3^-$ and ClO$_4^-$ have similar solvation numbers in 2,2,2-trifluoroethanol.

On a qualitative scale, solvation numbers can be estimated for the anions and bases, assuming that the large R$_n$N$^+$ cations undergo negligible solvation relative to the anion, by linking our fundamental IR results with the overtone work. Examination of the vC=O band for acetone shows the presence of two bands which is taken to indicate the presence of two
FIGURE 6.7
Effect of Bases on the LN-% (OH)\textsubscript{free} of 2,2,2-Trifluoroethanol after deconvolution and after dilution correction.

Temperature = 25°C ± 0.1
FIGURE 6.8
Effect of Salts on the LN-% (OH)_{free} of 2,2,2-Trifluoro-ethanol after deconvolution.
Temperature = 25°C ± 0.1
different solvates (Figure 6h). The band at 1707 cm$^{-1}$ is assigned to the mono-solvate and that at 1690 cm$^{-1}$ to the di-solvate. Figure 6i shows that for DMA, two solvates are also present, only this time it is mainly the di-solvate present at 1613 cm$^{-1}$, the mono-solvate having $v_{\text{max}}$ at 1633 cm$^{-1}$. DMA being a relatively stronger base than acetone, it is not surprising that it should favour the di-solvate, more than acetone, hence if acetone is assigned a solvation number of 1 and DMA 2 from the fundamental results, by comparing the gradients in Table 1, solvation numbers can be estimated which are listed in Table 2. Curve analysis revealed approximately 79% mono-solvate and 21% di-solvate for acetone in trifluoroethanol (Figure 6j), by comparing peak heights, and 78% di-solvate, 22% mono-solvate for DMA in trifluoroethanol, (Figure 6k).

Curve analysis was applied to each system studied, to obtain a clearer picture as to the effect on the (OH)$_{\text{free}}$ band when a salt or base is added. Figure 6.9 shows the component bands of 2,2,2-trifluoroethanol changing in absorbance as a function of temperature, the most notable features being the rapid rise in the (OH)$_{\text{free}}$ band with

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Solvation Number</th>
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<tr>
<td>CH$_3$NO$_2$</td>
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</tr>
<tr>
<td>CD$_3$CN</td>
<td>~ 1</td>
</tr>
<tr>
<td>Acetone</td>
<td>~ 1</td>
</tr>
<tr>
<td>DMSO</td>
<td>~ 2</td>
</tr>
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<td>~ 2</td>
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<td>DMF</td>
<td>~ 2</td>
</tr>
<tr>
<td>DMA</td>
<td>~ 2</td>
</tr>
<tr>
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<td>&gt; 2</td>
</tr>
<tr>
<td>But$_4$NBr</td>
<td>&gt; 2</td>
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<td>&gt; 2</td>
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<tr>
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<td>&gt; 2</td>
</tr>
<tr>
<td>But$_4$NClO$_4$</td>
<td>&gt; 2</td>
</tr>
</tbody>
</table>
FIGURE 6h
Monitoring the $\nu_{C=O}$ of Acetone in 2,2,2-Trifluoroethanol.
Temperature = 25°C ± 0.1

Molefraction of Acetone
1. 0.021
2. 0.055
3. 0.084
4. 0.105

Absorbance

Wavenumber (cm$^{-1}$)

-171-
FIGURE 6i
Monitoring the $\nu_{C=O}$ of DMA in 2,2,2-Trifluoroethanol.
Temperature = 25°C ± 0.1
The deconvolution of the $\nu_C=0$ band of acetone in CF$_3$CH$_2$OH at 25°C.

[M.F. Acetone = 0.105]
FIGURE 6k
The deconvolution of the νC=O band of DMA in CF₃CH₂OH at 25°C.
[M.F. DMA = 0.085]
FIGURE 6.9
Intensities of bands obtained by deconvolution of the spectrum of 2,2,2-Trifluoroethanol in the 2νOH region as a function of temperature.

Band 1 = (OH) free
(7114 cm⁻¹)

Band 2 = Very weak H-bonds
(7030 cm⁻¹)

Band 3 = Weak H-bonds
(6717 cm⁻¹)

Band 4 = Strong H-bonds
(6364 cm⁻¹)
increasing temperature and loss of strong H-bonds, band 4. The effect on the deconvoluted bands when DMSO is added is shown in Figure 6.10, highlighting the considerable decrease in (OH)$_\text{free}$ groups relative to the two weakly bound bands. The bulk band actually shows an increase in absorbance which could be due to strong DMSO---HO- interactions coming up close to bulk fluoroalcohol.

The effect CD$_3$CN has on the deconvoluted bands is shown in Figure 6.11, both (OH)$_\text{free}$ and strong H-bonds decrease in absorbance with increasing base concentration. The weakly bound bands increase in absorbance due to weak CD$_3$CN---HO- bonds growing up close to the (OH)$_\text{free}$ band. The CD$_3$CN system was deconvoluted using a minimum of 4 bands, however CH$_3$NO$_2$ (Figure 6.12) needed an extra band at 7040 cm$^{-1}$ (1420 nm) to account for weak CH$_3$NO$_2$---HO- bonds growing up close to (OH)$_\text{free}$.

Figure 6.13 shows the effect Bu$_4$NClO$_4$ has on the component bands of trifluoroethanol. The (OH)$_\text{free}$ band falls off rapidly, as does the bulk band, (6370 cm$^{-1}$). A significant increase in the weakly bound region is observed, due to weak ClO$_4^-$---HO- species growing up. Bu$_4$NI (Figure 6.14) shows a similar effect to that of Bu$_4$NClO$_4$, except growth due to I$^-$---HO- interactions (ca. 6725 cm$^{-1}$), is at lower frequency than ClO$_4^-$---HO- species (ca. 7030 cm$^{-1}$), i.e. closer to the strong H-bond region, (ca. 6370 cm$^{-1}$).

Very dilute 2,2,2-trifluoroethanol in CCl$_4$ was studied in the first overtone region, showing a monomer peak at 7087 cm$^{-1}$, (1411 nm). [This is about identical with band I, assigned to (OH)$_\text{free}$ groups.] A plot of absorbance versus fluoroalcohol concentration (Figure 6.15), shows that Beers Law is obeyed and yields an extinction coefficient of 17.50 mol$^{-1}$ dm$^2$. The percentage (OH)$_\text{free}$ concentration in 2,2,2-trifluoroethanol at 25°C can then be estimated if we assume that the absorbance
FIGURE 6.10

Intensities of bands obtained by deconvolution of the spectrum of 2,2,2-Trifluoroethanol in the $2\nu_\text{OH}$ region, on addition of DMSO, after dilution correction and after correcting for volume change on mixing.

Temperature = $25^\circ\text{C} \pm 0.1$
FIGURE 6.11

Intensities of bands obtained by deconvolution of the spectrum of 2,2,2-Trifluoroethanol in the 2vOH region, on addition of CD3CN, after dilution correction and after correcting for volume change on mixing. Temperature = 25°C ± 0.1

Band 3 = Weak H-bonds
(6711 cm⁻¹)

Band 4 = Strong H-bonds
(6360 cm⁻¹)

Band 2 = Very weak H-bonds
(7030 cm⁻¹)

Band 1 = (OH)free
(7114 cm⁻¹)
FIGURE 6.12

Intensities of bands obtained by deconvolution of the spectrum of 2,2,2-Trifluoroethanol in the $2\nu_{OH}$ region, on addition of CH$_3$NO$_2$, after dilution correction and after correcting for volume change on mixing.

Temperature = 25°C ± 0.1
FIGURE 6.13
Intensities of bands obtained by deconvolution of the spectrum of 2,2,2-Trifluoroethanol in the $2\nu_{OH}$ region on addition of Bu$_4$NClO$_4$ after dilution correction. Temperature = $25^\circ C \pm 0.1$

Band 3 = Weak H-bonds (6725 cm$^{-1}$)
Band 4 = Strong H-bonds (6370 cm$^{-1}$)
Band 2 = Very weak H-bonds (7030 cm$^{-1}$)
Band 1 = (OH)$_{free}$ (7114 cm$^{-1}$)
FIGURE 6.14
Intensities of bands obtained by deconvolution of the spectrum of 2,2,2-Trifluoroethanol in the \(2\nu_{OH}\) region on addition of \(\text{Bu}_4\text{NI}\) after dilution correction.
Temperature = 25°C ± 0.1
FIGURE 6.15
Plot showing the increase in monomer absorbance for 2,2,2-Trifluoroethanol diluted in CCl₄.
Temperature = 25°C ± 0.1
for the (OH)$_{\text{free}}$ groups in the pure alcohol is equal to that for the monomer. [This may not be correct.]

Using Beer's Law: \[ A = \varepsilon c \ell. \]

where \( A \) = absorbance of pure 2,2,2-trifluoroethanol (OH)$_{\text{free}}$ band at 25°C (different from methanol's absorbance in the same region, i.e. MeOH has no (OH)$_{\text{free}}$).

\[ \varepsilon = 17.5 \text{ mol}^{-1} \text{ dm}^2 \]
\[ \ell = 0.02 \text{ dm} \]

\[ 0.342 = 17.5 \times c \times 0.02 \]

\[ c = 0.97714 \text{ mol dm}^{-3} \]

The number of moles of CF$_3$CH$_2$OH per litre = \( \frac{1000 \times 1.288}{100.04} \)

\[ \therefore \text{mols per litre} = 12.8749 \text{ mol dm}^{-3} \]

\[ \therefore \% (\text{OH})_{\text{free}} = \frac{0.97714}{12.8749} = 7.6\% \]

**Calculation of Equilibrium Constant, \( k \)**

The concentration of [(OH)$_{\text{free}}$] in 2,2,2-trifluoroethanol at 25°C has been calculated to be ca. 7.6%, i.e. 0.076 molefraction of (OH)$_{\text{free}}$, using \( \varepsilon \) calculated from a Beer's Law plot, (Figure 6.15), for dilute CF$_3$CH$_2$OH in CCl$_4$. Hence an equilibrium constant can be calculated for the equilibrium:

\[ (\text{F}/\text{OH})_{\text{bound}} \rightleftharpoons (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}} \]

The equation used for calculating the equilibrium constant, \( k \), is:

\[ k = \frac{[(\text{OH})_{\text{free}}].[(\text{LP})_{\text{free}}]}{[(\text{F}/\text{OH})_{\text{bound}} - (\text{OH})_{\text{free}}]} \]

on a molefraction scale:

\[ \therefore k = \frac{(0.076)^2}{(1 - 0.076)} = 0.005776 = 0.0062511 \]

\[ (0.924) \]
To check the equilibrium constant, \( k \), the concentration of \((\text{OH})_{\text{free}}\) in molefraction terms can be re-calculated using \( k \). 

I.e. \((\text{F/OH})_b \rightleftharpoons (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}}\)

at equilibrium: \((1-x)\text{mols} \quad x\text{mols} \quad x\text{mols}\)

\[ k = \frac{x^2}{1-x} \]

\[ k - xk = x^2 \]

\[ x^2 + xk - k = 0 \quad .... [1] \]

Converting equation [1] into quadratic form, it becomes:-

\[ x = -k + \frac{\sqrt{k^2 + 4k}}{2} \]

Substituting \( k = 0.0062511 \)

\[ x = -0.0062511 + \frac{\sqrt{(0.0062511)^2 + 4(0.0062511)}}{2} \]

\[ x = -0.0062511 + \frac{\sqrt{0.000391 + 0.0250}}{2} \]

\[ x = -0.0062511 + 0.15825 \]

\[ x = 0.076 \]

Hence, using a value for \( k = 0.0062511 \), the concentration of \((\text{OH})_{\text{free}}\) in CF\(_3\)CH\(_2\)OH at 25°C has been re-calculated at ca. 7.6%. This result of 7.6% \((\text{OH})_{\text{free}}\) in 2,2,2-trifluoroethanol would appear to be low in view of the sharp "free" peak at ca. 1411 nm. However, it infers that at 0.076 molefraction of solute, the ratio of salt/base to \((\text{OH})_{\text{free}}\) groups is 1:1.

As mentioned earlier, computerised curve analysis was used to correct the difference spectra for loss of [OH] oscillator, as solute is introduced into the pure fluoroalcohol. This is accomplished by
FIGURE 6L

Effect of DMF in the First Overtone spectrum, 2v\textsubscript{OH}, of 2,2,2-Trifluoroethanol after normalising to 100% [OH].

Temperature = 25°C ± 0.1
FIGURE 6M

Effect of CD\textsubscript{3}CN on the First Overtone spectrum, 2v\textsubscript{OH}, of 2,2,2-Trifluoroethanol, after normalising to 100% [OH].

Temperature = 25°C ± 0.1
FIGURE 6N
Effect of Bu₄NCl on the First Overtone spectrum, 2νOH, of 2,2,2-Trifluoroethanol after normalising to 100% [OH].
Temperature = 25°C ± 0.1
Effect of Bu⁺₄NCLO₄ on the First Overtone spectrum, 2ν₉H, of 2,2,2-Trifluoroethanol after normalising to 100% [OH].

Temperature = 25°C ± 0.1
normalising the absorbance of each spectrum to 100% [OH]. The results of this technique are shown in Figs. 6L, 6M, 6N, 6P for DMF, CD$_3$CN, But$_4$NCl and But$_4$NClO$_4$ respectively. DMF, (6L), shows the expected loss of (OH)$_{\text{free}}$ and evidence for a band growing up in the bulk region (6370 cm$^{-1}$), due to DMF—HO- strong interactions. CD$_3$CN (6M) shows a growth in the very weak H-bond region, with isosbestic points at ca. 6685 cm$^{-1}$, for loss of bulk and growth of weak H-bonds, and at ca. 7050 cm$^{-1}$ for loss of (OH)$_{\text{free}}$ and growth of weak H-bonds.

But$_4$NCl (6N), shows loss of (OH)$_{\text{free}}$ groups and evidence for a band growing up in the strong H-bond region (ca. 6200 cm$^{-1}$), probably due to Cl$^-$—HO- strong interactions. But$_4$NClO$_4$ (6P) highlights the considerable growth in the weakly bound region, due to weak ClO$_4^-$—HO- bonds with a large decrease in bulk absorbance and (OH)$_{\text{free}}$. Although the growth due to ClO$_4^-$—HO- species reduces the loss of (OH)$_{\text{free}}$, curve analysis accounts for this and shows ClO$_4^-$ to have a similar solvation number to Cl$^-$, Br$^-$, I$^-$ and NO$_3^-$. Isosbestic points are observed at ca. 6750 cm$^{-1}$ and ca. 7100 cm$^{-1}$.

6.4.2 Cations

Metal salts were found to be insoluble in 2,2,2-Trifluoroethanol, hence a study of cation solvation was not possible.

6.5 CONCLUDING REMARKS

Fluoroalcohols are stronger acids and weaker bases than water, methanol and other alcohols. The concentration of cross-linked species in fluoroalcohols probably tends to zero because of the low basicity of the oxygen atom, hence terminal (OH)$_{\text{free}}$ groups are present. By monitoring the change in the concentration of (OH)$_{\text{free}}$ groups on adding various solutes and comparing the changes relative to each other,
solvation numbers have been proposed for anions and bases.

The solvation numbers proposed for anions are lower than those found in other protic solvents, i.e. MeOH, H_2O. We suggest that the key lies in the very strong H-bonding. When, say, Cl^- binds to two fluoroalcohol molecules these are such strong bonds that there is no further tendency for "Cl^-" to donate electrons.

Fundamental IR results indicate acetone is predominantly mono-solvated and DMA di-solvated. This result has been used as an internal reference point in the overtone work in fixing a scale for solvation numbers.
REFERENCES FOR CHAPTER 6

CHAPTER

7

A Near-Infrared Study of Hexafluoroisopropanol
7.1 **INTRODUCTION**

This work looks at the effect of added salts and bases on the first overtone spectra (1650-1300 nm) of Hexafluoroisopropanol and also examines the fundamental region (3750-3000 cm\(^{-1}\)) to a lesser extent. Hexafluoroisopropanol shows a doublet at 7052 cm\(^{-1}\), (1418 nm) and 7125 cm\(^{-1}\), (1404 nm) assigned to (OH)\_free groups. The doublet is as a result of two conformers, which will be discussed later. It is the effect of added solutes on the (OH)\_free doublet that is the main concern of this study, which leads to a qualitative analysis on base and anion solvation numbers.

7.2 **PREVIOUS WORK**

7.2.1 **Relative Acidity**

The increased acidity of fluoroalcohols relative to typical alcohols has been discussed in the previous chapter on 2,2,2-Trifluoroethanol, hence will not be discussed further.

7.2.2 **Band Assignments and Conformations of Hexafluoroisopropanol**

Purcell et al. [1], found the IR spectra of Hexafluoroisopropanol in CCl\(_4\) showed two nearly resolved and sharp bands of almost equal intensity at 3608 cm\(^{-1}\) and 3572 cm\(^{-1}\). They stated the peaks may be due to rotational isomers involving "free" and/or intramolecularly hydrogen bonded Hexafluoroisopropanol. They studied Et\(_3\)N in Hexafluoroisopropanol and found the "bonded" OH frequency falls below 3000 cm\(^{-1}\) in a region obscured by a multitude of alcohol and base CH vibrations. The absorption maximum for the Et\(_3\)N + fluoroalcohol adduct can be located at 2570 cm\(^{-1}\).

Two conformers of symmetry species Cs and Cl have been proposed for Hexafluoroisopropanol [2,3,4]. Murto et al. [4], assumed that there is
a more stabilising intramolecular \( \text{OH}--F \) interaction in the \( \text{Cs} \) conformer of Hexafluoroisopropanol than in the \( \text{Cl} \) conformer, thus the lower frequency \( \nu_{\text{OH}} \) peak corresponds to the \( \text{Cs} \) conformer. Murto et al. [3], recorded the IR spectra of Hexafluoroisopropanol and assigned two bands to \( \text{Cl} \) and \( \text{Cs} \) conformers in the \( \text{OH} \) stretching region. They state the molecule should possess 30 fundamental modes of vibration of which 11 are stretching, 16 deformation and 3 torsion vibrations. If the rotations around the \( \text{C-C} \) and \( \text{C-O} \) bonds are relatively free, the point group is \( \text{Cs} \). The higher frequency band has been assigned to the "free" conformer \( \text{Cl} \).

Murto et al. [5], studied the IR of hexachloro-2-propanol and found the alcohol exhibits two conformers in vapour and solution. The situation found for Hexachloro-2-propanol is somewhat analogous to that found for the fluoroalcohol.
Their results imply the Cs conformer (which corresponds to the lower frequency $v_{OH}$ peak) of Hexafluoroisopropanol is the more stable both in 
$CCl_4$ and vapour. In contrast, Truax et al. [6], referred to the 
"trans lone-pair interaction with a C-H bonds" which predicts the Cl 
conformer of Hexafluoro and Hexachloro alcohols to have lower energy 
and higher $v_{OH}$ frequency than the Cs conformer. Truax et al. [6] did 
a conformational analysis on Hexafluoropropan-2-ol:

![Geometry of Hexafluoroisopropanol](image)

They said this compound has no OH-00 gauche interaction, only the 
trans lone-pair effect and intramolecular hydrogen bonding are important 
as conformational determinants.

7.2.3 NMR and IR Studies

Purcell et al. [7], measured OH shifts in Hexafluoroisopropanol on 
addition of Lewis electron donors using $^1H$ NMR. The change in OH 
stretching frequency upon 1:1 adduct formation with a base is a measure 
of the extent of donor-acceptor interaction. They correlate the 
frequency change with shielding constant change for Hexafluoroisopropanol 
and compare with those for phenol and 2,2,2-Trifluoroethanol and use 
this to index the acidities of these alcohols and the magnitude of acid-
base interaction. A recent study on fluoroalcohols by Ganguly et al. 
[8], reports on the electronic and IR absorption spectra of fluoro-
alcohols in binary and ternary solution in cyclohexane and dioxane. 
Although an extensive literature exists on fluoroalcohols, little work
appears to have been done, regarding determining solvation numbers for anions and bases. This work attempts to shed some light on the relative basicities of anions and bases in Hexafluoroisopropanol.

7.3 EXPERIMENTAL

All first overtone spectra were recorded on a Perkin-Elmer 340 UV/VIS/NIR spectrophotometer. All spectra were recorded at 25°C ± 0.1, using a 3 minute time scan and a λ exp of x 5. A photometric scale of 0 - 0.6 was used. Hexafluoroisopropanol obtained from Fluorochem Ltd. was used without further purification. Salts used were of the highest Analar grade and were dried under vacuum and stored over silica gel in a desiccator before use. All solvents used were purified by distillation over CaH₂ and dried over CaH₂ before use. Deuterated fluoroalcohol was not available, hence all systems studied were recorded using difference spectra. For salt systems, a stock solution of fluoroalcohol + salt was made up by weight to a known volume. Sample solutions were prepared using a known volume of base or fluoroalcohol + salt solution and made up to the 5 ml volume mark with fluoroalcohol. The reference solutions consisted of the same volume of added solute as in the sample, but were made up to the 5 ml mark with CCl₄. If the salts were insoluble in CCl₄, MeOD was used instead. The systems studied were checked for changes in volume on mixing. A maximum change of 2% was observed for 0.25 mole-fraction of base in Hexafluoroisopropanol. The spectra were subsequently corrected for any volume change on mixing. No apparent volume change was found for fluoroalcohol/salt solution added to fluoroalcohol.

The absorbance of each spectrum has to be corrected for loss of [OH] oscillator in the sample, in a similar manner to the 2,2,2-Trifluoroethanol work previously discussed in Chapter 6.

All fundamental Infrared spectra were recorded on a Perkin-Elmer 580
spectrometer. The solutions were made up in the same manner as the first overtone solutions. All fundamental spectra were recorded using demountable CaF₂ cells with a 12µ spacer at 25°C. A variable vertical expansion and a horizontal expansion of ×5 was used. Glass cells with a 2mm pathlength were used in the first overtone work.

7.4 RESULTS

7.4.1 Anions/Bases

Figures 7a-e show examples of typical Hexafluoroisopropanol spectra in the first overtone region, on addition of various solutes. Figure 7a shows the effect of temperature change on the Hexafluoroisopropanol spectrum. Both conformer "free" bands increase in absorbance linearly with increasing temperature. Very little bulk absorbance remains at 55°C, indicating mainly (OH)free and very weak H-bonds to be present. An isosbestic is apparent at ca. 6887 cm⁻¹, (1452 nm). The Hexafluoroisopropanol spectrum at 25°C, shows a greater concentration of (OH)free than is found for 2,2,2-Trifluoroethanol at 25°C.

The effect of a strong base on the Hexafluoroisopropanol spectrum is shown in Figure 7b. A similar result to that found in the trifluoroethanol study is observed, showing loss of (OH)free with a rise in bulk absorbance at lower frequency, which is probably due to relatively strong DMA—HOCH(CF₃)₂ bonds. Figure 7c shows the effect that a weaker base, CH₃NO₂, has on the spectrum. Throughout most of the bases studied, the two "free" bands appeared to be scavenged to the same extent with a slight preference for the 1418 nm peak to fall in absorbance faster than the 1404 nm peak. However, in the case of CH₃NO₂, the 1404 nm peak shows a larger fall in absorbance. This is due to relatively weak CH₃NO₂—HO- interactions growing up close to the 1418 nm peak apparently reducing the scavenging of this "free" peak by base, to some extent. Curve analysis
FIGURE 7a
Effect of Temperature on 2\nuOH
of Hexafluoroisopropanol.

Absorbance

0.7

0.35

0

1300 1400 1500 1600
Nanometers (nm)

(\text{OH})_{\text{free}} \quad \text{ca. 1452 nm}
Figure 7b: Effect of DMA on 2VoH of Hexafluoroisopropanol (Difference Spectra).

Temperature = 25°C ± 0.1

Growth due to DMA: \( -\text{HOCH}_2\text{CF}_3 \)

Loss of (OH)-free

DMA Molefraction

Absorbance

Nanometers (nm)
FIGURE 7c
Effect of CH$_3$NO$_2$ on 2$v_{OH}$ of Hexafluoroisopropanol (Difference Spectra).
Temperature = 25°C ± 0.1
FIGURE 7e
Effect of Bu$_4$NClO$_4$ on 2νOH of Hexafluoroisopropanol (Difference Spectra).
Temperature = 25°C ± 0.1
is required to see the true effect on the two "free" peaks.

Figure 7d shows that in the case of Bu^tNCl, the 1418 nm "free" peak falls in absorbance faster than the 1404 nm band. As previously mentioned, this trend is found throughout most of the salts and bases studied, however Bu^tNCl shows this effect more clearly than most other systems, as does Bu^tNNO_3 and Et_3N. Figure 7e shows the effect Bu^tNClO_4 has on the spectrum. As is found in the 2,2,2-Trifluoroethanol work, there is evidence for growth close to the "free" peaks due to weak ClO_4^----HO- interactions.

The two "free" peaks ca. 1418 nm and 1404 nm are due to two rotamers in fast equilibrium. This presents problems interpreting results when salts and bases are added. Curve analysis is required to see both peaks clearly and the effect of solutes thereon. Each spectra recorded was digitised, converted from a nanometer scale to a wavenumber scale and curve analysed by following the same procedure described in detail in Chapter 4. An example of a deconvoluted Hexafluoroisopropanol spectrum is shown in Figure 7f. The spectrum is simulated using a minimum number of five bands, representing a range of OH oscillators from strongly H-bonded to "free". We do not infer the bands have any precise significance. The two "free" peaks come up at 7125 cm^{-1} and 7052 cm^{-1}, representing the Cl and Cs conformers respectively [3,4].

The deconvoluted (OH)\textit{free} peaks, i.e. bands 1 and 2 (Figure 7f), are added together so that the total "free" absorbance is being monitored when a solute is added. Band 2 is also monitored individually for comparison (ca. 7052 cm^{-1}). Figure 7.1 shows a linear change in the total (OH)\textit{free} absorbance of Hexafluoroisopropanol as a function of temperature. Figure 7.1a shows the change in the deconvoluted 7052 cm^{-1} "free" peak absorbance with temperature change. A similar linear trend
FIGURE 7f

The deconvolution of the OH band of (CF₃)₂CHOH at 25°C.
FIGURE 7.1
Effect of temperature on $2\nu_{\text{OH}}$ (OH)$_{\text{free}}$ of Hexafluoroisopropanol, after deconvolution.
FIGURE 7.1a

Effect of temperature on $2\nu_{OH}$ (7052 cm$^{-1}$) (OH)free band of Hexafluoroisopropanol after deconvolution.

Absorbance Units

Temperature °C
is observed to that found for the change in the total \((\text{OH})_{\text{free}}\) absorbance (Figure 7.1).

Figure 7.2 shows the effect of bases on the total \((\text{OH})_{\text{free}}\) absorbance after deconvolution and after correcting for increase in "free" absorbance due to the dilution effect of added base. This was examined by adding \(\text{CH}_2\text{Cl}_2\) to the fluoroalcohol and monitoring change in the "free" absorbance. [\(\text{CCl}_4\) was found to be immiscible, as in the 2,2,2-Trifluoroethanol study.] The 7052 cm\(^{-1}\) peak showed no apparent change in absorbance, whilst the 7125 cm\(^{-1}\) "free" peak gave a 2.5% increase in absorbance up to 0.2 \(\text{CH}_2\text{Cl}_2\) molefraction (Figure 6.4). The relatively stronger bases (Figure 7.2), DMA, DMF, Et\(_3\)N scavenge \((\text{OH})_{\text{free}}\) groups faster than weaker bases, i.e. \(\text{CH}_3\text{NO}_2\), \(\text{CD}_3\text{CN}\). However, \(\text{CH}_3\text{NO}_2\) and \(\text{CD}_3\text{CN}\) show a substantial growth in the weakly bound region, close to the \((\text{OH})_{\text{free}}\) bands, thus reducing loss of \((\text{OH})_{\text{free}}\).

Figure 7.2a shows the change in the 7052 cm\(^{-1}\) "free" peak absorbance due to added bases. A similar trend is observed to the effect of bases on the total "free" absorbance (Figure 7.2). Although monitoring only the 7052 cm\(^{-1}\) "free" peak, shows the absorbance to fall fractionally faster than the total "free" absorbance, [i.e. when both 7215 cm\(^{-1}\) and 7052 cm\(^{-1}\) "free" bands are added].

The effect of added tetraalkylammonium salts on the total \((\text{OH})_{\text{free}}\) concentration of Hexafluoroisopropanol is shown in Figure 7.3, after deconvolution. Qualitatively, within experimental error, all the salts appear to scavenge \((\text{OH})_{\text{free}}\) groups to the same extent. Monitoring the effect of added salts on the 7052 cm\(^{-1}\) "free" band individually, (Figure 7.3a), shows the anions to scavenge this lower frequency band faster than the total \((\text{OH})_{\text{free}}\) absorbance, although overall the same trends are observed within the series of salts.
FIGURE 7.2
Effect of Bases on $2\nu_0\text{H -(OH)}_\text{free}$ of Hexafluoroisopropanol measured relative to Pure Hexafluoroisopropanol after deconvolution and after dilution correction.
Temperature = $25\degree C \pm 0.1$
FIGURE 7.2a
Effect of Bases on $2\nu_\text{OH}$, 7052 cm$^{-1}$, (OH)$_{\text{free}}$ band of Hexafluoroisopropanol measured relative to pure Hexafluoroisopropanol after deconvolution and after dilution correction.
Temperature = 25°C ± 0.1
FIGURE 7.3
Effect of Salts on $2v_{OH} (OH)_{free}$ of Hexafluoroisopropanol, measured relative to pure Hexafluoroisopropanol after deconvolution and after dilution correction.

Temperature = 25°C ± 0.1
FIGURE 7.3a

Effect of Salts on $2\nu_{OH}$, 7052 cm$^{-1}$, $(OH)_{free}$ band of Hexafluoroisopropanol measured relative to pure Hexafluoroisopropanol after deconvolution and after dilution correction.

Temperature = 25°C ± 0.1

% $(OH)_{free}$ vs Salt Molefraction

- $Bu^+_4$ClO$_4$
- $Bu^+_4$NNO$_3$
- $Bu^+_4$NI
- $Bu^+_4$NBr
- $Me^+_4$NBr
- $Bu^+_4$NCl
Figures 7.4 and 7.5 show the change in LN-% (OH)\textit{free} absorbance for bases and salts in Hexafluoroisopropanol, respectively. The trends observed for the tetraalkylammonium salts are taken as representing the extent of anion solvation, since the large bulky $R_4N^+$ cations are assumed to undergo negligible solvation relative to the anion [although this may be incorrect].

The gradients for the change in LN-% (OH)\textit{free} absorbance for the addition of bases and salts to Hexafluoroisopropanol are listed in Table 1.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
\textbf{LN-% (OH)\textit{free} gradients} & \\
\hline
$\text{CH}_3\text{NO}_2$ & -2.17 \\
$\text{CD}_3\text{CN}$ & -2.58 \\
Acetone & -3.42 \\
DMSO & -3.39 \\
DMA & -4.69 \\
DMF & -4.25 \\
$\text{Et}_3\text{N}$ & -4.67 \\
$\text{Bu}_4\text{NClO}_4$ & -6.33 \\
$\text{Bu}_4\text{NNO}_3$ & -6.75 \\
Me$_4\text{NBr}$ & -9.25 \\
$\text{Bu}_4\text{NCl}$ & -8.42 \\
$\text{Bu}_4\text{NBr}$ & -8.40 \\
$\text{Bu}_4\text{NI}$ & -6.72 \\
\hline
\end{tabular}
\caption{LN-% (OH)\textit{free} gradients}
\end{table}

On a qualitative scale, the relatively stronger bases bring the (OH)\textit{free} absorbance down approximately twice as fast as the weaker bases, indicating a solvation number twice as large for the strong bases compared to the weak bases. The gradients for the salts come down approximately twice as fast as for the strong bases.

There has been no correction made for any increase in (OH)\textit{free} due to the dilution effect of bulky $R_4N^+$ cations being present. $\text{Bu}_4\text{Sn}$ and TMS were thought to be ideal for examining this problem, however, both were immiscible in Hexafluoroisopropanol. The increase in (OH)\textit{free} due to $R_4N^+$ cations being present is probably small, comparable to the
FIGURE 7.4
Effect of Bases on $2\nu_{\text{OH}}$ LN-$\%$ (OH)$_{\text{free}}$ of Hexafluorooisopropanol, after deconvolution and after dilution correction.

Temperature = 25°C ± 0.1
FIGURE 7.5

Effect of Salts on 2vOH IN-% (OH)free of Hexafluoroisopropanol, after deconvolution and after dilution correction.

Temperature = 25°C ± 0.1
relatively small effect CH$_2$Cl$_2$ showed on the "free" bands.

Figure 7.6 shows the change in the deconvoluted bands of Hexafluoroisopropanol as a function of temperature. The main feature being the rapid increase in both "free" bands as temperature increases. The 7052 cm$^{-1}$ "free" band appears to be more sensitive to temperature change than the 7125 cm$^{-1}$ "free" band, showing a larger gradient over the temperature range 55°C - 0°C. The strong H-bonds decrease in absorbance with increasing temperature, as expected.

Figure 7.7 shows the change in the deconvoluted bands when DMF is added as solute. The main feature being the rapid fall in the (OH)$_{free}$ bands due to scavenging by base. The strong H-bonds increase in absorbance, probably due to strong DMF--HOCH(CF$_3$)$_2$ species occurring in this region (ca. 6500 cm$^{-1}$). DMF being a relatively strong base forms H-bonds of a comparative if not stronger nature than normal H-bonds between fluoroalcohol molecules as evidenced by Figure 7.7. Again the 7052 cm$^{-1}$ "free" band is scavenged at a faster rate than the 7125 cm$^{-1}$ "free" peak.

A weak base, CH$_3$NO$_2$, is examined in Figure 7.8. There is substantial growth in the weakly bound region due to weak CH$_3$NO$_2$--HOCH(CF$_3$)$_2$ interactions occurring close to the "free" bands, which reduces the rate at which the 7052 cm$^{-1}$ "free" band falls in absorbance. Hence both (OH)$_{free}$ bands appear to be scavenged in a parallel sense, whereas in most other systems studied, the 7052 cm$^{-1}$ "free" is scavenged at a faster rate. The minimum number of 5 bands were used to obtain a good "fit" between experimental and simulated envelopes, without needing to incorporate additional bands to account for the growth of weak CH$_3$NO$_2$--HOCH(CF$_3$)$_2$ species, as was also the case for CD$_3$CN.

The analogous situation for salts in Hexafluoroisopropanol is
FIGURE 7.6
Intensities of bands obtained by deconvolution of the spectrum of Hexafluoroisopropanol in the $2\nu_{OH}$ region as a function of temperature.

- 7052 cm$^{-1}$ "free" band
- 7125 cm$^{-1}$ "free" band

Very weak H-bonds
(7000 cm$^{-1}$)

Weak H-bonds
(6766 cm$^{-1}$)

Strong H-bonds
(6495 cm$^{-1}$)

Absorbance Units

Temperature °C
Intensities of bands obtained by deconvolution of the spectrum of Hexafluoroisopropanol in the $2\nu_{OH}$ region, on addition of DMF, after dilution correction. Temperature = 25°C ± 0.1

**FIGURE 7.7**

- Strong H-bonds (6500 cm$^{-1}$)
- Weak H-bonds (6777 cm$^{-1}$)
- Very weak H-bonds (7005 cm$^{-1}$)
- 7125 cm$^{-1}$ (OH)$_{\text{free}}$ band
- 7052 cm$^{-1}$ (OH)$_{\text{free}}$ band
FIGURE 7.8
Intensities of bands obtained by deconvolution of the spectrum of Hexafluoropropanol in the $2v_{OH}$ region, on addition of CH$_3$NO$_2$, after dilution correction.

Temperature = $25^\circ$C ± 0.1
Buffer (Figure 7.9). Weak ClO$_4^-$…HOCH(CF$_3$)$_2$ bonds occur in the very weak (ca. 7000 cm$^{-1}$) and weak (ca. 6770 cm$^{-1}$) H-bond regions. No additional bands were required to deconvolute the spectra, to account for these weak ClO$_4^-$…HOCH(CF$_3$)$_2$ species growing up. The effect of Bu$_4$NI on the deconvoluted bands of Hexafluoroisopropanol is shown in Figure 7.10. There is a loss of (OH)$_{free}$ concentration with increasing salt molefraction, allied with a reduction in weakly bound absorbance. However, the strong H-bond region increases in absorbance, providing evidence for I$^-$…HOCH(CF$_3$)$_2$ bonds in this region.

The fundamental IR region (3700-3300 cm$^{-1}$) was used to determine a position for the weak CH$_3$NO$_2$…HOCH(CF$_3$)$_2$ oscillator (Figure 7g). The $\nu_{OH}$ stretch of Hexafluoroisopropanol at very low concentration in CH$_3$NO$_2$ was examined at 25$^\circ$C and revealed a shoulder on the high frequency side of the bulk band (ca. 3571 cm$^{-1}$), assigned to weak CH$_3$NO$_2$…HOCH(CF$_3$)$_2$ species. In the first overtone region this weak oscillator occurs in the 7000 cm$^{-1}$ region of very weakly bound H-bonds (Figure 7.8), which compares favourably with CH$_3$NO$_2$…HOCH$_2$CF$_3$ species occurring at ca. 7040 cm$^{-1}$, in 2,2,2-Trifluoroethanol.

Monitoring the carbonyl stretch of DMA in Hexafluoroisopropanol, in the fundamental region (1700-1500 cm$^{-1}$) (Figure 7h), shows one peak (ca. 1605 cm$^{-1}$), assigned as being the di-solvate species. Figure 7i shows two bands when monitoring the carbonyl stretch of acetone in hexafluoroisopropanol. The mono-solvate has a $\nu_{max}$ at 1705 cm$^{-1}$ and the di-solvate $\nu_{max}$ occurs at 1687 cm$^{-1}$. Curve analysis revealed 100% di-solvate for DMA (Figure 7j) and ~55% mono-solvate, ~45% di-solvate for acetone (Figure 7k), by comparing peak heights.

These fundamental IR results can be used together with the overtone data to qualitatively estimate solvation numbers for bases and anions in
FIGURE 7.9
Intensities of bands obtained by deconvolution of the spectrum of Hexafluoroisopropanol in the $2\nu_{\text{OH}}$ region, on addition of $\text{Bu}^+\text{NCIO}_4^-$, after dilution correction.
Temperature = $25^\circ\text{C} \pm 0.1$. 

Very weak H-bonds (7000 cm$^{-1}$)
7125 cm$^{-1}$ (OH)$^\text{free}$ band
Weak H-bonds (6770 cm$^{-1}$)
7052 cm$^{-1}$ (OH)$^\text{free}$ band
Strong H-bonds (6495 cm$^{-1}$)

Absorbance Units

$\text{Bu}^+\text{NCIO}_4^-$ Molefraction

-219-
FIGURE 7.10
Intensities of bands obtained by deconvolution of the spectrum of Hexafluoroisopropanol in the $2v_{OH}$ region, on addition of Bu$_4$NI, after dilution correction.

Temperature = 25°C ± 0.1
FIGURE 7q
The deconvolution of the νOH band of very dilute \((\text{CF}_3)_2\text{CHOH}\) in \text{MeNO}_2 (<2% \text{ V/V}) at 25°C.
Molefraction of DMA

1. 0.011
2. 0.023
3. 0.045
4. 0.067

FIGURE 7h
Monitoring the $v_{C=0}$ of DMA in Hexafluoroisopropanol.
Temperature = 25°C ± 0.1
FIGURE 7i
Monitoring the $\nu_{C=O}$ of Acetone in Hexafluoroisopropanol.
Temperature = 25°C ± 0.1
FIGURE 7j

The deconvolution of the $\nu_C=0$ band of DMA in $(CF_3)_2CHOH$ at 25°C.

[M.F. DMA = 0.045]
<table>
<thead>
<tr>
<th>Band</th>
<th>Height</th>
<th>Position</th>
<th>Guage</th>
<th>Half Band Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.720</td>
<td>1705.000</td>
<td>80.000</td>
<td>6.000</td>
</tr>
<tr>
<td>2</td>
<td>0.000</td>
<td>1680.500</td>
<td>80.000</td>
<td>10.000</td>
</tr>
</tbody>
</table>

**FIGURE 7k**

The deconvolution of the νC=O band of acetone in (CF₃)₂CHOH at 25°C.

[M.F. Acetone = 0.11]
Hexafluoroisopropanol. [Assuming that the large \( R^N \) cations undergo negligible solvation relative to the anion.] Hence if DMA is assigned a solvation number of 2 and acetone a number of 1-2 from the fundamental results, solvation numbers are estimated (Table 2) by directly comparing \( \ln \% \) \((\text{OH})_\text{free}\) gradients (Table 1) for the salts and bases with the DMA result.

**TABLE 2**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{NO}_2 )</td>
<td>(~1)</td>
</tr>
<tr>
<td>( \text{CD}_3\text{CN} )</td>
<td>(~1)</td>
</tr>
<tr>
<td>Acetone</td>
<td>1-2</td>
</tr>
<tr>
<td>DMSO</td>
<td>1-2</td>
</tr>
<tr>
<td>DMA</td>
<td>2</td>
</tr>
<tr>
<td>DMF</td>
<td>2</td>
</tr>
<tr>
<td>( \text{Et}_3\text{N} )</td>
<td>2</td>
</tr>
<tr>
<td>( \text{Bu}^t\text{NClO}_4 )</td>
<td>(~3)</td>
</tr>
<tr>
<td>( \text{Bu}^t\text{NNO}_3 )</td>
<td>(~3)</td>
</tr>
<tr>
<td>( \text{Me}_2\text{NBr} )</td>
<td>(~4)</td>
</tr>
<tr>
<td>( \text{Bu}^t\text{NCl} )</td>
<td>(~4)</td>
</tr>
<tr>
<td>( \text{Bu}^t\text{NBr} )</td>
<td>(~4)</td>
</tr>
<tr>
<td>( \text{Bu}^t\text{NI} )</td>
<td>(~3)</td>
</tr>
</tbody>
</table>

Curve analysis was used to correct the difference spectra for \( \text{CD}_3\text{CN} \), \( \text{DMF} \), \( \text{Bu}^t\text{NCl} \) and \( \text{Bu}^t\text{NClO}_4 \) by normalising each spectrum's absorbance to 100\% \((\text{OH})\). Figure 7L shows the true effect on the Hexafluoroisopropanol spectrum when \( \text{CD}_3\text{CN} \) is added as solute. The main features being a decrease in \((\text{OH})_\text{free}\) absorbance and a rise in the strong H-bond region, surprising since \( \text{CD}_3\text{CN} \) is regarded as being a relatively weak base. However, results imply \( \text{CD}_3\text{CN} \) has a low basicity but forms relatively strong \( \text{CD}_3\text{CN}--\text{HOCH(\text{CF}_3)}_2 \) bonds. \( \text{CH}_3\text{NO}_2 \), which is also regarded as being a weak base, does form weak \( \text{CH}_3\text{NO}_2--\text{HOCH(\text{CF}_3)}_2 \) bonds (Figures 7c and 7.8) which occur close to the \((\text{OH})_\text{free}\) bands.

DMF (Figure 7M), on the other hand, provides evidence for base--\( \text{HOCH(\text{CF}_3)}_2 \) bonds occurring at a lower frequency than Hexafluoroisopropanol bulk H-bonds (i.e. ca. 6100 cm\(^{-1}\)). This implies the alcohol is a very...
FIGURE 7.1
Effect of CD$_3$CN on the First Overtone spectrum, 2$\nu_{\text{OH}}$, of Hexafluoroisopropanol, after normalising to 100% [OH].
Temperature = 25°C ± 0.1
FIGURE 7M

Effect of DMF on the First Overtone spectrum, $2\nu_{OH}$, of Hexafluoroisopropanol, after normalising to 100% [OH].

Temperature = 25°C ± 0.1
weak base. The analogous situation for salts is highlighted by Bu⁺₄NCl (Figure 7N), clearly showing growth at a lower frequency (ca. 6100 cm⁻¹), than bulk Hexafluoroisopropanol, probably due to strong Cl⁻—HOCH(CF₃)₂ interactions.

Figure 7P shows a growth close to (OH)free for ClO₄⁻—HOCH(CF₃)₂ species, when Bu⁺₄NClO₄ is added as solute, analogous to CH₃NO₂ in the study on bases. There is no apparent change in the strong H-bond region, in comparison to Bu⁺₄NClO₄ in trifluoroethanol which shows clear loss in strong H-bond absorbance. Likewise, CD₃CN in trifluoroethanol shows a loss in strong H-bond absorbance, but in Hexafluoroisopropanol a growth in the bulk region is observed. These results imply that bases and anions generally form stronger H-bonds with Hexafluoroisopropanol than with 2,2,2-Trifluoroethanol, as expected.

Very dilute Hexafluoroisopropanol in CCl₄ was studied in the first overtone region, showing monomer peaks at 7077 cm⁻¹ (1413 nm) and 7037 cm⁻¹ (1421 nm) [very close to the 7052 cm⁻¹ (OH)free band II]. A plot of absorbance versus fluoroalcohol concentration (Figure 7.11), shows that Beers Law is obeyed and yields an extinction coefficient of 8.33 mol⁻¹ dm² for the 1421 nm band and 7.91 mol⁻¹ dm² for the 1413 nm monomer peak. The percentage (OH)free concentration in Hexafluoroisopropanol at 25°C can be estimated if we assume that the absorbance for the (OH)free groups in the pure alcohol is equal to that for the monomer [this may be incorrect].


where  A = Absorbance of Pure Hexafluoroisopropanol (OH)free band at 25°C (different from methanol's absorbance in the same region, i.e. MeOH has no (OH)free).
FIGURE 7
Effect of Bu$_4$NCl on the First Overtone spectrum, $2\nu_{\text{OH}}$, of Hexafluoroisopropanol, after normalising to 100% [OH].

Temperature = $25^\circ C \pm 0.1$
FIGURE 7P

Effect of $\text{Bu}_4\text{NClO}_4$ on the First Overtone spectrum, $2\nu_{\text{OH}}$, of Hexafluoroisopropanol, after normalising to 100% [OH].

Temperature = $25^\circ\text{C} \pm 0.1$

Bu$^+_4\text{NClO}_4$ Molefraction

Absorbance

Wavenumber (cm$^{-1}$)

0 0.1 0.2 0.3 0.4 0.5 0.6

7200 7400 7600 7800 8000 8200
FIGURE 7.11
Plot showing the increase in monomer absorbance for Hexafluoroisopropanol in CCl₄.
Temperature = 25°C ± 0.1

\[ \varepsilon \cdot l = \frac{A}{C} \]

1421 nm \( \varepsilon = 8.33 \text{ mol}^{-1} \text{ dm}^2 \)
1413 nm \( \varepsilon = 7.91 \text{ mol}^{-1} \text{ dm}^2 \)

(= 0.1 dm
(lcm cells used)
\[ \varepsilon_{1421\text{nm}} = 8.33 \text{ mols}^{-1} \text{ dm}^2 \]
\[ \varepsilon_{1413\text{nm}} = 7.91 \text{ mols}^{-1} \text{ dm}^2 \]
\[ \ell = 0.02 \text{ dm} \]

(i) 1421 nm band

\[ 0.36 = 8.33 \times C \times 0.02 \]
\[ \therefore C = 2.1609 \text{ mols dm}^{-3} \]

No. moles (CF\(_3\))\(_2\)CHOH per litre = 1000 \times 1.596 = 9.4977 mols dm\(^{-3}\)

\[ \therefore \% \text{(OH)free} = \frac{2.1609}{9.4977} = 22.8\% \]

(ii) 1413 nm band

\[ 0.347 = 7.91 \times C \times 0.02 \]
\[ \therefore C = 2.1934 \text{ mols dm}^{-3} \]

\[ \therefore \% \text{(OH)free} = \frac{2.1934}{9.4977} = 23.1\% \]

Thus, by taking the average from these two results, there is ~23% (OH)\(_{\text{free}}\) in Hexafluoroisopropanol at 25°C. Although the two monomer peaks in CCl\(_4\) solution have slightly different extinction coefficients, both produce a result of ca. 23% (OH)\(_{\text{free}}\), inferring that at 0.23 molefraction of base or salt, the ratio of (OH)\(_{\text{free}}\) to solute is 1:1.

Calculation of Equilibrium Constant, \(k\)

The concentration of [(OH)\(_{\text{free}}\)] in Hexafluoroisopropanol at 25°C, has been calculated to be ca. 23%, i.e. 0.23 molefraction of (OH)\(_{\text{free}}\), using \(\varepsilon\) calculated from a Beer's Law plot (Figure 7.11) for dilute (CF\(_3\))\(_2\)CHOH in CCl\(_4\). Hence an equilibrium constant can be calculated for the equilibrium:

\((F/OH)_{\text{bound}} \rightleftharpoons (OH)_{\text{free}} + (LP)_{\text{free}}\)

The equation used for calculating the equilibrium constant, \(k\), is:-
\[ k = \frac{[(\text{OH})_{\text{free}}] \cdot [(\text{LP})_{\text{free}}]}{[(\text{F/OH})_{\text{b}}] - (\text{OH})_{\text{free}}} \]

on a molefraction scale:-

\[ k = (0.23)^2 = \frac{0.0687}{1 - 0.23} \]

to check the equilibrium constant, \( k \), the concentration of (OH)\(_{\text{free}}\) in molefraction terms, can be re-calculated using \( k \), i.e.

\[ (\text{F/OH})_{\text{b}} = (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}} \]

at equilibrium: \((1-x)\text{mols}\) \(\text{x mols}\) \(\text{x mols}\)

\[ k = \frac{x^2}{1-x} \]

\[ k - xk = x^2 \]

\[ x^2 + xk - k = 0 \quad .... [1] \]

Converting equation [1] into quadratic form, it becomes:-

\[ x = \frac{-k + \sqrt{k^2 + 4k}}{2} \]

substituting; \( k = 0.0687 \)

\[ x = \frac{-0.0687 + \sqrt{(0.0687)^2 + 4(0.0687)}}{2} \]

\[ x = \frac{-0.0687 + \sqrt{0.0047197 + 0.2748}}{2} \]

\[ x = 0.23 \]

Hence, using a value for \( k = 0.0687 \), the concentration of [(OH)\(_{\text{free}}\)] in \((\text{CF}_3)\text{CHOH}\) at 25°C has been re-calculated at ca. 23%.

7.4.2 Cations

Metal salts were found to be insoluble in Hexafluoroisopropanol, hence a study of cation solvation was not possible.
7.5 CONCLUDING REMARKS

Hexafluoroisopropanol is a stronger acid than 2,2,2-Trifluoroethanol and Near-Infrared results infer it forms relatively stronger H-bonds to bases and anions than 2,2,2-Trifluoroethanol. Evidence is shown in the form of strong solute---HOCH(CF₃)₂ bands, growing up in the strong H-bond region (ca. 6200 cm⁻¹) and in some cases (i.e. strong bases, Cl⁻, etc.), growing up at lower frequencies than normal bulk fluoroalcohol H-bonds.

Strong bases are estimated to be predominantly di-basic in Hexafluoroisopropanol and weaker bases, monobasic. Anions were found to have larger solvation numbers, with the average being tetra-solvated. A fundamental IR study showed DMA to be di-basic and acetone, mono/di-basic in Hexafluoroisopropanol. This result has been used as an internal reference point in the overtone work in fixing a scale for solvation numbers.
REFERENCES FOR CHAPTER 7

CHAPTER

8

A Near-Infrared/NMR Study of Tert-butyl Alcohol
8.1 INTRODUCTION

This work examines the effect on the $2v_{OH}$ stretch of tert-butyl alcohol (t-BuOH) of added bases, esters, ketones, d-alcohols and tetraalkylammonium salts at 27°C. The main concern is the effect on the $2v_{OH}$ (OH)$_{free}$ peak ca. 7062 cm$^{-1}$ (1416 nm) by added solutes, leading to a qualitative estimate of solvation numbers for the solutes in t-BuOH.

The hydroxyl proton resonance of t-BuOH is also monitored on addition of alcohols, bases and tetraalkylammonium salts at 27°C.

8.2 PREVIOUS WORK

Numerous works have been devoted to revealing the hydration structure in the t-butanol-water system in relation to the co-existence of the hydrophilic hydroxyl group and the hydrophobic t-butyl group in the molecule. Various techniques have been used, such as vibrational spectroscopy [1-6], NMR [7-13], light scattering [14-19], ultrasonic absorption or relaxation [20-25], dielectric relaxation [26-28], other physico-chemical or thermodynamic data [29-34], X-ray diffraction [35] and Neutron scattering [36].

8.2.1 Band Assignments

Bourdon and Sandorfy [37] identified the first OH overtone bands for methanol, ethanol and tert-butyl alcohol even though they were overlapped by CH+OH combination bands. They noted that t-butanol shows an appreciable increase in [(OH)$_{free}$] relative to methanol and ethanol. They studied the spectra of the related deuterated alcohols and examined the second overtone bands also. Luck and Ditter [38] pointed out that combinations of the CH+OH type are strong and overlap the first overtones of the 'polymer' OH stretching vibrations. However, in a preliminary note
on hydrogen bonding in methanol [39], Bourderon et al. took the opposite view, namely that CH+OH combinations are weak and do not seriously interfere with overtone measurements. The contribution of intermolecular CH+OH combination bands to the $2v_{\text{OH}}$ stretch of t-BuOH is discussed later in this Chapter.

The fundamental spectrum of liquid t-BuOH, shows a broad band centred at 3370 cm$^{-1}$ [37]. Liquid C$_4$D$_9$OH has practically an identical spectrum to C$_4$H$_9$OH in the fundamental. In the first overtone region, the "free" OH band is observed at 7062 cm$^{-1}$ [37] and compensating the $2v_{\text{OH}}$ t-BuOH spectrum with C$_4$H$_9$OD showed clearly that the contribution of CH absorption, although by no means negligible, is not as important as for MeOH or EtOH.

The second overtone $3v_{\text{OH}}$ [37] of C$_4$D$_9$OH exhibits a free band even stronger than in the first overtone region. The broad 9880 cm$^{-1}$ band is assigned to the second overtone of oligomers, the "free" band coming at ca. 10,320 cm$^{-1}$.

8.2.2 $^1$H NMR Studies on Tert-butyl Alcohol

There are many $^1$H NMR studies in the literature pertaining to t-BuOH/H$_2$O systems and many works comment on strongly increasing hydrogen bonding in the early t-BuOH molefraction range. Glew et al. [40] observed initial downfield shifts, which provided evidence for the strengthening of water-water hydrogen bonding. This was assigned to water shell formation around weakly interacting-interstitial t-BuOH molecules. They postulated that this water structuring effect is most likely to occur in the 0.03-0.06 t-BuOH molefraction range, where there is sufficient water to form completely H-bonded water shells around all the solute molecules. They observed an overall shift to high fields over the full molefraction range of co-solvent, which they claimed was due to weak solute H-bonds being formed, resulting in the loss of strong water-water H-bonds. Blandamer
et al. [21] reported that the hydroxyl proton resonance shift in water + t-BuOH mixtures passes through a minimum at 0.05 t-BuOH molefraction. Symons and co-workers [7,10,13,41-44] have been involved in many studies on t-BuOH/water systems relating to the strongly increasing H-bonding phenomenon in the early t-BuOH molefraction range. They also noted that this effect is greatly enhanced on cooling. They [43,44] proposed that the initial downfield shift in t-BuOH/H_2O mixtures was due to the scavenging of (OH)_free groups in water by t-BuOH as well as to clathrate cage formation. This phenomenon also occurs in other alcohol/water mixtures, the alcohols utilising both lone-pairs on the oxygen atom, hence acting as di-bases. However, overall their effect would be that of a monobase, since the alcohol OH group participates in hydrogen bonding as a monoacid.

Oakes [11] postulated an alternative theory to clathrate cage formation, i.e. that the low-field shift of the coalesced proton peak for alcohol/water was due to alcohol-water hydrogen bonding. He said this effect increases with the alcohols basicity, i.e. strong alcohol hydrogen bonds, strengthened water-water hydrogen bonds by a co-operative effect.

Wen and Hertz [2] measured the hydroxyl proton chemical shift of alcohol/H_2O mixtures and found large downfield shifts particularly for t-BuOH/H_2O in the water-rich region. They attributed the large downfield shifts to 'polar effects' and 'non-polar group' effects, thus disagreeing with Oakes [11]. Marciacq-Rousselot and Lucas [12] studied various alcohol/water mixtures and observed initial downfield shifts for the water proton (calculated from the coalesced alcohol/water signal) in dilute alcohol solution at low temperature and an opposite highfield shift at high temperature. From these observations, they claimed that at low temperatures alcohols behaved as structure makers, while at higher
temperatures they were structure breakers. However, Kingston and Symons [10] explained these trends as being due to the temperature dependence of the water clathrate cage which diminishes with temperature increase.

Kuppers et al. [45,46] said the maximum low-field shift of the coalesced OH proton signal for t-BuOH/H2O mixtures occurred at concentrations for which thermodynamic properties suggested the highest degree of water structuring. For all alcohols studied the greatest degree of structuring occurred at low alcohol concentrations.

Symons et al. [10] studied the methyl proton resonance of t-butyl alcohol/H2O mixtures and found very small shifts. Saunders and Hynne [47] studied the hydroxyl NMR frequency of various alcohols in CCl4, including tert-butanol. They obtained data which fitted with theoretical data for a monomer-trimer equilibrium model of association for t-BuOH. Davis et al. [48] claimed to have fixed the monomer shift for dilute t-BuOH in CCl4, relative to bulk t-BuOH at 280 c.p.s. on a 60 MHz instrument.

A recent 1H NMR study on the effect of sodium alkoxides on the hydroxyl proton resonance [49] of alcohols, including t-BuOH, revealed that the average number of solvent molecules H-bonded to alkoxide ions, decreases down the series MeOH, EtOH, t-BuOH. Results indicated 3 MeOH molecules were H-bonded to alkoxide ions, but only 1.6 t-BuOH molecules. They also noted that hydroxy deuteration of the solvent leads in all cases to a small upfield shift of the resonance of the residual hydroxyl proton.

8.2.3 Separation of Alcohol/Water Peaks

A major problem of looking at alcohol/water or alcohol/alcohol mixtures by 1H NMR spectroscopy, is that of fast exchange between the protons of both species which leads to only one peak corresponding to both hydroxyl species.
Shuiskii and Naberkuhn [50] found that using D₂O rather than H₂O enabled separation of the two OH peaks in t-BuOH/D₂O mixtures down to 0.075 molefraction of t-BuOH. This limit being due to difficulty in observing the weak signal of t-BuOH and not due to any fast exchange causing the peaks to coalesce. Harvey et al. [13] used a combination of deuteration and low temperatures to separate the two alcohol/water peaks over the full molefraction range. By separating the alcohol/water peaks, results showed that the downfield shift is due to water and not the alcohol.

8.2.4 Relative Acidity/Basicity of Alcohols and Water

Shuiskii et al. [50] claimed that water was the stronger base since both alcohol and water ¹H NMR hydroxyl peaks were shifted to low fields with increasing water concentration. Harvey et al. [13] suggested that alcohols were more acidic than water since the corresponding peaks for the alcohols were to lower fields than water, hence they claimed that alcohols formed stronger H-bonds with bases. This would imply a trend for alcohols with methanol at lowest fields since it is the most acidic of the alcohols. However, Oakes [11] found no real correlation between chemical shift and acidity for alcohols relative to water at 0°C.

Kamlet and Taft [52,53] using a solvatochromic comparison method, involving the measurement of v max values for two substrates of different H-bonding ability in a series of solvents of varying polarity, showed the relative hydrogen bond donating ability of the alcohols and water to be:

Water > MeOH > EtOH > n-propanol > n-Butanol > t-Butanol

Increasing acidity

Morrison and Boyd [54] stated that water was a stronger acid than alcohols in solution. Alcohols would appear to be stronger bases and water a
stronger acid, a possible explanation being the electron donating alkyl
groups increasing the negative charge around the oxygen atom, thus making
it more basic.

8.2.5 Infrared and Other Studies on Tert-Butyl Alcohol

Iwasaki et al. [19] obtained light scattering spectra of t-BuOH/water
solutions and from their results proposed that the clathrate structure
was \((H_2O)_{21} \text{TBA}\) at \(<\frac{1}{2}\) alcohol mole fraction and \((H_2O)_{15} \text{TBA}\) at \(>\frac{1}{2}\)
alcohol mole fraction. Yastremskii et al. [55] studied dielectric
properties of aqueous t-BuOH. They stated that hydrophobic hydration
of the alcohol molecule reduced the rotational mobility of the \(H_2O\) mole-
cule and increased structure formation. They also add that hydrophobic
hydration decreases with decreasing number of non-polar groups in the
series t-BuOH \(\rightarrow\) MeOH.

Smith [51] studied HDO/t-BuOH mixtures in the second overtone \(2\nu_{OH}\)
stretch region (1100 nm - 800 nm). His results imply that t-BuOH scavenges
"(OH)\text{free}" groups in the water-rich region. Perelygin et al. [56]
examined the effect of halide anions, \(\text{CCl}_4\), \(\text{MeCN}\), \(\text{Me}_2\text{CO}\) and pyridine on
the \(2\nu_{OH}\) stretch of \(\text{CD}_3\text{OH}\), EtOH and t-BuOH. They stated that formation
of H-bonds caused low frequency shifts of these overtone bands, the
displacement increased in the order \(I^- < Br^- < Cl^-\) and the band intensities
decreased with increasing displacement.

Tanabe [57] recently measured the isotropic Raman linewidth of t-butanol
at 753 cm\(^{-1}\), in aqueous solution and in cyclohexane solution. He inter-
preted the concentration dependence of the linewidths in aqueous solution
in terms of a model where the extent of H-bond formation is estimated from
the partial molar volume of t-butanol. From the concentration dependence
of the linewidths, he noted that t-BuOH H-bonded clusters start to break
down on diluting with cyclohexane around the 0.1 t-BuOH molefraction, i.e. the ratio of free non-bonded solute molecules becomes higher. The maximum linewidths for the t-BuOH/H₂O system occurred at 0.05 molefraction of t-BuOH, hence it was deduced that the amount of H-bonded t-BuOH molecules is largest at this concentration.

8.2.6 Theoretical Studies on t-BuOH

Brink [58] used the empirical potential EPEN (empirical potential based on interaction of electrons and nuclei), claiming to establish the structure of isolated H-bonded clusters in t-BuOH. The most stable form of the dimer has a trans open (non-cyclic) form, similar to that in methanol. The most stable form of the trimer is essentially closed, but with one of the H-bonds being long and very non-linear. The tetramer also has a closed form, but the H-bonds are not all equal. The results are compared with the H-bonding in methanol and are discussed in terms of the steric factors which affect the H-bonding in tert-butyl alcohol.

Nakanishi et al. [59] has recently carried out Monte-Carlo calculations on an infinitely dilute aqueous solution of t-BuOH in water at 298.15 K, to obtain energetic and structural information on the hydration structure of t-BuOH. They state that the potential energy and structure of water tend to be stabilized by the introduction of one t-BuOH molecule, and two strong H-bonds between t-BuOH and the surrounding water molecules favour the formation of a bulky and stable hydration shell, which includes co-operatively connected hydrophobic hydration structures.

8.3 EXPERIMENTAL

All the first overtone t-BuOH spectra (1650 - 1300 nm) were recorded on a Perkin-Elmer 340 UV/VIS/NIR spectrophotometer. Spectra were recorded
at 27°C ± 0.1 on a photometric scale of 0-0.08, a λ expansion of ×5 and a 3-minute scan time. All salts used were of Analar grade and were dried under vacuum and stored in a dessicator over silica gel before use. Cosolvents, of the best available grades, were purified by distillation over CaH2 and dried over CaH2. Tert-butyl alcohol-d, >98%, was used without further purification. Each sample contained 25% t-BuOH by volume, a known volume of cosolvent or salt/t-BuOD solution was added and, finally, t-BuOD added to make up to the 5 ml mark. The reference contained the same volume of cosolvent or salt/t-BuOD solution; then t-BuOD was added to make up to the 5 ml mark. Stock solutions of t-BuOD + salt were prepared by weight so that the molefraction of salt was established.

It is useful to keep the concentration of [OH] oscillators constant in the sample solutions so that spectral changes are only a result of salt or base effects on the solvent and not due to an imbalance of [OH] groups. Glass cells with a 2 mm pathlength were used in this work. Absorbance due to the cells was recorded into the baseline correction before each system was studied.

All the 1H NMR spectra were recorded on a Jeol PS 100 spectrometer. Sample solutions were prepared in a similar manner to those used in the overtone work. TMS (<1% v/v) in very dilute concentration, was used as internal reference in each sample. Sidebands of TMS were dialled up at 400 Hz and 485 Hz downfield from the TMS reference signal. The hydroxyl proton resonance of t-BuOH appears at ca. 465 Hz downfield from TMS at 27°C. Hence using TMS side-bands enables a much narrower sweep to be used, i.e. 85 Hz, for measuring accurately the t-BuOH hydroxyl resonance shift on adding solutes. Each spectrum was recorded at 27°C.
8.4 RESULTS (SPECTRAL ANALYSIS)

8.4.1 Effect of Temperature Change

The effect of temperature change on the $2\nu_{OH}$ t-BuOH spectrum is shown in Figure 8a which highlights the growth in [(OH)$_{\text{free}}$] and decrease in the strongly hydrogen bonded region ca. 1545 nm, with increasing temperature. An isosbestic point is apparent at ca. 1485 nm over the range 27-67°C. The effect of temperature change on t-BuOH is compared with the corresponding change in the HOD, MeOH, CF$_3$CH$_2$OH and (CF$_3$)$_2$CHOH $2\nu_{OH}$ spectra with temperature change in Section 8.5.1.

8.4.2 Inert Solvents

Figure 8b shows the effect Bu$_4$Sn has on the t-BuOH $2\nu_{OH}$ spectrum. Adding this inert solute generates [(OH)$_{\text{free}}$] groups, a similar result was also observed when neopentane (Me$_n$C) and TMS were added to t-BuOH, though not as dramatic.

This "steric-dilution" effect is usually neglected in other protic solvents, based on an NMR study on MeOH with added CCl$_4$ or (CH$_2$Cl)$_2$ at -80°C [60].

As the concentration of CH$_2$Cl$_2$ or CCl$_4$ increases, methanol remains effectively unchanged in the 0-0.9 CH$_2$Cl$_2$ molefraction range. This can
FIGURE 8a
Effect of temperature change on the $2\nu_{\text{OH}}$ spectrum of t-BuOH/OD (25% v/v).

Isosbestic point ca. 1485 nm

(OH)$_2$ free groups
FIGURE 2d
Effect of Tetra-n-Butyl tin on the 2um spectrum of t-BuCl/OD (25% v/v) at 27°C.
be explained by taking the view that the dimer is linear (1) rather than cyclic (2), making it both more basic and more acidic than the monomer.

![Diagram of structures](image)

Thus it should react more strongly with monomers than do other monomers which will lead to a loss of dimers and a gain of oligomers. Eventually, tetramers or pentamers form and cyclisation ensues (3) giving fully bonded methanol molecules that are spectroscopically almost indistinguishable from bulk methanol.

![Diagram of structure](image)

Eventually with increasing [CH₂Cl₂], i.e. >0.9 molefraction, these cyclic structures begin to break up inducing a drastic shift to high fields. However, Figure 8.1 shows an immediate upfield shift on adding CCl₄ or Bu₄Sn to t-BuOH at 27°C. This upfield shift is consistent with [(OH)₄] free generation as observed in the ₂νOH stretch study (Figure 8b).

The observed loss of t-BuOH [(OH)₄] due to added bases (Figure 8.4) is subsequently corrected for any corresponding increase in [(OH)₄] due to the "steric-dilution" effect of adding large base molecules, i.e. Et₃N, DMA, DMF and DMSO to t-BuOH. The correction is related to the extent to which TMS generates [(OH)₄] in t-BuOH (Figure 8.2). This is subtracted from the original observed loss of [(OH)₄] due to base:-
FIGURE 8.1

$^1$H NMR plot showing the upfield shift of the t-BuOH hydroxyl resonance on adding diluents, measured relative to pure t-BuOH at 27°C.
FIGURE 8.2
Effect of inert solvents on the $2\nu_{\text{OH}}$ (OH)$_{\text{free}}$ peak of t-BuOH/OD measured relative to pure t-BuOH/OD after deconvolution.
Temperature = 27°C $\pm$ 0.1
Corrected % loss of = Original % loss - % Increase in [(OH)\text{free}] of [(OH)\text{free}] measured relative to pure t-BuOH due to "steric-dilution" effect.

This correction is not applied when adding smaller base molecules, i.e. CH\textsubscript{3}NO\textsubscript{2}, CD\textsubscript{3}CN, Me\textsubscript{2}CO to t-BuOH.

The extent to which Bu\textsuperscript{4}Sn generates [(OH)\text{free}] (Figure 8.2) when added to t-BuOH, is used to correct the loss of [(OH)\text{free}] due to added tetra-alkylammonium salts (Figure 8.8). The gradient for [(OH)\text{free}] increase due to Et\textsubscript{4}N\textsuperscript{+} cations being present in t-BuOH is obtained from the difference between the extent to which Bu\textsuperscript{4}SnCl and Et\textsubscript{4}NCl scavenge t-BuOH (OH)\text{free} groups (Figure 8.7), i.e. both salts contain the same anion hence the difference in the results is a measure of the cation effect on the solvent structure.

8.4.3 Basic Aprotics

Figures 8d and 8e indicate the extent of the 2\nu\textsubscript{OH} spectral change, on adding strong bases; DMSO and DMF to t-BuOH/OD. Both systems show a similar effect, i.e. dramatic loss of [(OH)\text{free}] due to base scavenging, also a reduction in the strong H-bonded region absorbance ca. 1545 nm, but an increase in the weakly bound region at ca. 1475 nm. In the methanol 2\nu\textsubscript{OH} study (Chapter 5), (LP)\text{free} groups were detected at 1475 nm, i.e. in the same region as the growth in weakly bound H-bonds when DMSO and DMF are added to t-BuOH. Hence the growth at ca. 1475 nm (6780 cm\textsuperscript{-1}) in the 2\nu\textsubscript{OH} t-BuOH spectrum, may be due to a growth in [(LP)\text{free}], as (OH)\text{free} groups are scavenged by base. Alternatively, it may be accountable to relatively weak Base-\textsubscript{---}HO\textsubscript{Me}, H-bonds growing up in this region.

In the fluoroalcohol work in Chapters 6 and 7, it was observed that Base-\textsubscript{---}HO\textsubscript{CH\textsubscript{2}}CF\textsubscript{3}, and Base-\textsubscript{---}HO\textsubscript{CH(CF\textsubscript{3})\textsubscript{2}} bands occurred close to bulk fluoroalcohol. The fluoroalcohols are very strong acids relative to
FIGURE 8c
Effect of $\text{Bu}_4^+\text{NCl}$ on the $2\nu_\text{OH}$ spectrum of $t$-$\text{BuOH}/\text{OD}$ (25% $\text{v/v}$) at 27°C.

Molefraction $\text{Bu}_4^+\text{NCl}$
1. 0
2. 0.024
3. 0.036
4. 0.048

Absorbance

I = Isosbestic point
ca. 1505 nm

Nanometers (nm)
FIGURE 83
Effect of DMSO on the 20OH spectrum of t-BOOH/OD (508, 4V)

Molefraction DMSO
1. 0
2. 0.065
3. 0.128
4. 0.25
5. 0.36
6. 0.47

Absorbance

Nanometers (nm)

Increase in weakly bound
region, ca. 1475 nm

Isosbestic point
ca. 1430 nm

Decrease in (OH)free groups

0.15
0.075
0.04
0.01
0.005
0.002
0.001
0.0005
0.0002
0.0001
0.00005
0.00002
0.00001
0.000005
0.000002
0.000001
0.0000005
0.0000002
0.0000001
0.00000005
0.00000002
0.00000001
0.000000005
0.000000002
0.000000001
0.0000000005
0.0000000002
0.0000000001
0.00000000005
0.00000000002
0.00000000001
0.000000000005
0.000000000002
0.000000000001
0.0000000000005
0.0000000000002
0.0000000000001
0.00000000000005
0.00000000000002
0.00000000000001
0.000000000000005
0.000000000000002
0.000000000000001
0.0000000000000005
0.0000000000000002
0.0000000000000001
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0.00000000000000000000000000000000002
0.00000000000000000000000000000000001
0.00000000000000000000000000000000000005
0.00000000000000000000000000000000002
0.00000000000000000000000000000000001
0.000000000000000000000000000000000000005
0.00000000000000000000000000000000002
FIGURE 8e.
Effect of DMF on the $2\nu_{\text{OH}}$ spectrum of t-BuOH/OD (25% $\nu$/v) at 27°C.

- Isosbestic point ca. 1490 nm
- Increase in Weakly bound region ca. 1475 nm
- Decrease in [(OH)$_{\text{free}}$] groups
FIGURE 8f
Effect of D₂O on the 2νOH spectrum of t-BuOH/OD (25% v/v) at 27°C.

Absorbance

Molefraction D₂O
1. 0
2. 0.11
3. 0.21
4. 0.29
5. 0.36

Nanometers (nm)
1300 1400 1500 1600

Loss of strong H-bonds
Isosbestic point ca. 1503 nm
Increase in weak H-bonds ca. 1460 nm
Loss of coupled band
t-BuOH, which is a much stronger base. Hence it is possible that Base-HOCMe$_3$ bands may occur in the weakly bound region ca. 1475 nm, even for relatively strong bases, i.e. DMSO, DMF, when they may have been expected to occur closer to the strongly H-bonded region ca. 1545 nm.

The effect on the $2\nu_{OH}$ t-BuOH spectrum when CD$_3$CN is added as solute is shown in Figure 8g. A reduction in the strong H-bonded absorbance is accompanied by a dramatic growth in the weakly bound t-BuOH region. The growth is such that the (OH)$_{free}$ peak would appear to actually increase in absorbance, whereas the relatively weak base CD$_3$CN is probably scavenging (OH)$_{free}$ groups to some extent. Curve analysis is required to separate the two conflicting features, i.e. decrease in [(OH)$_{free}$] and growth in weak H-bonds due to weak CD$_3$CN-HOCMe$_3$ species, with possibly a small growth in [(LP)$_{free}$] groups also contributing.

Figure 8h shows the effect on the $2\nu_{OH}$ t-BuOH/CD spectrum when the very weak base, CH$_3$NO$_2$, is added as solute. The most noticeable feature is a growth in very weak H-bonds close to the (OH)$_{free}$ peak (ca. 1420 nm). This is attributable to weak CH$_3$NO$_2$-HOCMe$_3$ H-bonds, which results in the apparent increase in [(OH)$_{free}$] groups, although they are probably being scavenged, albeit slightly, by the weak base molecules. Hence curve analysis is required to see the true rate of [(OH)$_{free}$] scavenging by CH$_3$NO$_2$.

The effect of adding ketones and esters on the $2\nu_{OH}$ t-BuOH/CD spectrum has also been examined. Acetone (Figure 8i) is shown as an example, again highlighting the considerable growth in weak H-bonds, due mainly to Me$_2$CO-HOCMe$_3$ bonds, with a growth in [(LP)$_{free}$] groups possibly contributing. Again curve analysis is required to separate the growth in weak H-bonds from the actual effect on the [(OH)$_{free}$].
Molefraction $\text{CH}_3\text{NO}_2$
1. 0
2. 0.051
3. 0.10
4. 0.132
5. 0.16

FIGURE 8h
Effect of $\text{CH}_3\text{NO}_2$ on the $2\nu_\text{OH}$ spectrum of $t$-$\text{BuOH/OD}$ (25% $\nu$/$\nu$) at 27°C.

Absorbance

Isosbestic point ca. 1500 nm

Growth in very weak H-bonds

Nanometers (nm)
FIGURE 81
Effect of Acetone on the 2νOH spectrum of t-BaOH/OD (258 νv)
at 27°C.

Molefraction Acetone
1. 0
2. 0.090
3. 0.175
4. 0.245
5. 0.300

Absorbance
0.04
0.08
1.300
1.400
1.500
1.600
Nanometers (nm)

-259-
8.4.4 d-Alcohols and D₂O

Figure 8f shows the effect of adding D₂O to t-BuOH on the 2νOH spectrum. The main features are a decrease in strong H-bonds (1545 nm) and [(OH)free], but a dramatic increase in weak H-bonds at ca. 1460 nm. Inevitably there will be OH/OD exchange between D₂O and t-BuOH molecules. The extent to which OH/OD exchange affects the 2νOH spectral measurements has been examined thus:–

Consider the following system:–

\[
t-BuOH + t-BuOD + ROH + ROH \rightleftharpoons t-BuOH + t-BuOD + ROH + ROH
\]

at \( T = 0 \):

\[
X_1 \quad Y_1 \quad Z_1 \quad 0
\]

at \( T = t \):

\[
X_{1-a} \quad Y_{1+a} \quad Z_{1-\alpha} \quad \alpha
\]

Assume statistical distribution

\[
\therefore \frac{X_{1-a}}{Y_{1+a}} = \frac{\alpha}{Z_{1-\alpha}}
\]

where: \( \alpha \) = number of moles of O-H bonds or O-D bonds

\[
X_1, Y_1 \text{ and } Z_1 = \text{number of moles of O-H bonds or O-D bonds}
\]

\[
\therefore \alpha(Y_{1+a}) = (X_{1-a})(Z_{1-\alpha})
\]

\[
\therefore \alpha Y_1 + \alpha^2 = X_1Z_1 - \alpha X_1 - \alpha Z_1 + \alpha^2
\]

\[
\therefore \alpha Y_1 = X_1Z_1 - \alpha X_1 - \alpha Z_1
\]

\[
\therefore \alpha Y_1 + \alpha X_1 + \alpha Z_1 = X_1Z_1
\]

\[
\therefore \alpha (Y_1 + X_1 + Z_1) = X_1Z_1
\]

\[
\therefore \alpha = \frac{X_1Z_1}{Y_1 + X_1 + Z_1}
\]

NB:– The 2νOH (OH)free peak position is identical for t-BuOH and HOD, i.e. ca. 1416 nm [61]. Hence loss of t-BuOH [OH] and a gain in HOD [OH] cancels out and does not effect spectral measurements.

Thus:

\[
[OH] = \frac{X_{1-a} + \alpha}{X_1}
\]

\[
\therefore [OH] = 1 - \frac{\alpha + \alpha}{X_1 X_1}
\]

(i.e. no correction is needed to the spectral measurements).
There is also an apparent band growing up at ca. 1390 nm on the high frequency side of the t-BuOH (OH)\textsubscript{free} band. This may be due to H\textsubscript{2}O in the system. The increase in weakly bound absorbance (ca. 1460 nm) is probably due to a combination of increasing weak D\textsubscript{2}O--HOCMe\textsubscript{3} bonds and [(LP)\textsubscript{free}]. Curve analysis is required to deduce the actual effect on the [(OH)\textsubscript{free}].

Figure 8L shows a comparison of the $2\nu_{OH}$ spectra for (CH\textsubscript{3})\textsubscript{3}CCH/OD and (CD\textsubscript{3})\textsubscript{3}COH/OD at 27°C. On deuterating the butyl C-H groups, the broad band at ca. 1545 nm for (CD\textsubscript{3})\textsubscript{3}COH/OD is diminished in absorbance relative to (CH\textsubscript{3})\textsubscript{3}COH/OD, indicating that the broad band at 1575 nm in t-BuOH is due to a CH\textsubscript{3}+OH intermolecular combination band and hence is not the strong H-bonded band. The actual strong H-bonded band is at ca. 1545 nm based on the (CD\textsubscript{3})\textsubscript{3}COH/OD result.

Figure 8j shows the effect of adding MeOD to t-BuOH/OD on the $2\nu_{OH}$ spectrum. There is a loss of [(OH)\textsubscript{free}] accompanied by an increase in absorbance in the 1545 nm region, with an isosbestic point at ca. 1495 nm. The effect of iPrOD on the t-BuOH $2\nu_{OH}$ spectrum is shown in Figure 8K. It is noticeable that iPrOD scavenges the t-BuOH [(OH)\textsubscript{free}] to a lesser extent than MeOD and also shows a smaller increase in the 1545 nm region. As ROH is added, the number of t-BuOH/t-BuOH bonds falls and therefore the probability of breaking falls, but they are replaced by ROH---t-BuOH bonds and these are "stronger" for MeOH than for iPrOH for steric reasons. Since ROH is bound into the H-bond frame no "steric-dilution" correction is made on the spectral measurements.

8.4.5 Tetraalkylammonium Salts

The effect on the $2\nu_{OH}$ t-BuOH spectrum on adding a tetraalkylammonium salt is shown in Figure 8c for Bu\textsuperscript{+}NCl. There appears to be little effect on the strong H-bonded region (ca. 1545 nm), but there is an appreciable
FIGURE 81
Effect of MeOD on the 2νOH spectrum of t-BuOH/OD (50% V/V) at 27°C.

- Growth in strong H-bonds
- Isosbestic point ca. 1495 nm
- Decrease in (OH) free groups

Molefraction MeOD
1. 0
2. 0.11
3. 0.20
4. 0.29
5. 0.37

Absorbance
0.075
0.1300
0.15

Nanometers (nm)
1300
1400
1500
1600
FIGURE 8L
Comparison of the $2v_{OH}$ spectra of $(CD_3)_3COH/OD$ against $(CH_3)_3COH/OD$
at $27^\circ C$.

Absorbance

Nanometers (nm)
decrease in \([\text{(OH)}_{\text{free}}]\). However, it has to be considered that the
Bu\(^{+}\)N\(^{+}\) ion may be generating \([\text{(OH)}_{\text{free}}]\) for "steric" reasons previously
discussed. Hence the actual decrease in \([\text{(OH)}_{\text{free}}]\) will be slightly
larger than is observed. This is accounted for in the final analysis,
discussed in the curve analysis section.

8.4.6 Metal Cations

Metal salts were found to be insoluble in t-BuOH/OD, hence a study
of cation solvation was not attempted.

8.5 RESULTS (CURVE ANALYSIS)

The next stage in analysing the results discussed in the spectral
analysis section (8.4) is to use a curve analysis technique on the
observed \(2\nu_{\text{OH}}\) t-BuOH spectra. This technique is the same as previously
described in Chapter 4 and so is not detailed here.

Each \(2\nu_{\text{OH}}\) t-BuOH/OD spectrum can be simulated by placing a minimum of
five bands under the total band envelope. Figure 8M(i) shows a typical
example of a deconvoluted spectrum. Band 1 is assigned as being
essentially due to \((\text{OH})_{\text{free}}\) groups and is kept at a constant position,
7072 cm\(^{-1}\) (1414 nm), constant half-band width at half-height, 20 cm\(^{-1}\),
and 100% Gaussian in all the systems studied. Only the height of band 1
is allowed to change as solute is titrated into the t-BuOH/OD system. The
other four bands are allowed small changes in height and position to
obtain a good fit between observed and simulated envelopes. It is
important to note that no physical significance is attached to the five
bands used to simulate \(2\nu_{\text{OH}}\) t-BuOH/OD spectra. They only represent a
range of hydrogen bonds varying from strong H-bonds at lower frequency to
weak H-bonds and ultimately \((\text{OH})_{\text{free}}\) at higher frequency. Band 5 is
assigned to a \(\text{CH}_{3}+\text{OH}\) intramolecularly coupled band as previously
The deconvolution of the OH band of t-BuOH in t-BuOD (25% Vv) at 27°C.

<table>
<thead>
<tr>
<th>BAND</th>
<th>HEIGHT</th>
<th>POSITION</th>
<th>STRETCH</th>
<th>HALF BAND WIDTH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.048</td>
<td>7072.000</td>
<td>100.000</td>
<td>20.000</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>6975.000</td>
<td>80.000</td>
<td>150.000</td>
</tr>
<tr>
<td>3</td>
<td>0.030</td>
<td>6760.000</td>
<td>60.000</td>
<td>122.000</td>
</tr>
<tr>
<td>4</td>
<td>0.029</td>
<td>6592.000</td>
<td>40.000</td>
<td>112.000</td>
</tr>
<tr>
<td>5</td>
<td>0.055</td>
<td>6352.000</td>
<td>20.000</td>
<td>148.000</td>
</tr>
</tbody>
</table>

FIGURE 8M(i)

The deconvolution of the OH band of t-BuOH in t-BuOD (25% Vv) at 27°C.
FIGURE 8M(ii)

The deconvolution of the OH band of \((\text{CD}_3)_3\text{COH}\) in \((\text{CD}_3)_3\text{COD}\) at 27°C.
discussed. Figure 8M(ii) shows the deconvoluted spectrum of \((\text{CD}_3)_3\text{COH/OD}\) using four bands. Bands 1 and 2 are identical to those used in the t-BuOH deconvoluted spectrum, in terms of position, half-band width at half-band height and % Gaussian. One broad band is used to simulate the strong H-bonded region, ca. 6510 cm\(^{-1}\), now that the CH\(_3\)+OH coupled band has been removed.

The curve analysis procedure was undertaken for each \(2\nu_\text{OH}\) t-BuOH/OD system, primarily to separate the \((\text{OH})\text{free}\) band from weakly bound bands and thus obtain a clearer picture as to the effect of added solutes on the \([\text{(OH)}\text{free}]\) absorbance.

8.5.1 Effect of Temperature Change

Figure 8.3 compares the relative change in \([\text{(OH)}\text{free}]\) absorbance, as a function of temperature, for t-BuOH, with other alcohols and HOD. The plot is a measure of the relative hydrogen bond energies for the different solvents. The weaker the H-bonding in the solvent, the easier it is for bonds to break with increasing temperature. The fluoroalcohols contain the largest concentration of \((\text{OH})\text{free}\) groups at room temperature, relative to HOD, t-BuOH and MeOH. They also show the steepest increase in \([\text{(OH)}\text{free}]\) with increasing temperature. t-BuOH shows a linear change in \([\text{(OH)}\text{free}]\) with increasing temperature as do the other solvents. It is interesting to note that t-BuOH lies between HOD and MeOH in terms of temperature gradient.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CF}_3)_2\text{CHOH})</td>
<td>(9.8 \times 10^{-3})</td>
</tr>
<tr>
<td>(\text{CF}_3\text{CH}_2\text{OH})</td>
<td>(3.7 \times 10^{-3})</td>
</tr>
<tr>
<td>HOD</td>
<td>(3.0 \times 10^{-3})</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>(0.75 \times 10^{-3})</td>
</tr>
<tr>
<td>MeOH</td>
<td>(0.40 \times 10^{-3})</td>
</tr>
</tbody>
</table>

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FIGURE 8.3
Change in the (OH)$_{free}$ band absorbance as a function of temperature, after deconvolution; for MeOH, t-BuOH, HOD, CF$_3$CH$_2$OH and (CF$_3$)$_2$CHOH.
8.5.2 Inert Solvents

The effect of adding inert solvents to t-BuOH and the subsequent effect on the \([\text{OH}]_{\text{free}}\), has already been discussed in Section 8.4.2. Figure 8.2 shows the relative increase in \([\text{OH}]_{\text{free}}\) for TMS, Me₄C, Bu₄Sn and CCl₄ in t-BuOH after curve analysing the respective \(2\nu_{\text{OH}}\) spectra.

8.5.3 Basic Aprotics

The effect of bases on the \(2\nu_{\text{OH}}\) t-BuOH \((\text{OH})_{\text{free}}\) band is shown in Figure 8.4 after deconvolution and correcting for base "steric-dilution" effects as previously discussed in Section 8.4.2. The relatively stronger bases, i.e. DMSO, DMA, DMF, scavenge \((\text{OH})_{\text{free}}\) groups at a quicker rate than weaker bases, i.e. CD₃CN, CH₃NO₂. Et₃N is a strong base, however it behaves as a weak base in t-BuOH, because the nitrogen lone-pair is hindered by ethyl groups, hence the bulky t-BuOH molecules cannot get to the nitrogen lone-pair. Acetone and Et₃N scavenge \((\text{OH})_{\text{free}}\) at a rate in-between strong bases and weak bases.

Figure 8.5 shows the effect of ketones and esters on the \(2\nu_{\text{OH}}\) \([\text{(OH)}_{\text{free}}]\) after deconvolution and correcting for "steric-dilution" effect due to esters. No correction is made for ketone "steric-dilution" effects due to the relatively smaller size of these molecules compared to the esters. The observed trends show that the esters produce slightly steeper gradients for loss of \([\text{(OH)}_{\text{free}}]\) compared to the ketones.

8.5.4 d-Alcohols and D₂O

The effect of adding MeOD, EtOD, iPrOD and D₂O to t-BuOH on the \(2\nu_{\text{OH}}\) spectrum has already been discussed with reference to OH/OD exchange in Section 8.4.4. Figure 8.6 shows the effect of d-alcohols and D₂O on the t-BuOH \(2\nu_{\text{OH}}\) \([\text{(OH)}_{\text{free}}]\) after curve analysing the spectra over the full
FIGURE 8.4
Effect of bases on the $2v_{\text{OH}}$ (OH)$_{\text{free}}$ band of t-BuOH/OD measured relative to pure t-BuOH/OD, after deconvolution and dilution correction for Et$_3$N, DMA, DMF, DMSO. Temperature = 27°C ± 0.1
FIGURE 8.5
Effect of ketones and esters on the $2\nu_{\text{OH}} (\text{OH})_{\text{free}}$ band of t-BuOH/OD measured relative to pure t-BuOH/OD after deconvolution and correcting for esters dilution effect. Temperature = 27°C ± 0.1
FIGURE 8.6
Effect of D$_2$O and d-alcohols on the 2ν$_{OH}$ (OH)$_{free}$ band of t-BuOH/OD measured relative to pure t-BuOH/OD after deconvolution.
Temperature = 27°C ± 0.1

* D$_2$O molefraction calculated on the basis of two available OH groups.
i.e. $x_{D_2O} = \frac{2nD_2O}{2nD_2O + nt-BuOH}$

Change in Estimated % (OH)$_{free}$

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cosolvent molefraction range. MeOD scavenges the [(OH)\text{free}] down to approximately zero concentration at 0.9 MeOD molefraction. EtOD produces a similar result, except it does not scavenge the [(OH)\text{free}] down to zero concentration, since EtOD contains a small amount of (OH)\text{free}, i.e. <1\% at room temperature. \textsuperscript{1}PrOD follows "ideal behaviour" in the 0-0.5 cosolvent molefraction range; "ideal" means the ROH is all bound but t-BuOH remains unaffected. The plot indicates that relative to t-BuOH, \textsuperscript{1}PrOD contains about 1\% (OH)\text{free} at room temperature. The 3\% (OH)\text{free} value for t-BuOH is obtained from inert solvent work discussed in Section 8.6.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Estimated % (OH)\text{free} at 27\textdegree C</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuOH</td>
<td>3%</td>
</tr>
<tr>
<td>\textsuperscript{1}PrOD</td>
<td>1%</td>
</tr>
<tr>
<td>EtOD</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>MeOD</td>
<td>~0%</td>
</tr>
</tbody>
</table>

The result for adding D\textsubscript{2}O to t-BuOH is the most dramatic. D\textsubscript{2}O scavenges t-BuOH [(OH)\text{free}] in the 0-0.5 cosolvent molefraction range. As [D\textsubscript{2}O] increases the 2\textsubscript{vOH} (OH)\text{free} peak absorbance shows a dramatic increase in absorbance as the system tends towards D\textsubscript{2}O. The complete D\textsubscript{2}O molefraction range was not studied since in the limit of pure HOD in D\textsubscript{2}O (25\% \textsubscript{v/v}), the relatively large increase in HOD weakly bound obscures the true effect on the (OH)\text{free} peak, thus making curve analysis unreliable.

8.5.5 Tetraalkylammonium Salts

Figures 8.7 and 8.8 show the effect of tetraalkylammonium salts on the 2\textsubscript{vOH} t-BuOH [(OH)\text{free}], before and after "steric-dilution" correction, respectively. This correction has been discussed previously in Section 8.4.5, regarding the extent to which large butyl groups and Et\textsubscript{4}N\textsuperscript{+} cause [(OH)\text{free}] increase. It is assumed that large tetraalkylammonium groups undergo negligible solvation relative to the smaller more active anions.
FIGURE 8.7
Effect of tetraalkylammonium salts on the $2\nu_0\text{H (OH)}$ free band of t-BuOH/OD measured relative to pure t-BuOH/OD, after deconvolution.
Temperature = 27°C ± 0.1
FIGURE 8.8
Effect of tetraalkylammonium salts on the $2\nu_{OH} (OH)_{\text{free}}$ band of t-BuOH/OD, measured relative to pure t-BuOH/OD, after deconvolution and cation dilution correction.

Temperature = 27°C ± 0.1
Hence tetraalkylammonium salts are generally used to examine the effect of various anions on the $2\nu_{\text{OH}}$ t-BuOH/OD spectrum.

All the salts studied appear to scavenge $[(\text{OH})_{\text{free}}]$ to a similar extent in the $0$-$0.05$ salt molefraction range. Beyond this range there is a significant difference between Cl$^-$ and Br$^-$, i.e. Cl$^-$ scavenges (OH)$_{\text{free}}$ groups quicker. Other tetraalkylammonium salts were tried but found to be insoluble in t-BuOH, e.g. Et$_4$NBr, Et$_4$NI, Bu$_4$NClO$_4$, and all Me$_n$N$^+$ salts.

Table 1 contains the LN-% (OH)$_{\text{free}}$ gradients for the various bases, ketones, esters, alcohols and tetraalkylammonium salts studied in t-BuOH. Some of the graphs for these gradients are shown in Figures 8.9-8.11.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Initial LN-% (OH)$_{\text{free}}$ Gradients [Arbitrary Units]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NO$_2$</td>
<td>-0.55</td>
</tr>
<tr>
<td>CD$_3$CN</td>
<td>-0.75</td>
</tr>
<tr>
<td>Et$_3$N</td>
<td>-1.95</td>
</tr>
<tr>
<td>Acetone</td>
<td>-1.75</td>
</tr>
<tr>
<td>DMF</td>
<td>-3.10</td>
</tr>
<tr>
<td>DMA</td>
<td>-3.55</td>
</tr>
<tr>
<td>DMSO</td>
<td>-3.10</td>
</tr>
<tr>
<td>Diethyl Ketone</td>
<td>-1.55</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>-1.95</td>
</tr>
<tr>
<td>Cyclopentanone</td>
<td>-2.35</td>
</tr>
<tr>
<td>Isopropyl Acetate</td>
<td>-3.05</td>
</tr>
<tr>
<td>Tert-butyl Acetate</td>
<td>-3.35</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>-3.05</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>-3.95</td>
</tr>
<tr>
<td>MeOD</td>
<td>-6.95</td>
</tr>
<tr>
<td>EtOD</td>
<td>-6.95</td>
</tr>
<tr>
<td>t-PrOD</td>
<td>-3.30</td>
</tr>
<tr>
<td>Bu$_4$NI</td>
<td>-4.50</td>
</tr>
<tr>
<td>Bu$_4$NBr</td>
<td>-4.15</td>
</tr>
<tr>
<td>Bu$_4$NCl</td>
<td>-5.30</td>
</tr>
<tr>
<td>Bu$_4$NCH$_3$COO</td>
<td>-6.10</td>
</tr>
<tr>
<td>Et$_4$NCl</td>
<td>-6.00</td>
</tr>
</tbody>
</table>

8.5.6 Solvation Numbers

Having obtained the initial LN-% (OH)$_{\text{free}}$ gradients, measured over the $0$-$0.05$ base molefraction range, it is possible to estimate solvation
FIGURE 8.9
Effect of bases on the $2\nu_{OH} \text{LN-8 (OH)}_{\text{free}}$ of t-BuOH/OD measured relative to pure t-BuOH/OD after deconvolution and dilution correction for DMA, DMF, DMSO, Et$_3$N.
Temperature = 27°C ± 0.1
FIGURE 8.10
Effect of ketones and esters on the 2νOH LN-% (OH) free of t-BuOH/OD measured relative to pure t-BuOH/OD after deconvolution and after dilution correction on the esters.
Temperature = 27°C ± 0.1
FIGURE 8.11

Effect of tetraalkylammonium salts on the $2\nu_0\text{H} \text{LN-}$
(OH)$_\text{free}$ of t-BuOH/OD, measured relative to pure t-BuOH/OD
after deconvolution and cation dilution correction.
Temperature = 27°C ± 0.1
Eaton and Symons [62] monitored the vC=O stretch of acetone and DMA in methanol. They found that acetone gave a doublet, assigning the 1718 cm\(^{-1}\) peak to the "free" species and the 1708 cm\(^{-1}\) peak to the mono-solvate. By comparing peak heights the mono-solvate was estimated at 90% concentration with only 10% "free". DMA also produced a doublet, they assigned the di-solvate species to the 1615 cm\(^{-1}\) peak and the mono-solvate to the 1631 cm\(^{-1}\) peak. Relative peak heights gave an estimated value of 70% mono-solvate and 30% di-solvate.

Figures 8N and 8P show the vC=O stretch for acetone and DMA in t-BuOH respectively. Curve analysis on the t-BuOH/acetone system revealed a peak at ca. 1712 cm\(^{-1}\) assigned to the mono-solvate and a peak at 1742 cm\(^{-1}\) assigned to "free" base. Relative peak heights reveal an estimated value of 94% mono-solvate and 6% "free" (Figure 8Q). Figure 8R reveals a peak at 1639 cm\(^{-1}\), assigned to mono-solvated species and a peak at 1618 cm\(^{-1}\) assigned to the di-solvate for the t-BuOH/DMA system. Relative peak heights reveal an estimated value of 80% mono-solvate and 20% di-solvate. These assignments are made by referring to Eaton and Symons' [62] methanol assignments.

Using these results as references, other solvation numbers can be estimated using the \(2v_{OH}\) results. These are listed in Table 2. The solvation numbers are calculated by comparing the LN-% (OH)\textsubscript{free} gradients for all the systems studied with the LN-% (OH)\textsubscript{free} gradients for DMA and acetone.
FIGURE 8N
Monitoring the νC=O stretch of Acetone in t-BuOH at 27°C.

Molefraction Acetone
1. 0.013
2. 0.026
3. 0.051
4. 0.075
5. 0.10
FIGURE 8P
Monitoring the νC=O stretch of DMA in t-BuOH at 27°C.

Molefraction DMA
1. 0.01
2. 0.02
3. 0.04
4. 0.061

Absorbance

Wavenumber (cm⁻¹)
FIGURE 8Q

The deconvolution of the $\nu\text{C}=0$ band of acetone in t-BuOH at 27°C.
[M.F. Acetone = 0.075]
FIGURE 8R

The deconvolution of the \( \nu_{C=O} \) band of DMA in t-BuOH at 27°C.
[M.F. DMA = 0.06]
### TABLE 2

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Estimated Solvation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NO$_2$</td>
<td>0.4</td>
</tr>
<tr>
<td>CD$_3$CN</td>
<td>0.4</td>
</tr>
<tr>
<td>Et$_3$N</td>
<td>1.0</td>
</tr>
<tr>
<td>DMF</td>
<td>1.1</td>
</tr>
<tr>
<td>DMA</td>
<td>1.2</td>
</tr>
<tr>
<td>DMSO</td>
<td>1.1</td>
</tr>
<tr>
<td>Diethyl Ketone</td>
<td>0.9</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.0</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>1.0</td>
</tr>
<tr>
<td>Cyclopentanone</td>
<td>1.1</td>
</tr>
<tr>
<td>Isopropyl Acetate</td>
<td>1.1</td>
</tr>
<tr>
<td>Tert-butyl Acetate</td>
<td>1.2</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>1.1</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>1.3</td>
</tr>
<tr>
<td>Me$_2$O</td>
<td>2.0</td>
</tr>
<tr>
<td>Et$_2$O</td>
<td>2.0</td>
</tr>
<tr>
<td>$^4$Pr$_2$OD</td>
<td>1.2</td>
</tr>
<tr>
<td>Bu$_4$NII</td>
<td>1.4</td>
</tr>
<tr>
<td>Bu$_4$NBr</td>
<td>1.3</td>
</tr>
<tr>
<td>Bu$_4$NCl</td>
<td>1.6</td>
</tr>
<tr>
<td>Bu$_4$NCH$_3$COO</td>
<td>1.7</td>
</tr>
<tr>
<td>Et$_4$NCl</td>
<td>1.7</td>
</tr>
</tbody>
</table>

8.5.7 Changes in Other Spectral Regions

Figures 8.12-8.14 show the changes in the deconvoluted peaks of t-BuOH in t-BuOD in the first overtone region on addition of DMF, CH$_3$NO$_2$ and Bu$_4$NCl respectively. DMF being a strong base produced a dramatic loss of [(OH)$_{free}$] and also a loss of absorbance in the strong H-bond region, accompanied by a growth in weak H-bonds $\text{ca. 6758 cm}^{-1}$. This growth may be due to increasing [(LP)$_{free}$] or DMF---HOCMe$_3$ species or both. Figure 8.13 shows how CH$_3$NO$_2$, a very weak base, affects the t-BuOH/OD deconvoluted peaks. An additional sixth band is needed to obtain a good fit between experimental and simulated spectra. This additional band is assigned to CH$_3$NO$_2$---HOCMe$_3$ species (ca. 7040 cm$^{-1}$), which occurs close to the (OH)$_{free}$ band. There is also a large growth in very weak bonds (ca. 6975 cm$^{-1}$). Figure 8.14 shows how a tetraalkylammonium salt changes the deconvoluted peaks, i.e. Bu$_4$NCl. There is a loss of (OH)$_{free}$ groups and weak H-bonds (ca. 6975 cm$^{-1}$), with little effect on the more strongly
FIGURE 8.12

Change in the deconvoluted peaks of t-BuOH in t-BuOD in the first overtone region on addition of DMF.

Temperature = 27°C ± 0.1

- Strong H-bonds (6350 cm⁻¹)
- (OH) free (7072 cm⁻¹)
- Weak H-bonds (6758 cm⁻¹)
- Weak H-bonds (6975 cm⁻¹)
- Weak H-bonds (6590 cm⁻¹)

Absorbance Units

DMF Molefraction

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FIGURE 8.13
Change in the deconvoluted peaks of t-BuOH/OD in the first overtone region on addition of CH$_3$NO$_2$.
Temperature = 27°C ± 0.1

**KEY**
- Band 1 = (OH)free (7072 cm$^{-1}$)
- Band 2 = Very Weak H-bonds (6975 cm$^{-1}$)
- Band 3 = Weak H-bonds (6758 cm$^{-1}$)
- Band 4 = Weak H-bonds (6590 cm$^{-1}$)
- Band 5 = Strong H-bonds (6350 cm$^{-1}$)
- Band 6 = CH$_3$NO$_2$---HOCMe$_3$ (7040 cm$^{-1}$)
FIGURE 8.14
Change in the deconvoluted peaks of t-BuOH in t-BuOD in the first overtone region on addition of Bu₄NCl.
Temperature = 27°C ± 0.1

Absorbance Units

Bu₄NCl Molefraction

Strong H-bonds (6350 cm⁻¹)
(7072 cm⁻¹)

Weak H-bonds (6758 cm⁻¹)
(6590 cm⁻¹)

Very Weak H-bonds (6975 cm⁻¹)
bound region of the spectrum.

Table 3 lists the "best" cm\(^{-1}\)/nm values for all the t-BuOH/OD deconvoluted bands at 27°C, averaged from the systems studied.

**TABLE 3**

Infrared Parameters for deconvoluted band maxima in the 2\(\nu_{OH}\) region for t-BuOH at 27°C

<table>
<thead>
<tr>
<th>Band</th>
<th>(\nu) cm(^{-1})</th>
<th>(\nu) cm(^{-1})</th>
<th>cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (OH)(^{\text{free}})</td>
<td>1414 (1414)</td>
<td>7072</td>
<td></td>
</tr>
<tr>
<td>2. Very Weak H-bonds</td>
<td>1434 (1434)</td>
<td>6975</td>
<td></td>
</tr>
<tr>
<td>3. Weak H-bonds</td>
<td>1478 (1478)</td>
<td>6764</td>
<td></td>
</tr>
<tr>
<td>4. Strong H-bonds</td>
<td>1517 (1536)</td>
<td>6590</td>
<td></td>
</tr>
<tr>
<td>5. CH(_3) +OH coupled band</td>
<td>1575</td>
<td>6350</td>
<td></td>
</tr>
<tr>
<td>CH(_3)NO(_2)---HOCMe(_3)</td>
<td>1420</td>
<td>7040</td>
<td></td>
</tr>
</tbody>
</table>

* Values for (CD\(_3\))\(_3\)COH in (CD\(_3\))\(_3\)COD

8.6 **CALCULATION OF % (OH)\(^{\text{free}}\) IN t-BuOH**

An extinction coefficient, \(\varepsilon\), was calculated for very dilute t-BuOH in CCl\(_4\) (i.e. monomer concentration), shown in Figure 8.15. A value for \(\varepsilon = 24.6\) is very close to the value for MeOH in CCl\(_4\), calculated at \(\varepsilon = 24.5\) by Pay [63]. This extinction coefficient can be used to calculate a value for % (OH)\(^{\text{free}}\) in t-BuOH at 27°C.

Using Beers Law: \(A = \varepsilon . c . \ell\).

where \(A\) = Absorbance of pure t-BuOH (OH)\(^{\text{free}}\) peak (i.e. the deconvoluted (OH)\(^{\text{free}}\) absorbance)

\(\varepsilon = 24.6\) mols\(^{-1}\) dm\(^2\)

\(\ell = 0.02\) dm

Thus: \(A = 0.152\) absorbance units for 100% [t-BuOH]

\[0.152 = 24.6 \times c \times 0.02\]

\[c = 0.309\ \text{mols dm}\(^{-3}\)\]

Number of moles in neat t-BuOH = \(1000 \times 0.786 = 10.6044\) mols dm\(^{-3}\)

\[\frac{74.12}{10.6044}\]

\[\therefore \% \ (OH)\(^{\text{free}}\) = \frac{0.309 \times 100}{10.6044} = \text{ca. 3%}\]
FIGURE 8.15
Beers Law plot of [t-BuOH] against 'monomer' absorbance for t-BuOH in CCl₄ at 27°C ± 0.1.

\[ \xi = \frac{A}{C \cdot l} \]

\[ \xi = 24.6 \text{ mol}^{-1} \text{ dm}² \]

\[ [l = 0.02 \text{ dm}] \]
This value of 3% (OH)\text{free} in t-BuOH appears to be low in view of the sharp 2νOH peak at ca. 1416 nm, however the ε value appears to be reasonable, in relation to the methanol ε value.

8.7 \textbf{1H NMR RESULTS}

A study was made on the effect of adding inert solvents, bases, alcohols and tetraalkylammonium salts to t-BuOH on the observed δ(t-BuOH) hydroxyl resonance at 27°C, which is the weighted average of bulk H-bonds, (OH)\text{free} and (LP)\text{free} species.

\begin{center}
\begin{tikzpicture}
    \node (a) at (0,0) {δ(t-BuOH)\text{observed}};
    \node (b) at (-1.5,1.5) {bulk};
    \node (c) at (1.5,1.5) {(LP)\text{free}};
    \node (d) at (-1.5,-1.5) {(OH)\text{free}};
    \draw[->] (a) -- (b);
    \draw[->] (a) -- (c);
    \draw[->] (a) -- (d);
\end{tikzpicture}
\end{center}

8.7.1 \textbf{Inert Solvents}

The effect of Bu\textsubscript{4}Sn, CCl\textsubscript{4} and TMS on the observed δ(t-BuOH) hydroxyl resonance has already been discussed in Section 8.4.2 (Figure 8.1). The immediate upfield shift indicates that CCl\textsubscript{4} is effecting the t-BuOH structure, whereas in MeOH, cyclisation ensues producing species similar to bulk MeOH. As a result, CCl\textsubscript{4} does not effect the MeOH structure until >0.9 [CCl\textsubscript{4}] molefraction.

The most stable form of the t-BuOH dimer has a trans open (non-cyclic) form similar to that in methanol, as discussed by Brink [58], who did a theoretical study on isolated H-bonded clusters in t-BuOH.
In the trimer there may be a "protected" OH held between large butyl groups and unavailable for bonding due to steric reasons:

Hence if cyclisation did not occur in t-BuOH/CCl₄ systems to the same extent as MeOH/CCl₄ systems, unbonded OH groups would give rise to the observed immediate upfield shift.

A shift upfield from $\delta(t\text{-BuOH})_{\text{obs}}$ of 333 Hz was measured at infinite t-BuOH dilution in CCl₄. There is a gradual upfield shift up to about 0.8 [CCl₄] molefraction. A more dramatic shift is observed thereafter as hydrogen bonding is increasingly weakened, resulting in increased shielding of the hydroxyl proton. The C-H proton resonance occurred at ca. 123 Hz downfield from TMS and showed a negligible shift over the full molefraction range.

8.7.2 Basic Aprotics

Trends in the OH proton resonance of t-BuOH with molefraction of added cosolvent are shown in Figure 8.16. Strong bases, i.e. DMA, DMSO and DMF all show similar upfield shifts, while MeCN produces a relatively large
FIGURE 8.16
$^1$H NMR plot showing the shift of the t-BuOH hydroxyl resonance on adding various bases, measured relative to pure t-BuOH at 27°C.
upfield shift. Et₃N produces a downfield shift in the 0-0.5 base mole-
fraction region, thereafter a high-field trend in the 0.5-1.0 mole-
fraction range. The controlling factor is probably steric, reducing the
rate of formation of hydrogen bonds due to the narrow cone of approach
to the protected lone-pair of electrons on nitrogen. Pineau et al. [64]
have commented on the steric difficulty of forming hydrogen bonds to
triethylamine. However, the limiting NMR shift for t-BuOH in pure Et₃N
falls close to DMA, DMSO and DMF. This implies that when [t-BuOH] is
high, the steric factor is not so significant, probably because the
equilibrium is biased towards the bonded form.

Limiting NMR shifts for t-BuOH in pure bases are listed below, as well
as initial slopes measured over the 0-0.1 [base] molefraction region;
measured relative to δ(t-BuOH)_{obs} for pure t-BuOH at 27°C.

<table>
<thead>
<tr>
<th>Base</th>
<th>Limiting Shift (ppm)</th>
<th>Initial Gradient (Arbitrary Units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>+ 1.96</td>
<td>+ 2.05</td>
</tr>
<tr>
<td>Me₂CO</td>
<td>+ 1.27</td>
<td>+ 1.12</td>
</tr>
<tr>
<td>DMSO</td>
<td>+ 0.46</td>
<td>+ 0.71</td>
</tr>
<tr>
<td>DMF</td>
<td>+ 0.48</td>
<td>+ 0.92</td>
</tr>
<tr>
<td>DMA</td>
<td>+ 0.25</td>
<td>+ 0.35</td>
</tr>
<tr>
<td>Et₃N</td>
<td>+ 0.32</td>
<td>- 0.51</td>
</tr>
</tbody>
</table>

These shifts are a measure of base strength, thus:–

MeCN < Acetone < DMF ≈ DMSO ≈ DMA < Et₃N

Increasing base strength

A similar study by Symons et al. [65], for bases in methanol, indicates
steeper initial slopes than observed for bases in t-BuOH. This can be
explained by the following schemes:
(i) Methanol + Base

There is negligible [(OH)\text{free}] in methanol, hence addition of base generates [(LP)\text{free}] and B\textsuperscript{−}—HOMe species which act to shift the \( \delta \) (MeOH)\text{obs} resonance upfield.

(ii) t-BuOH + Base

The presence of [(OH)\text{free}] in t-BuOH and the fact that (OH)\text{free} groups are scavenged by base, counteracts to some extent the gain in [(LP)\text{free}] and B\textsuperscript{−}—HOCMe\textsubscript{3} species, hence the shift upfield is less pronounced.

Figure 8.17 shows trends in the proton resonance shifts (from the bulk methanol value) for methanol at 25\degree C as a function of the molefraction of added basic aprotic cosolvents [65].
FIGURE 8.17
Effect of added bases on the methanol proton resonance at 25°C.
8.7.3 Alcohols and H<sub>2</sub>O

Figure 8.18 shows the effect of adding alcohols and H<sub>2</sub>O to t-BuOH, on the time averaged shift of the hydroxyl resonance over the full mole-fraction range. For t-BuOH/EtOH and t-BuOH/PrOH systems, both hydroxyl resonance signals were observed. However, the t-BuOH/MeOH system produced a time averaged single peak, thus for comparative reasons the time averaged shift is plotted for each system.

The t-BuOH/MeOH system shows a maximum downfield shift in the 0.5 molefraction range. This might indicate that the strongest hydrogen bonding environment around both t-BuOH and MeOH protons occurs in the mid-molefraction range. The t-BuOH/EtOH and t-BuOH/PrOH systems indicate the t-BuOH structure changes markedly towards a stronger hydrogen bonded environment around the t-BuOH proton on going from t-BuOH into the cosolvent rich region.

The limiting shifts for the pure cosolvents are listed below, measured relative to pure t-BuOH at 27°C.

<table>
<thead>
<tr>
<th>Cosolvent</th>
<th>Limiting Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuOH</td>
<td>0</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-0.1</td>
</tr>
<tr>
<td>MeOH</td>
<td>-0.26</td>
</tr>
<tr>
<td>PrOH</td>
<td>-0.60</td>
</tr>
<tr>
<td>EtOH</td>
<td>-0.68</td>
</tr>
</tbody>
</table>

The limiting shifts are probably controlled by competition between the [(OH)<sub>free</sub>] present in each pure cosolvent and the alkyl group inductive effect. The alkyl groups have a downfield effect on the cosolvent hydroxyl resonance and [(OH)<sub>free</sub>] an upfield contribution. The magnitude of the inductive effect is proportional to the size of the alkyl group. Of all the alcohols studied t-BuOH is the most basic due to the large butyl groups pushing electron density onto the oxygen, thus making the OH proton less acidic.
FIGURE 8.18

$^1$H NMR plot showing the time averaged shift of the hydroxyl resonance on mixing t-BuOH with H$_2$O and various alcohols; 27°C.
The t-BuOH hydroxyl resonance occurs at highest field relative to all the alcohols, because it contains more [(OH)\text{free}] than \(^1\text{PrOH}, \text{EtOH}\) and \(\text{MeOH}\) which offsets the downfield shift contribution of the relatively large butyl groups.

It would appear that for methanol, there is a loss of [(OH)\text{free}] and a gain of MeOH bound giving the observed downfield shift. The pure methanol shift relative to t-BuOH is a measure of the methyl group inductive effect since MeOH contains no [(OH)\text{free}]. \(^1\text{PrOH}\) has a larger alkyl group than EtOH, however the \(^1\text{PrOH}\) resonance occurs at higher field relative to EtOH because \(^1\text{PrOH}\) contains more [(OH)\text{free}], as found in the \(2\nu_0\text{H}\) study, which offsets the alkyl groups downfield contribution.

A small downfield shift is observed over the water cosolvent range, reaching a maximum shift at ca. 0.05 [t-BuOH] molefraction. Harvey et al. [13] showed this enhanced H-bonding to be due to water shell formation around weakly interacting interstitial t-BuOH molecules. The trend for the t-BuOH/H\(_2\)O system infers loss of [(OH)\text{free}] and a gain of 2OH---bound species. Compared to the alcohols, the \(\delta(H_2O)_{\text{obs}}\) shift in pure water is expected to occur at higher fields due to the relatively high [(OH)\text{free}]. However, water is anomalous in that it is three-dimensional compared to alcohols two-dimensional structure and also contains two OH groups. Thus the water 'bulk' contribution to the \(\delta(H_2O)_{\text{obs}}\) shift, which provides the largest contribution to the shift, cannot be discussed in the same terms as the alcohols 'bulk' term.
8.7.4 Tetraalkylammonium Salts

Whereas the $2\nu_{OH}$ overtone study provided information on the relative basicity of anions in t-BuOH, a $^1$H NMR study reveals information about the relative strengths of anion----solvent interaction, i.e. base strength. The $2\nu_{OH}$ study revealed a similar solvation number for Cl$^-$, Br$^-$ and I$^-$ anions. However, Figure 8.19 shows the dramatic effect on the $\delta(t$-BuOH)$_{obs}$ hydroxyl resonance caused by $R_nN^+X^-$ salts, the shifts being a measure of the strength of anion----HOCHMe$_3$ interaction.

Large butyl groups have a diluent effect on the t-BuOH solvent structure, i.e. Figure 8.1 shows how Bu$^+$_Sn causes an upfield shift of the hydroxyl resonance. This result is used as a correction factor in the final hydroxyl resonance shifts for $R_nN^+X^-$ salts (Figure 8.19). Hence the corrected shifts are a measure of the anion interaction with t-BuOH separate from any cation effect. Figure 8.19 shows that I$^-$ produces an upfield shift indicating a relatively weak interaction between I$^-$---HOCHMe$_3$, compared to Br$^-$ which produces no significant shift and Cl$^-$ which shows a large downfield shift:

i.e. $\text{Cl}^- \gg \text{Br}^- \gtrsim \text{I}^-$

Increasing base strength

8.7.5 $^1$H NMR/IR Correlation

Figure 8.20 shows a correlation plot between infrared shifts, $\nu$(OH), and proton resonance shifts, $\nu'$(OH), for very dilute t-BuOH in various solvents at 27°C. The plot can be used to obtain NMR shifts for species whose infrared shift is known but for which no NMR shift can be obtained. The $2\nu_{OH}$ region was used to check if there is any [(OH)$_{free}$] present when dilute t-BuOH is present in the various solvents. No [(OH)$_{free}$] was observed, hence the points on the correlation plot need not be corrected, since the presence of any [(OH)$_{free}$] would act to push the points upfield,
FIGURE 8.19

$^1$H NMR plot showing the effect on the hydroxyl resonance of t-BuOH on adding tetraalkylammonium salts, after correcting for cation dilution effect, measured relative to pure t-BuOH.

Temperature = $27^\circ C \pm 0.1$
FIGURE 8.20

$\nu$ ppm/$\nu$ cm$^{-1}$ correlation plot for very dilute $t$-BuOH in various solvents, 27°C (using $\nu_{OH}$ IR data).
i.e. off the slope. A similar correlation plot was obtained for methanol in CCl₄ + added bases [60].

Table 4 lists the limiting infrared and proton resonance shifts for very dilute t-BuOH in various solvents which have been used to construct the correlation plot (Figure 8.20). Some 2ν₉₂₉ infrared shifts for very dilute t-BuOH in solvents, are also listed. This set of overtone infrared shifts has been used to construct a ν ppm/ν cm⁻¹ correlation plot (Figure 8.21). The t-BuOH position is upfield, off the slope due to [(OH)free] being present.

**TABLE 4**

Limiting hydroxyl resonance shifts for very dilute t-BuOH in various solvents, measured relative to (OH)free at 27°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Δ ν ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>0</td>
</tr>
<tr>
<td>MeCN</td>
<td>1.36</td>
</tr>
<tr>
<td>Me₂CO</td>
<td>2.06</td>
</tr>
<tr>
<td>DMF</td>
<td>2.85</td>
</tr>
<tr>
<td>DMA</td>
<td>3.07</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>3.33</td>
</tr>
</tbody>
</table>

Limiting νOH IR shifts for very dilute t-BuOH in various solvents at 27°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ν cm⁻¹</th>
<th>Δ ν cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₁₂</td>
<td>3621</td>
<td>0</td>
</tr>
<tr>
<td>MeCN</td>
<td>3548</td>
<td>73</td>
</tr>
<tr>
<td>Me₂CO</td>
<td>3520</td>
<td>91</td>
</tr>
<tr>
<td>DMF</td>
<td>3455</td>
<td>166</td>
</tr>
<tr>
<td>DMA</td>
<td>3445</td>
<td>176</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>3360</td>
<td>261</td>
</tr>
</tbody>
</table>

Limiting 2νOH IR shifts for very dilute t-BuOH in various solvents at 27°C

- (OH)free = 7072 cm⁻¹
- (CD₃)₃COH bulk band = 6765 cm⁻¹
- DMSO = 6850 cm⁻¹
- MeCN = 6975 cm⁻¹
Figure 8.21

$\nu_{ppm}/\nu_{cm}^{-1}$ correlation plot for very dilute $t$-BuOH in various solvents, 27°C (using $2\nu_{OH}$ IR data).

- $t$-BuOH
- MeCN
- DMSO
- (OH)$_{free}$
This correlation could be useful for the reconstruction of NMR shifts for t-BuOH with added bases, as discussed for water in Chapter 9.

8.8 THEORETICAL CONSIDERATION FOR LOSS OF \( (\text{OH})_{\text{free}} \) GROUPS

Using simple Law of Mass Action theory;

Consider the equilibrium:

\[
(t-\text{BuOH})_{\text{bulk}} = (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}}
\]

at equilibrium \( 2\bar{n}(t-\text{BuOH})_b = \bar{n}(\text{OH})_f + \bar{n}(\text{LP})_f \)

\[
\therefore \text{Total no. moles} = n_T = 2\bar{n}(t-\text{BuOH})_b + \bar{n}(\text{OH})_f + \bar{n}(\text{LP})_f
\]

\[
\therefore 2\bar{n}(t-\text{BuOH})_b = n_T - \bar{n}(\text{OH})_f - \bar{n}(\text{LP})_f
\]

On a molefraction scale:

\[
K = \frac{\bar{n}(\text{OH})_f \cdot \bar{n}(\text{LP})_f}{2\bar{n}(t-\text{BuOH})_b} \frac{n_T}{n_T}
\]

In pure t-BuOH: \( \bar{n}(\text{OH})_f = \bar{n}(\text{LP})_f \)

\[
\therefore K = \left( \frac{\bar{n}(\text{LP})_f}{n_T} \right)^2 
\]

\[
\therefore K = \left( \frac{[y(\text{LP})_f]}{1 - 2[x(\text{LP})_f]} \right)^2
\]

\[
\% (\text{OH})_{\text{free}} = \frac{\bar{n}(\text{OH})_f}{n_T} \times 100
\]

Add Base

Assume each mole of base bonds to \( Z \) moles of \( (\text{OH})_{\text{free}} \) (where \( Z \) = basicity).

At equilibrium: \( n_s = 2\bar{n}(t-\text{BuOH}) + \bar{n}(\text{OH})_{\text{free}} + \bar{n}(\text{LP})_{\text{free}} + \bar{n}[B(\text{OH})] \)

\( (n_s = \text{total no. moles}) \)

also: \( \bar{n}(\text{OH})_{\text{free}} \neq \bar{n}(\text{LP})_{\text{free}} \)
\[ n(LP)_{\text{free}} = n(\text{OH})_{\text{free}} + Zn[B(\text{OH})] \]

\[ \therefore \quad n_s = 2n(t\text{-BuOH}) + n(\text{OH})_{\text{free}} + n(\text{OH})_{\text{free}} + Zn[B(\text{OH})] + n[B(\text{OH})] \]

\[ \therefore \quad n_s = 2n(t\text{-BuOH}) + 2n(\text{OH})_{\text{free}} + Zn[B(\text{OH})] + n[B(\text{OH})] \]

\[ \therefore \quad 2n(t\text{-BuOH}) = n_s - 2n(\text{OH})_{\text{free}} - Zn[B(\text{OH})] - n[B(\text{OH})] \]

\[ \therefore \quad 2n(t\text{-BuOH}) = n_s - 2n(\text{OH})_{\text{free}} - (1+2)n[B(\text{OH})] \]

\[ K = \frac{n(\text{OH})_{\text{free}} + Zn[B(\text{OH})]}{ns - 2n(\text{OH})_{\text{free}} - (1+2)n[B(\text{OH})]} \]

\[ \therefore \quad K = \frac{n(\text{OH})_{\text{free}} + Zn[B(\text{OH})]}{1 - 2n(\text{OH})_{\text{free}} - (1+2)n[B(\text{OH})]} \]

\[ \therefore \quad K = \frac{\alpha (\alpha + nb)}{1 - 2\alpha - b - nb} \quad \ldots \quad (1) \]

\( \alpha = \bar{x}(\text{OH})_{\text{free}} \)

\( b = \bar{x}[B(\text{OH})] \)

\( n = Z \)

Converting (1) into quadratic form:

\[ K - 2\alpha - Kb - Knb = \alpha^2 + nb \]

\[ \therefore \quad \alpha^2 + nb + 2K\alpha + Kb + Knb - K = 0 \]

\[ \therefore \quad \alpha^2 + \alpha(nb + 2K) + K(b + nb - 1) = 0 \]

\[ \therefore \quad \alpha = \frac{-(nb + 2K) + \sqrt{(nb + 2K)^2 - 4K(b + nb - 1)}}{2} \quad \ldots \quad (2) \]

Equation (2) is only valid at low base concentration, whilst the equilibrium between bulk (t-BuOH) and (OH)_{free}, (LP)_{free} groups remains constant. By fixing a value for K (equilibrium constant), \( \alpha \) can be calculated for different concentrations of base. The basicity of the base can also be changed to give results for mono-, di-, tri- bases, etc., assuming the concentration of (OH)_{free} is known in t-BuOH at 27°C.

If the inert solvent result (8.6) is used, i.e. 3% (OH)_{free} in t-BuOH.
to fix a value for K in equation (2), theoretical gradients are produced, which are much steeper than the experimental results:

\[
\ln \% \text{(OH)}_{\text{free}} \text{ gradients}
\]

<table>
<thead>
<tr>
<th></th>
<th>Monobase</th>
<th>Dibase</th>
<th>Tribase</th>
</tr>
</thead>
<tbody>
<tr>
<td>for ~3% \text{(OH)}_{\text{free}}</td>
<td>-16.47</td>
<td>-27.97</td>
<td>-35.97</td>
</tr>
</tbody>
</table>

Two possible explanations are: (i) that the \( \epsilon \) extinction coefficient giving 3% \( \text{(OH)}_{\text{free}} \) is incorrect and (ii) cross-linking, however improbable for steric reasons, may occur in t-BuOH which would increase the number of \( \text{(LP)}_{\text{free}} \)/weakly bound groups relative to \( \text{(OH)}_{\text{free}} \) groups. This would mean that the simple equilibrium:

\[
(t-\text{BuOH}) \rightleftharpoons (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}}
\]

is inappropriate and a new equilibrium is required;

\[
\begin{align*}
\text{(Bulk)} \Rightarrow & \quad -\text{O}-\text{H} & -\text{O}-\text{H} & + \quad -\text{O}-\text{H} \\
& | & | & | & \text{(OH)}_{\text{free}} \\
& \text{H} & \text{H} & \text{H} & \\
& \text{O} & \text{R} & \text{O} & \text{R}
\end{align*}
\]

(cross-linking structure)

The first possible explanation can be examined by using the NMR/IR correlation (Figure 8.20) to calculate the \% \( \text{(OH)}_{\text{free}} \) in t-BuOH, using equation (3).

\[
\delta(t-\text{BuOH}) = \frac{a \nu a + b \nu b + c \nu c}{a + b + c} \quad \ldots \quad (3)
\]

This equation applies to the following species:
\( \delta(t-\text{BuOH}) \) is the weighted mean of \((\text{OH})_{\text{free}}\), \((\text{LP})_{\text{free}}\) and bulk species.

The terms in the equation are defined thus:

\[
\begin{align*}
\delta(t-\text{BuOH}) &= 3.333 \ \text{ppm from} \ (\text{OH})_{\text{free}} \ \text{[from NMR/IR correlation]} \\
a &= [\ (\text{OH})_{\text{free}}] \\
\nu_a &= \text{taken as reference point, i.e. Zero} \iff a, \nu_a \text{ term disappears} \\
b &= [\ (\text{LP})_{\text{free}}] \\
\nu_b &= \text{position from} \ (\text{OH})_{\text{free}} \\
c &= [\text{bulk}] \\
\nu_c &= 4.5 \ \text{ppm from} \ (\text{OH})_{\text{free}} \ \text{[from NMR/IR correlation]} \\
a + b + c &= \text{moles of t-BuOH}
\end{align*}
\]

Consider the simple equilibrium:

\[
\begin{align*}
\text{(Bulk)} &\rightleftharpoons (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}} \\
(c-a-b) \text{ moles} &
\end{align*}
\]

\[
\begin{align*}
\text{no. moles } [\text{t-BuOH}] &= 1000 \times 0.786 = 10.604 \text{ mols dm}^{-3} \\
\frac{74.12}
\end{align*}
\]

If \[ [\ (\text{OH})_{\text{free}}] = [(\text{LP})_{\text{free}}] \]

\[
\Rightarrow a \text{ moles} = b \text{ moles}
\]

\[
\Rightarrow \ [\text{bulk}] = c = (10.604 - 2b \text{ moles})
\]

The \( \delta(\text{LP})_{\text{free}} \) ppm shift in t-BuOH is estimated by using the methanol \( \delta(\text{LP})_{\text{free}} \) shift from bulk methanol (+1.4 ppm) obtained by Symons et al. [65], using a methanol NMR/IR correlation plot. By using this MeOH \( \delta(\text{LP})_{\text{free}} \) value from bulk t-BuOH, a shift of 3.1 ppm for \( \delta(\text{LP})_{\text{free}} \) measured from \( \delta(\text{OH})_{\text{free}} \) in t-BuOH is estimated. Thus the \( \delta(\text{OH})_{\text{free}} \) in
t-BuOH can be calculated using equation (3).

\[ 3.333 = 3.1b + 4.5c \]

\[ \frac{10.604}{10.604} \]

substituting \( c = (10.604 - 2b) \)

\[ 3.333 = \frac{3.1b + 4.5(10.604 - 2b)}{10.604} \]

\[ 35.343 = 3.1b + 47.718 - 9b \]

\[ b = 2.062 \text{ mols dm}^{-3} = [(\text{OH})_{\text{free}}] = [(\text{LP})_{\text{free}}] \]

\[ \% (\text{OH})_{\text{free}} = \frac{2.062 \times 100}{10.604} = \text{ca. } 19.5\% \]

Hence if this new estimate for \([(\text{OH})_{\text{free}}]\) in t-BuOH is used to fix a value for \( K \) in equation (2), new theoretical gradients for loss of \([(\text{OH})_{\text{free}}]\) are produced, which tie in extremely well with the experimental results; i.e. DMA, DMF, DMSO were all found to be primarily monobasic and all have a gradient of \(-3\), which fits in with the new theoretical gradients listed below:

<table>
<thead>
<tr>
<th>LN-% (OH)_{free} Gradients</th>
</tr>
</thead>
<tbody>
<tr>
<td>[for (-20% (\text{OH})_{\text{free}})]</td>
</tr>
<tr>
<td>Monobase</td>
</tr>
<tr>
<td>Dibase</td>
</tr>
<tr>
<td>Tribase</td>
</tr>
</tbody>
</table>

Figure 8.22 shows both sets of theoretical gradients calculated using

\(~3\% (\text{OH})_{\text{free}}\) and \(~20\% (\text{OH})_{\text{free}}\).

The cross-linking postulate can also be considered, by using the NMR/IR correlation to calculate the \%(\text{LP})_{free}\) in t-BuOH which would be present if cross-linking did occur.

Consider a new equilibrium, assuming \(3\% (\text{OH})_{\text{free}}\) but a larger \([(\text{LP})_{\text{free}}]\) due to cross-linking.

\[ \text{Bulk} = (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}} \]

\[ (c-a-b) \text{ moles} \quad a \text{ mols} \quad b \text{ mols} \]

\[ \text{[t-BuOH] moles} = 10.604 \text{ mols} \text{ dm}^{-3} \]
FIGURE 8.22
Plot showing theoretical change in \([\text{OH}]\text{free}\) for t-BuOH on adding base at 27°C.

**KEY**
- --- Assuming 20% (OH)\text{free} in t-BuOH
- --- Assuming 3% (OH)\text{free} in t-BuOH

<table>
<thead>
<tr>
<th>Relative Drop in % (OH)\text{free}</th>
<th>Base Molefraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.04</td>
</tr>
<tr>
<td>80</td>
<td>0.02</td>
</tr>
<tr>
<td>60</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

- monobase
- dibase
- tribase
\[ \text{now: } a \neq b \]

\[ [\text{bulk}] = c = (10.604 - 0.318 - b) \]

\[ [\text{bulk}] = c = (10.286 - b) \]

**hence: using equation (3)**

\[
3.333 = \frac{3.1b + 4.5(10.286 - b)}{10.604}
\]

\[
35.346 = 3.1b + 46.29 - 4.5b
\]

\[
b = 7.815 \text{ mols dm}^{-3}
\]

\[
\% [(\text{LP})_{\text{free}}] = \frac{7.815 \times 100}{10.604} = 73.7\%
\]

This result shows that if cross-linking occurred in t-BuOH, then \(~74\%\) \((\text{LP})_{\text{free}}\) would be present, which cannot be the case. Hence it would seem that the \(c\) extinction coefficient is incorrect and that there is \(~20\%\) \((\text{OH})_{\text{free}}\) in t-BuOH at 27°C. This ties in with the sharp peak at ca. 1416 nm, in the \(2\nu_{\text{OH}}\) region, which indicates more \([(\text{OH})_{\text{free}}]\) to be present than \(~3\%\).

### 8.9 CONCLUDING REMARKS

Results imply that when H-bonds are formed, they are on average reasonably strong and that Base---HOCMe\(_3\) bonds are relatively weak. This work has estimated solvation numbers for various solutes in t-BuOH, and has found bases to be primarily monobasic and salts and other alcohols mainly dibasic. NMR results have indicated relative base strengths for anions and bases in t-BuOH. An NMR/IR correlation has been constructed and has proved useful in estimating the \([(\text{OH})_{\text{free}}]\) in t-BuOH, indicating the inert solvent result of ca. 3\% \((\text{OH})_{\text{free}}\) to be too low. An estimate of \(~20\%\) \((\text{OH})_{\text{free}}\) ties in the theoretical and experimental results for loss of \([(\text{OH})_{\text{free}}]\) due to added base.
REFERENCES FOR CHAPTER 8

REFERENCES FOR CHAPTER 8 (Continued)

REFERENCES FOR CHAPTER 8 (Continued)

CHAPTER 9

NMR/IR Study of Aqueous Electrolyte Systems
Many studies have been made on the effect of dissolved electrolytes on the chemical shift of water [1-6]. Rapid proton exchanges occur between the various possible water environments hence a single resonance is observed between 0°C and 100°C, which can be displaced upfield or downfield from the pure water resonance depending on the electrolyte or temperature. The main component species which contribute to the single resonance are bulk water, $(\text{OH})_{\text{free}}$ and $(\text{LP})_{\text{free}}$ groups:

Interpretation of results is difficult when a solute is added, since the contributions made by anionic and cationic hydration, ion-pairing and solvent structure changes are not individually known and the different effects oppose each other hence making the solution shifts small overall [7]. This work attempts to explain solution shifts by using a model which accounts for anionic and cationic hydration and consequent changes in $[(\text{OH})_{\text{free}}]$, $[(\text{LP})_{\text{free}}]$ and $[\text{bulk}]$. The model makes use of an NMR/IR correlation plot to estimate the contributing shifts from Anion---HO and Base---HO species to the observed solution shift.

9.2 PREVIOUS WORK

9.2.1 Anion/Cation Hydration

According to Schoolery and Alder [8] the chemical shift produced by
ions in aqueous solution is the sum of at least two factors; polarisation of water molecules and structure breaking of the water hydrogen bonded network. Frank and Wen [9] discussed proton NMR water shifts in terms of a competing effect between the cation and anion [10]. They argued that the larger the cation the more it behaves as a structure former and the larger the anion the more it behaves as a structure breaker.

Since Frank and Wen [9] introduced the concept of water structure promotion by tetrabutylammonium bromide, aqueous solutions of tetraalkylammonium halides have been extensively studied [4]. Rousselot et al. [11] attempted to clarify the effect of tetraalkylammonium salts on water structure. They found at low temperatures the downfield shift of the water protons increases in the order \( \text{Br}^- < \text{Cl}^- < \text{F}^- \) and \( \text{Me}_4\text{N}^+ < \text{Pr}_4\text{N}^+ < \text{Bu}_4\text{N}^+ \) which is consistent with an increase in water structure promotion, i.e. increased H-bonding when the alkyl chains of the quaternary ammonium salts are lengthened. They state also that at higher temperatures the order remains the same for the anions but is reversed for cations.

Davies, Ormondroyd and Symons [12] attempted to derive absolute shifts for tetraalkylammonium cations in water and stated that the larger chain quaternary ammonium ions exhibit a downfield shift at low temperatures, but the shifts pass through zero and become positive on heating. Salt shifts are additive in ionic contributions and scales of absolute ionic molal shifts were proposed by Symons et al. [13] for methanol and for water [14]. Determination of ion shifts in methanol [13] was based on Taube's discovery [15] of signals from methanol molecules directly bonded to cations at low temperatures. This method is difficult to apply to aqueous solutions, because, to prevent freezing, it is necessary to use high salt concentrations, or to add co-solvents [2,15]. However, for methanolic solutions the cation solvation shell and residual hydroxyl
signals shift equivalently when the salt concentration is varied [16]. In a later study, Symons et al. [3] determined the NMR salt shifts for a range of electrolytes in water at 273 K and 298 K and assigned an absolute shift to the chloride ion. This was used to set up scales of absolute ionic shifts which they discuss in terms of ion-solvent interactions.

Akitt [5] states that the total cationic water shift contains two contributions: a downfield one from the electric field and a smaller upfield one from a structural effect. He estimated the proton shift of hydration water of group I and II cations from a correlation between the downfield shifts of the hydration complexes of some group II, III and IV cations with shift increments calculated to arise from the electric field of the ion. Akitt then estimated anion contributions by comparing the contribution of cationic hydration to molal shifts of salt solutions. Further studies by Akitt [17,18] looked at the effect of electrolytes and temperature on water structure and, in particular, anion effects in aqueous solution.

9.2.2 Models/Solvation Numbers

Symons et al. [19] calculated solvation numbers for halide ions in methanol, by using an estimated position for the anion solvation shell and the anion molal shift of a given halide. Akitt [5] proposes a model for explaining solution shifts, mentioning a contribution from "effectively free water" as one of the factors in his model. These were thought to be produced by anions which he says have a structure breaking effect, reducing H-bonding in the solvent and giving an upfield contribution to the overall shift. A solvation number of six is proposed by Akitt [5] for Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, four for alkali-metal ions and zero for Me$_3$N$^+$ in water. Nakamura et al. [20] determined Mg$^{2+}$ to have a solvation number
of six in methanol. Covington et al. [21] obtained a solvation number of six for Mg$^{2+}$ in acetone, with low water concentration, in agreement with the results of other workers. Taube et al. [15,24] calculated the solvation number to be six in water, aqueous acetone and methanolic acetone solutions by measuring the area under the NMR lines for the resonance assigned to water molecules in the primary solvation shell at low temperatures and comparing the area with bulk solvent. Vogrin et al. [22] deduced total effective hydration numbers for some strong electrolytes from the temperature dependence of proton shifts and calculated a solvation number of three for Li$^+$, six for Mg$^{2+}$ and Ca$^{2+}$. Hindman [7] calculated effective hydration numbers for cations and noted a decrease in solvation number with increasing cation radius. He predicted a zero solvation number for the nitrate anion, and stated that only F$^-$ ion formed a hydrate, all other halides are supposed to break down the water structure, the effect increasing with increasing anionic radius. Hinton et al. [23] studied selective solvation of some cations and anions in water and found the relative degree of cation solvation to be: Al$^{3+}$ > Mg$^{2+}$ > Li$^+$, which correlates with Akitt's work [5], with expectation. Separate resonances have been observed for protons in the bulk solvent and in the cationic hydration complexes [2,25] of concentrated solutions of some group II, III and IV electrolytes, at low temperatures, and the cationic hydration numbers have been estimated. Stockton et al. [1] measured the hydroxyl proton NMR shifts for 1:1 complexes in methyl cyanide of some diamagnetic cations with various hydroxylic substrates including water and methanol. Their results follow a trend appropriate to a simple electrostatic association of the cation with the oxygen of the substrate. They proposed a model for accounting for molal shifts of small cations in water and methanol and calculated a solvation number near six.
for the cations in water. Stockton et al. [1] postulated that when ions are added to a hydroxylic solvent, those solvent molecules which interact with the ions undergo a change of state characterised by two effects; partial desolvation and polarisation by the ion.

Recently, the $^1$H NMR spectrum of ice has been studied. The first recording of the proton anisotropic chemical shift spectra of a single crystal of hexagonal ice has been recorded by Rhim et al. [26] who state that the isotropic shift is $-3 \pm 0.5$ ppm with respect to water at room temperature.

9.2.3 Fundamental IR Studies

Saumagne et al. [27] and Glew [28] observed a correlation between the symmetric and asymmetric OH stretching frequencies for water, symmetrically bonded to a H-bond acceptor. Later, Saumagne et al. compared these results with those for water singly bonded to one such acceptor molecule [29]. There is a good linear relationship between $\nu_{\text{symmetric}}$ and $\nu_{\text{asymmetric}}$ but the slope of the line is different. Bellamy et al. [30] studied the fundamental IR spectra of salt hydrates in HOD and H$_2$O. Their results correlate well with those reported by Saumagne for water symmetrically bonded to a range of H-bonded acceptors.

There have been a number of other IR studies made on water-ion interactions in aprotic solvents [31]. For example, Glew and Rath [32] list fundamental symmetric and asymmetric stretching bands for water dissolved in some solvents. From their values of $\nu_1$ and $\nu_3$, a mean value for $\Delta\nu$ can be calculated for various bases which we have added to the $^1$H ppm/\cm$^{-1}$ correlation plot obtained in this work. Holmes, Kivelson and Drinkard [33] also list stretching frequencies for water dissolved in various solvents and NMR chemical shifts of water protons in various solvents. Mohr, Wilk and Barrow [34], found from infra-red studies on
water in various bases in CCl₄ solution, that at high base concentration, 2:1 complexes could also be detected. These literature values for $\Delta \nu_{\text{ppm}}$ and $\Delta \nu_{\text{cm}^{-1}}$ hydroxyl shifts are used in this work to help define the slope of the $\nu_{\text{ppm}}/\nu_{\text{cm}^{-1}}$ correlation plot.

9.3 EXPERIMENTAL

9.3.1 Recording Spectra

All the $^1$H NMR spectra reported in this work have been recorded on a Jeol PS 100 instrument operating at 100 MHz. All infra-red measurements were carried out using a Perkin-Elmer 580 instrument. The details of both these instruments are documented in Chapter 2. The calibration of the sweep width on the Jeol PS 100 recorder chart was checked on each spectrum by means of electronically produced sidebands of TMS used as reference. Hence observed chemical shifts could be corrected for inaccuracies arising from this source, ensuring that shifts could be accurately measured to ±0.3 Hz.

In this work HOD (10% H₂O in D₂O) solutions are used rather than H₂O, which allows a higher amplitude on the instrument to be used producing a better resolution of the signals. It was found that HOD solutions produced the same shifts as water solutions at 25°C, in this work.

9.3.2 Materials

All materials used were of the highest Analar grade available. Water was purified by deionisation followed by passage through a Millipore "Milli-Q" system. Solvents were purified by fractional distillation over CaH₂ and dried over CaH₂ or molecular sieves. Salts were purchased from Aldrich Chemical Co. Limited and Fluorochem Limited, in most cases at >98% purity. They were dried at an appropriate temperature in vacuo for 48 hours before use and stored in a dessicator over silica gel. All
samples were prepared by weight and concentrations of the various components calculated in terms of molality or molefraction.

9.3.3 Referencing in NMR

All chemical shifts in this work are measured from the resonance position of a suitable chemical reference with a fixed resonant frequency. The most commonly used reference material is tetramethylsilane, TMS, which gives a sharp single peak at higher field than most substances. In this aqueous work, TMS could not be used since it is immiscible in water, hence 3(trimethylsilyl)-propanesulfonic acid sodium salt was used instead, in low concentration (<1%) dissolved in the aqueous solution being studied, and is assumed to be non-interacting. The peak position of this substance is taken arbitrarily as being at 0 ppm, as is usually the case for TMS. The reference is said to be 'internal'.

It has been shown that using an unsuitable internal reference can effect the observed shifts [35]. Because of this, some workers choose to use external referencing, whereby the reference material is usually contained in a central capillary or in the outer annulus of a coaxial cell. The sample and reference experience different fields hence bulk susceptibility corrections are necessary [36,37], which enables the actual separation between sample and reference signals. However, using an external reference is more complicated than internal referencing and susceptibility corrections can be several orders of magnitude greater than the observed chemical shift thus leading to inaccuracies.

9.3.4 Side-band Technique

A 540 Hz sweep width is used initially to examine the pure HOD system, (10% H_2O in D_2O v/v). The hydroxyl resonance is resolved relative to TMS as zero. The next stage involves generating a side-band of TMS at 400 Hz
downfield of the reference TMS signal centred at 0 ppm:

The 400 Hz TMS side-band is ca. 73 Hz upfield of the observed HOD hydroxyl resonance which appears at ca. 473 Hz downfield of TMS at 25°C. The field offset control is next adjusted to move the 400 Hz side-band upfield and centred on 0 ppm on the chart paper. Once this has been achieved, the sweep width is reduced from 540 Hz to 108 Hz for more accurate measurement of small shifts in the hydroxyl resonance due to added solutes. The 400 Hz TMS side-band is then recorded along with the hydroxyl resonance signal and another TMS side-band at ca. 500 Hz downfield of TMS generated to calibrate the spectrum:

The total sweep width now becomes 100 Hz and can be reduced further by suitable adjustment of the TMS side-band resonant frequencies, allowing for an even greater degree of accuracy. Also any change in field strength is reflected in the distance between the two side-bands.

All samples were recorded consecutively as accurately and efficiently as possible to reduce errors due to field change or temperature fluctuations, i.e. each sample was allowed 10 minutes to equilibrate with the thermostatically controlled temperature in the sample compartment between the magnets, before being recorded. The hydroxyl resonance was monitored
over a range of solute concentrations up to [1 molal].

9.3.5 Referencing in IR Studies

The Infra-red work was primarily aimed at determining the limiting shift for the fundamental, $\nu_{OH}$, stretch of HOD (<4% H$_2$O in D$_2$O V/V) at 25°C for a range of added solutes. The fundamental spectra were recorded using a variable vertical expansion and a horizontal expansion of $\times 5$.

The broad $\nu_{OH}$ spectra were measured as accurately as possible, for shifts due to added salts or bases, by taking several half-band width measurements and calculating the average shift position. The reference used in these studies was D$_2$O containing the same concentration of solute as used in the sample to remove absorption bands which might arise from solute/solvent interaction.

9.4 RESULTS AND DISCUSSION

The observed hydroxyl resonance signal of HOD is a fast-averaged singlet of several contributing species, primarily, in terms of our current theories; (OH)$_{free}$, (LP)$_{free}$ and bulk hydrogen bonds in pure water. On adding a salt or base, other contributing species have now to be considered, which produces an observed shift in the hydroxyl resonance position:

\[
\begin{align*}
\delta(\text{bulk H-bonds}) & \quad \delta(\text{LP})_{free} \quad \delta(\text{OH})_{free} \\
\delta(\text{B}---\text{HO}) & \quad \delta(\text{HOD})_{observed} \quad \text{Upfield shift}
\end{align*}
\]
Usually an upfield shift is observed when a salt is added or a weak base. Strong bases, i.e. DMSO, DMA show a negligible shift or a slight downfield shift. These shifts are discussed later in this work. The model now proposed to account for the observed shift in the hydroxyl resonance of water when solutes are added, is represented by the following equation:

\[
\nu_S \times \text{Bulk H}_2\text{O} = \nu^- S^- + \nu^+ S^+ + \nu_{\text{OH}_f}[\delta(\text{OH}_f)] + \nu_{\text{LP}_f}[\delta(\text{LP}_f)] + \nu_{\text{bulk}}[\delta(\text{Bulk})]
\]

where:

- \(\nu_S\) = Shift of the water hydroxyl resonance at 1 Molal solute concentration, measured from pure water resonance position at 25°C.
- \(\text{Bulk H}_2\text{O}\) = Concentration of \([O-H]\) bonds in terms of molality i.e. \((1000/18) \times 2 = 111.11\) molal.
- \(\nu^-\) = Anion shift in ppm or Base shift in ppm from \(\delta(\text{H}_2\text{O})\) observed.
- \(S^-\) = Anion solvation number in water at 25°C.
- \(\nu^+\) = Cation shift in ppm from \(\delta(\text{H}_2\text{O})\) observed.
- \(S^+\) = Number of lone-pairs scavenged by the cation in water at 25°C.
- \(\nu_{\text{OH}_f}\) = \((\text{OH})\) free shift in ppm from \(\delta(\text{H}_2\text{O})\) observed at 25°C.
- \([\delta(\text{OH}_f)]\) = Change in concentration of \((\text{OH})\) free groups at 1 molal solute concentration, measured relative to the original concentration of \([\text{(OH) free}]\) in pure water at 25°C.
- \(\nu_{\text{LP}_f}\) = \((\text{LP})\) free shift in ppm from \(\delta(\text{H}_2\text{O})\) observed at 25°C.
- \([\delta(\text{LP}_f)]\) = Change in concentration of \((\text{LP})\) free groups at 1 molal solute concentration, measured relative to the original concentration of \([\text{(LP) free}]\) in pure water at 25°C.
- \(\nu_{\text{bulk}}\) = Bulk H-bonds shift in ppm from \(\delta(\text{H}_2\text{O})\) observed at 25°C.
- \([\delta(\text{Bulk})]\) = Change in concentration of bulk H-bonds at 1 molal solute concentration measured relative to the original concentration of \([\text{Bulk H-bonds}]\) in pure water at 25°C, usually equal to the base solvation number.
Thus: (i) $V_{OH_f} \cdot [\delta (OH)_f] = \text{shift contribution of (OH)$_{\text{free}}$ groups}$
(ii) $V_{LP_f} \cdot [\delta (LP)_f] = \text{shift contribution of (LP)$_{\text{free}}$ groups}$
(iii) $V_{bulk} \cdot [\delta (bulk)] = \text{shift contribution of bulk H-bonds}$
(iv) $V^{-}.S^{-} = \text{shift contribution of Anions/Bases}$
(v) $V^{+}.S^{+} = \text{shift contribution of cations}$

9.4.1 Changes in $[(OH)_{\text{free}}]$ due to added solute

It is assumed (generally found to be justified for dilute aqueous solutions) that water brings out the maximum basicity, so that for reactions such as:

$$B_i + (OH)_{\text{free}} \rightleftharpoons B_i - HO$$

we assume $[B_i] \rightarrow \text{zero}$. Then for a monobase ($B_i$), at $[B_i] = \beta$, $\beta$ OH groups are scavenged. For an n-base ($B_n$), at $[B_n] = \beta$, $n\beta$ OH groups are scavenged. For a hypothetical mono-acidic "acid" $A_i$, at $[A_i] = \beta$, one LP$_{\text{free}}$ is scavenged and for $A_n$, $n\beta$ LP$_{\text{free}}$ groups are scavenged. For any salt $A_n^+ B_m^- \text{ (where n and m = solvation numbers)}$, $n$ LP$_{\text{free}}$ and $m$ OH$_{\text{free}}$ groups react.

The hydroxyl resonance shift on adding a salt is due to four contributing factors; cation solvation, anion solvation, change in [bulk H-bonds] and change in $[(OH)_{\text{free}}]$, $[(LP)_{\text{free}}]$ contribution. NMR 'sees' the weighted average of these species. An allowance has to be made for a change in $[(OH)_{\text{free}}]$ and $[(LP)_{\text{free}}]$ concentration on adding a solute. This can be expressed as follows, regarding the model postulated to explain solution shifts:

$$V_{OH_f} \cdot [\delta (OH)_{\text{free}}] = \frac{\text{Original } [(OH)_f] - \text{New } [(OH)_f]}{\text{Original } [(OH)_f]} \times \text{Original } [(OH)_f] \times V_{OH_f}$$

\[ \therefore V_{OH_{\text{free}}} \cdot [\delta (OH)_{\text{free}}] = [(OH)_{\text{free}} \text{ in pure water} - \text{New } [(OH)_{\text{free}}]].V_{OH_f} \]

This represents the (OH)$_{\text{free}}$ contribution to the observed salt shift. A neutral salt has a relatively minor effect on the (OH)$_{\text{free}}$, (LP)$_{\text{free}}$ shift.
contribution to the overall observed salt shift. By a 'neutral' salt, is meant the fact that the cation and anion affect the [(LP)\text{free}] and [(OH)\text{free}] respectively to an equal extent, i.e. they both have the same solvation numbers in water. However, a 'neutral' salt will affect the bulk contribution to the observed shift, since (OH)\text{free} groups are scavenged by anions and (LP)\text{free} groups scavenged by cations, hence bulk water concentration decreases to accommodate this effect. The bulk term is considered later.

9.4.2 Aqueous Anion/Cation Solvation: Basic Theory

(i) Anion Solvation

This occurs via a one proton interaction with the anion:

(ii) Cation Solvation

Cations solvate in two different ways in water:

A) A bond which removes both LP's from bonding to water.

B) Bonds via one lone-pair.

When 'B' type occurs, (OH)\text{free} is produced by breaking α bonds. A cation
can solvate by either 'A' or 'B'; for example, Na⁺ in water can have 6 water molecules around it, i.e. a solvation number of six, but it can be "scavenging" up to 12 lone-pairs. Hence in the 'model' postulated for explaining aqueous salt shifts the S⁻ term is the anion solvation number, since anions solvate only via a 1:1 interaction with water molecules, however the S⁺ term is the number of (LP)\text{free} groups scavenged by the cation and not necessarily the cation solvation number. Cations are probably solvated via a balance between 'A' and 'B';

**Example:**

![Diagram](image)

It depends on the charge/radius ratio. 'A' is probably favoured by the high charge and small radius. The NMR cation shift, v⁺, is the average of both these different ways of solvation.

In methanol there is no [(OH)\text{free}], which simplifies the model used to explain methanolic salt shifts. Also by using tetraalkylammonium salts and assuming negligible cation solvation, the v⁺.S⁺ term can be neglected. Adding RₙN⁺X⁻ salts to water results in loss of [(OH)\text{free}] because of strong anion solvation, and this fact, previously ignored, must be taken into consideration. Also RₙN⁺ cations probably undergo solvation to some extent, an alternative would be to use Mg²⁺ which has a solvation number of six, however Mg²⁺ solvates via one or two lone-pairs. Hence Mg²⁺ has a variable coordination number and therefore cannot be used as a standard.

-328-
To a first approximation, these residual protons can be considered as "bulk" protons. The two weak H-bonds counter-balance the strong H-bond, overall the net change in H-bonding being thought to be small.
The lone-pair term in the model, incorporates the modified proton. Again, however, we expect strong "compensation", so the overall effect may be small.

9.4.3 $\Delta \nu \text{ cm}^{-1}/\Delta \nu \text{ ppm}$ Correlation

As discussed previously, the water hydroxyl resonance shift is a fast time-average to which several species contribute. The $\Delta \nu \text{ cm}^{-1}/\Delta \nu \text{ ppm}$ plot (Figures 9.1 and 9.2) allows NMR parameters to be estimated for these species. Such a plot has already been obtained for methanolic systems [38], which is used to obtain NMR shifts for species whose infra-red shift is known, but for which no NMR shift can be obtained. In aqueous systems there is the formation of both 2:1 and 1:1 complexes which complicates the correlation. In the case of strong acceptors the 2:1 complex is probably present at relatively low water concentrations. Because an average NMR shift is observed, there is a problem of determining how much of each complex is present and their individual chemical shifts. The limiting shift observed for water is probably that of the 2:1 complex, except for very weak bases. Fundamental IR bands can be assigned to both 1:1 and 2:1 complexes for most bases. The 1:1 complex is usually characterised by bands assigned to bonded and non-bonded O-H oscillators, however adding further base results in a loss of the Base---HOH species contribution to the observed solution shift.

The slope of Figure 9.1 is determined by taking the best straight line fit through the (OH)$_{\text{free}}$, ice 1h points and the added data points for 2:1 B----H---O---H----B complexes, using Thomas' NMR data [39] and fundamental IR data from References [29,32-34]. Figure 9.2 uses the same slope as Figure 9.1 for comparative reasons since both plots use different NMR data. Preference is given to Thomas' NMR data (Figure 9.1), since it was obtained using a 100 MHz instrument as opposed to a
FIGURE 9.1

$\Delta \nu'$ ppm vs $\Delta \nu$ cm$^{-1}$ plot for dilute H$_2$O in various bases using $^1$H NMR data from V. K. Thomas [39] and IR data from references [29, 32, 33, 34].

-331-
FIGURE 9.2

$\Delta \nu'$ ppm vs $\Delta \nu$ cm$^{-1}$ plot for dilute H$_2$O in various bases using $^1$H NMR data from Holmes, Kivelson and Drinkard [33] and fundamental IR data from references [29,32,33,34].

- MeNO$_2$
- Dioxan
- MeCN
- Acetone

- MeNO$_2$
- P-Dioxan
- DMSO
- THF
- CCl$_4$

- MeNO$_2$
- MeCN
- P-Dioxan
- Acetone

- MeNO$_2$
- MeCN
- Dioxan
- Acetone

- (OH)$_{free}$

- H$_2$O

Ice 1h [26]
40 MHz instrument used by Holmes, Kivelson and Drinkard [33].

The respective IR/NMR shifts for each base are measured relative to dilute water in CCl₄, taken as being the limiting (OH)ₙ疁 value. The νₒH IR shifts are taken from averaged ν₁ and ν₃ water peaks for 2:1 complexes, giving Δν cm⁻¹ measured from (OH)ₙ疁. Table 1 contains the NMR/IR parameters for dilute water in bases used to help define the slope in Figures 9.1 and 9.2. The Ice 1h NMR position w.r.t. water at room temperature was estimated at -3 ppm ± 0.5 by Rhim et al. [26]. The Ice IR position was determined at 150 cm⁻¹ to low frequency from water by Glew et al. [32]. A shift of 3.75 ppm for (OH)ₙ疁 upfield from water, was determined by Holmes et al. [33]. The (OH)ₙ疁 IR shift from water has been determined by Glew et al. [32] and Saumagne [29] to be 250 cm⁻¹ to higher frequency.

**TABLE 1**

Frequencies (cm⁻¹) of the OH stretching mode absorption bands of the association complexes formed between dilute water and various bases [32].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ν₃</th>
<th>ν₁</th>
<th>Δν cm⁻¹</th>
<th>Δνₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>3705</td>
<td>3613</td>
<td>3659</td>
<td>0</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>3663</td>
<td>3579</td>
<td>3621</td>
<td>38</td>
</tr>
<tr>
<td>1,4 Dioxane</td>
<td>3580</td>
<td>3509</td>
<td>3544.5</td>
<td>114.5</td>
</tr>
<tr>
<td>DMSO</td>
<td>3490</td>
<td>3450</td>
<td>3470</td>
<td>189</td>
</tr>
<tr>
<td>Ice</td>
<td>3300</td>
<td>3220</td>
<td>3260</td>
<td>399</td>
</tr>
</tbody>
</table>

Infrared shifts Δνₛ (cm⁻¹) of the OH stretching mode absorption bands of the association complexes formed between dilute water in various bases measured relative to H₂O in CCl₄ [33].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Δνₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>0</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>38</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>75</td>
</tr>
<tr>
<td>Acetone</td>
<td>87</td>
</tr>
<tr>
<td>p-Dioxane</td>
<td>113</td>
</tr>
<tr>
<td>DMSO</td>
<td>194</td>
</tr>
</tbody>
</table>
TABLE 1 (Continued)

Frequencies (cm⁻¹) of the OH stretching mode absorption bands of the association complexes formed between dilute water and various bases in CCl₄ solution [34].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ν₂</th>
<th>ν₁</th>
<th>Δν cm⁻¹</th>
<th>Δνs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄ [32]</td>
<td>3705</td>
<td>3613</td>
<td>3659</td>
<td>0</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>3670</td>
<td>3580</td>
<td>3625</td>
<td>34</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>3640</td>
<td>3545</td>
<td>3592.5</td>
<td>66.5</td>
</tr>
<tr>
<td>Acetone</td>
<td>3610</td>
<td>3530</td>
<td>3570</td>
<td>89</td>
</tr>
<tr>
<td>Dioxane</td>
<td>3585</td>
<td>3525</td>
<td>3555</td>
<td>104</td>
</tr>
<tr>
<td>DMF</td>
<td>3550</td>
<td>3490</td>
<td>3520</td>
<td>139</td>
</tr>
</tbody>
</table>

Frequencies (cm⁻¹) of the OH stretching mode absorption bands of the association complexes formed between water and various bases [29].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ν₂</th>
<th>ν₁</th>
<th>Δν cm⁻¹</th>
<th>Δνs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>3708</td>
<td>3613</td>
<td>3660.5</td>
<td>0</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>3667</td>
<td>3580</td>
<td>3623.5</td>
<td>37</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>3625</td>
<td>3540</td>
<td>3582.5</td>
<td>78</td>
</tr>
<tr>
<td>Acetone</td>
<td>3615</td>
<td>3535</td>
<td>3575</td>
<td>85.5</td>
</tr>
<tr>
<td>Dioxane</td>
<td>3583</td>
<td>3512</td>
<td>3547.5</td>
<td>113</td>
</tr>
</tbody>
</table>

Proton Magnetic Resonance chemical shifts measured relative to pure water, for H₂O dissolved in various bases [33].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ppm</th>
<th>Δ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>3.75</td>
<td>0</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>2.66</td>
<td>-1.09</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>2.95</td>
<td>-0.8</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.08</td>
<td>-1.67</td>
</tr>
<tr>
<td>Dioxane</td>
<td>2.20</td>
<td>-1.55</td>
</tr>
<tr>
<td>DMSO</td>
<td>1.26</td>
<td>-2.49</td>
</tr>
<tr>
<td>THF</td>
<td>2.16</td>
<td>-1.59</td>
</tr>
</tbody>
</table>

Proton Magnetic Resonance chemical shifts measured relative to water diluted in CCl₄, for dilute H₂O on addition of various bases [39].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Δ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>0</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>-0.9</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>-1.42</td>
</tr>
<tr>
<td>Acetone</td>
<td>-1.77</td>
</tr>
<tr>
<td>DMF</td>
<td>-2.35</td>
</tr>
<tr>
<td>DMSO</td>
<td>-2.89</td>
</tr>
</tbody>
</table>
It is noticeable that the observed $\delta(H_2O)$ position does not lie on the line in Figures 9.1 and 9.2. The $\delta(H_2O)$ position lies upfield off the line, which is attributed to the concentration of (OH)$_{free}$ present in water. The (OH)$_{free}$ groups have a very large NMR shift from $\delta(H_2O)_{observed}$, i.e. +3.75 ppm upfield. This has a significant effect on the water peak position by moving it ca. +0.57 ppm further upfield than if there were no [(OH)$_{free}$] in water (see Figure 9.1). In the case of methanol, the $\delta(MeOH)$ peak position lies on the line since MeOH contains no (OH)$_{free}$.

9.4.4 Experimental Results

Table 2 lists molal $^1H$ NMR solution shifts for various bases in water at 25°C and $\nu_{OH}$ IR limiting shifts for bases in water. By limiting IR shift is meant the shift at a sufficiently high solute concentration such that B—HOH species predominate. The shifts are measured from pure water position.

**Example**

![Diagram showing limiting shift and pure water (Bulk)](image)

Limiting $\nu_{OH}$ base shift in water.

Shifts for tetraalkylammonium salts and metal salts are also included in Table 2.
TABLE 2

<table>
<thead>
<tr>
<th>Solute</th>
<th>Molal $^1H$ NMR shift (ppm) from $\delta(H_2O)_{obs}$ (298 K)</th>
<th>Limiting $\nu_{OH}$ cm$^{-1}$ shift from bulk H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>-0.01</td>
<td>2</td>
</tr>
<tr>
<td>DMA</td>
<td>-0.01</td>
<td>6</td>
</tr>
<tr>
<td>Acetone</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>Et$_4$NCl</td>
<td>+0.035</td>
<td>0</td>
</tr>
<tr>
<td>Et$_4$NBr</td>
<td>+0.05</td>
<td>17</td>
</tr>
<tr>
<td>Et$_4$NI</td>
<td>+0.08</td>
<td>38</td>
</tr>
<tr>
<td>Et$_4$NOCN</td>
<td>+0.01</td>
<td>8</td>
</tr>
<tr>
<td>Et$_4$NOCN</td>
<td>+0.015</td>
<td>10</td>
</tr>
<tr>
<td>NaCl</td>
<td>+0.11</td>
<td>-</td>
</tr>
<tr>
<td>NaI</td>
<td>+0.17</td>
<td>-</td>
</tr>
<tr>
<td>NaClO$_4$</td>
<td>+0.15</td>
<td>-</td>
</tr>
</tbody>
</table>

Literature Values [12] Ref. [40]

<table>
<thead>
<tr>
<th>Solute</th>
<th>Molal $^1H$ NMR shift (ppm) from $\delta(H_2O)_{obs}$ (298 K)</th>
<th>Limiting $\nu_{OH}$ cm$^{-1}$ shift from bulk H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_4$NCl</td>
<td>+0.038</td>
<td>0</td>
</tr>
<tr>
<td>Et$_4$NBr</td>
<td>+0.071</td>
<td>15</td>
</tr>
<tr>
<td>Et$_4$NI</td>
<td>+0.108</td>
<td>30</td>
</tr>
<tr>
<td>NaCl</td>
<td>+0.096</td>
<td>-</td>
</tr>
<tr>
<td>NaI</td>
<td>+0.175</td>
<td>-</td>
</tr>
<tr>
<td>NaClO$_4$</td>
<td>+0.14</td>
<td>40</td>
</tr>
</tbody>
</table>

Figures 9.3–9.7 show the plots for the experimental results, showing the molal NMR solution shifts and limiting IR base and salt shifts in water. The correlation plot (Figure 9.1) is constructed using IR/NMR data for 2:1 complexes, i.e. B—H—O—H—B. The experimental limiting IR shifts are for (1:1) B—H—O—H complexes. However, there should not be too much difference between these two species shifts, hence the correlation plot can be used to convert B---HOH IR limiting shifts into NMR shifts. Strauss [40] was able to resolve the fundamental water peak into its component features when a base is added, by using low temperature. The fundamental water peak is broad and featureless at room temperature. The results of Strauss [40] show IR shifts for individually H-bonded species, i.e. B---HOH tie in well with room temperature results obtained in this work, indicating we are valid in using these room temperature $\nu_{OH}$ shifts to obtain NMR shifts for individual B---HOH species by using.
FIGURE 9.3
Effect of bases on the hydroxyl resonance of HOD. Temperature = 25°C ± 0.1
FIGURE 9.4
Effect of tetraalkylammonium salts on the hydroxyl resonance of HOD.
Temperature = 25°C ± 0.1
FIGURE 9.5
Effect of metal salts on the hydroxyl resonance of HOOH.
Temperature = 25°C ± 0.1
FIGURE 9.6
Effect of bases on $v_{OH}$ of HOD.
Temperature = $25^\circ C \pm 0.1$

![Graph showing the effect of bases on $v_{OH}$ of HOD](image)

- Acetone
- DMA
- DMSO

Higher $\gamma_{cm^{-1}}$

$H_2O_{obs}$ vs Base Molality
FIGURE 9.7
Effect of tetraalkylammonium salts on vOH of HDO.
Temperature = 25°C ± 0.1
9.4.5 Calculation of $\delta(LP)_{\text{free}}$ and $\delta(\text{bulk})$ values

It is possible to calculate a value for the $\delta(LP)_{\text{free}}$ position relative to $\delta(H_2O)$ observed by using the correlation plot (Figure 9.1), in liaison with the model proposed in Section 9.4.1. The $\delta(LP)_{\text{free}}$ value from $\delta(H_2O)$ can be calculated using the model, in the case of adding a base to water. Both the $\delta(\text{OH})_{\text{free}}$ and $\delta(\text{bulk})$ values w.r.t. $\delta(H_2O)$ can be estimated from the correlation plot. The molal solution shift is known and the B---HOH NMR shift can be measured off the correlation plot by taking the point on the line where $\delta(H_2O)$ would be if no (OH)$_{\text{free}}$ were present and measuring the limiting IR B---HOH shift from this point. The limiting IR base shift is usually to higher frequency w.r.t. bulk H$_2$O, which provides an upfield NMR shift for B---HOH on the plot.

Example:

Converting $\nu_{\text{OH}}$ IR limiting B---HOH shifts into NMR B---HOH shifts, using the NMR/IR correlation plot.

The change in [(OH)$_{\text{free}}$] and [(LP)$_{\text{free}}$] terms in the model, on adding base, are obtained from theoretical considerations for loss of [(OH)$_{\text{free}}$] discussed in Chapter 4. Table 3 lists the theoretical loss of [(OH)$_{\text{free}}$]
in water on adding [base] at 1 molal, for varying basicities.

**TABLE 3**

<table>
<thead>
<tr>
<th>Basicity</th>
<th>% (OH) free</th>
<th>% (IP) free</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>1</td>
<td>7.07</td>
<td>8.87</td>
</tr>
<tr>
<td>2</td>
<td>6.31</td>
<td>9.91</td>
</tr>
<tr>
<td>3</td>
<td>5.63</td>
<td>11.03</td>
</tr>
<tr>
<td>4</td>
<td>5.04</td>
<td>12.24</td>
</tr>
<tr>
<td>5</td>
<td>4.52</td>
<td>13.52</td>
</tr>
<tr>
<td>6</td>
<td>4.06</td>
<td>14.86</td>
</tr>
</tbody>
</table>

The figures in Table 3 assume 8% [(OH) free] in pure water at 25°C. The corresponding increase in [(IP) free] is also listed.

Once the δ(IP) free value w.r.t. water has been calculated, the δ(bulk) shift can be recalculated for the pure water case using the δ(OH) free, δ(IP) free values. This procedure is repeated until fixed values for δ(IP) free and δ(bulk) are converged upon which 'fit' the requirements of both situations, i.e. pure water and water + base.

**Example:**

From the correlation plot, δ(OH) free = 3.75 ppm, δ(bulk) = -0.57 ppm w.r.t. water, hence the δ(IP) free value can be calculated thus:

(i) **Add Base** (e.g. DMSO)

Molal NMR shift = -0.01 ppm

νOH IR shift = 2 cm⁻¹ (equivalent to a 0.05 ppm shift w.r.t. (H₂O) on the correlation plot)

Hence using the proposed model:

\[ \text{111.11 × (-0.01)} = S^- × 0.05 + (3.75 × Δ[OH]) + (δLP × Δ[IP]) + (-Δ[bulk] × -0.57) \]

DMSO is a di-base in water [41], hence S^- = 2 and Δ[bulk] = -2 mols.

Using theoretical data for loss of [(OH) free] due to a di-base at [1 molal]:

\[ Δ[(OH)_{free}] = \text{new} [(OH)_{f}] - \text{original} [(OH)_{f}] \]
\[ \Delta \{ \delta \text{LP}_{\text{free}} \} = (111.11 \times 0.099) - (111.11 \times 0.08) = 2.11 \text{ mols} \]

\[ . \cdot -1.11 = 0.01 + (3.75 \times -1.888) + (\delta \text{LP}_{\text{free}} \times 2.11) + 1.14 \]

\[ \therefore \delta \text{LP}_{\text{free}} = 2.28 \text{ ppm w.r.t. } \delta (H_2O) \]

Now using this \( \delta \text{LP}_{\text{free}} \) value, a value for \( \delta \text{bulk} \) can be re-calculated for the pure water case to compare with the correlation plot \( \delta \text{bulk} \) value, i.e. -0.57 ppm w.r.t. \( \delta (H_2O) \).

(ii) Pure Water Case

Consider the simple equilibrium:

\[
\begin{align*}
(H_2O)_{\text{bound}} & \rightleftharpoons (OH)_{\text{free}} + \text{(LP)_{free}} \\
[H_2O] \times \delta_{\text{bulk}} & \quad [OH] \times 3.75 \quad [\text{LP}] \times 2.28
\end{align*}
\]

\[ . \cdot [111.11 \times 0.84] \times -\delta_{\text{bulk}} = [111.11 \times 0.08] \times 3.75 + [111.11 \times 0.08] \times 2.28 \]

\[ . \cdot 93.33 \times -\delta_{\text{bulk}} = 33.333 + 20.266 \]

\[ \therefore \delta_{\text{bulk}} = -0.57 \text{ ppm w.r.t. } \delta (H_2O) \]

These values for \( \delta \text{LP}_{\text{free}} \) and \( \delta \text{bulk} \) can be checked for other water/base systems using the same convergence method adopted for water/DMSO.

(iii) Add Base i.e. Acetone (assumed di-base)

\[ (111.11 \times 0) = 2 \times 0.35 + (3.75 \times -1.8904) + (\delta \text{LP} \times 2.124) - 2(-0.59) \]

\[ \therefore \delta \text{LP}_{\text{free}} = +2.45 \text{ ppm w.r.t. water} \]

i.e. for acetone/H_2O; \( \delta \text{bulk} = -0.59 \text{ ppm} \) and \( \delta \text{LP}_{\text{free}} = +2.45 \text{ ppm w.r.t. } \delta H_2O \).

(iv) Add Base i.e. DMA (assumed di-base)

\[ (111.11 \times -0.01) = 2 \times 0.1 + (3.75 \times -1.8904) + (\delta \text{LP} \times 2.124) - 2(-0.565) \]

\[ \therefore \delta \text{LP}_{\text{free}} = 2.19 \text{ ppm w.r.t. } \delta H_2O \]
i.e. for DMB/H$_2$O; $\delta_{\text{bulk}} = -0.565$ ppm and $\delta_{\text{LPfree}} = +2.19$ ppm w.r.t. H$_2$O.

Thus the average $\delta_{\text{LPfree}}$ and $\delta_{\text{bulk}}$ values w.r.t. H$_2$O can be taken:

<table>
<thead>
<tr>
<th>Base/H$_2$O System</th>
<th>$\delta_{\text{LPfree}}$</th>
<th>$\delta_{\text{bulk}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>+2.28</td>
<td>-0.57</td>
</tr>
<tr>
<td>Acetone</td>
<td>+2.45</td>
<td>-0.59</td>
</tr>
<tr>
<td>DMA</td>
<td>+2.19</td>
<td>-0.565</td>
</tr>
<tr>
<td><strong>Average value:</strong></td>
<td><strong>+2.3 ppm</strong></td>
<td><strong>-0.575 ppm</strong></td>
</tr>
</tbody>
</table>

The calculated $\delta_{\text{LPfree}}$ value from H$_2$O appears to be reasonable as it comes in between $\delta_{\text{OHfree}}$ and H$_2$O and the average $\delta_{\text{bulk}}$ value, i.e. -0.575 ppm w.r.t. H$_2$O fits well with the correlation plot value.

9.4.6 Calculation of $\%_{\text{OHfree}}$

The observed water resonance is the weighted average of bulk water, [(OH)$_{\text{free}}$] and [(LP)$_{\text{free}}$]. The $\%_{\text{OHfree}}$ in water can be calculated using the data obtained for these species in the previous section.

Using the weighted mean equation:

$$\delta_{\text{H2O}} = \frac{a \cdot \delta_{\text{va}} + b \cdot \delta_{\text{vb}} + c \cdot \delta_{\text{vc}}}{a + b + c}$$

- $a = [(\text{OH})_{\text{free}}]$
- $\delta_{\text{va}} = $ Zero (i.e. take (OH)$_{\text{free}}$ resonance position as zero)
- $b = [(\text{LP})_{\text{free}}]$
- $\delta_{\text{vb}} = -1.443$ ppm from $\delta_{\text{(OH)free}}$
\[ c = [\text{bulk}] \]
\[ \nu_c = -4.325 \text{ ppm from } \delta(\text{OH})_{\text{free}} \]
\[ a + b + c = 111.11 \text{ moles for bulk water} \]
\[ \therefore -3.75 = -1.443b - 4.325c \]
\[ \text{Consider: } \]
\[ \begin{align*}
(\text{H}_2\text{O})_{\text{bound}} & \Rightarrow (\text{OH})_{\text{free}} + (\text{LP})_{\text{free}} \\
111.11 \text{ mols} & \quad a \text{ mols} \quad b \text{ mols} \\
\text{in water} \quad [(\text{OH})_{\text{free}}] & = [(\text{LP})_{\text{free}}] \\
\therefore \quad a & = b \\
\therefore [(\text{H}_2\text{O})_{\text{b}}] = (111.11 - 2b) \\
\therefore \text{substitute } [(\text{H}_2\text{O})_{\text{b}}] = c = (111.11 - 2b) \\
\therefore -3.75 = (-1.443b - 4.325[111.11 - 2b]) / 111.11 \\
\therefore -3.75 = -1.443b - 480.55 + 8.65b \]
\[ \therefore b = 8.8646 \text{ mols} = [\text{OH}_{\text{free}}] = [\text{LP}_{\text{free}}] \]
\[ \therefore \% (\text{OH})_{\text{free}} = 8.8646 \times 100 = 8.86 \% \]

Thus using the values for \( \delta_{\text{bulk}}, \delta(\text{LP})_{\text{free}} \) and \( \delta(\text{OH})_{\text{free}} \) w.r.t. \( \delta(\text{H}_2\text{O}) \), obtained from the correlation plot and by calculation, a value of \( \sim 8\% \) (\( \text{OH} \))_{\text{free}} has been calculated using a simple weighted mean calculation. This result ties in well with the average literature value for estimated \% (\( \text{OH} \))_{\text{free}} in water (see Chapter 3) and adds validity to the slope used on the correlation plot.

If there were no [(\( \text{OH} \))_{\text{free}}] in water the observed \( \delta(\text{H}_2\text{O}) \) resonance position would occur further downfield. Figure 9.8 shows the observed upfield shift in the water hydroxyl resonance when acetone is added as base to water. The linear upfield shift can be extrapolated to zero [base], thus giving the downfield \( \delta(\text{H}_2\text{O}) \) shift when all [(\( \text{OH} \))_{\text{free}}] has been removed. From Figure 9.8 a downfield shift of \( \text{ca.} -9 \text{ Hz} \) would occur for the \( \delta(\text{H}_2\text{O}) \) position if all [(\( \text{OH} \))_{\text{free}}] were removed by base.
FIGURE 9.8
Plot showing the $^1$H NMR hydroxyl shift for HOD on adding acetone at 25°C.
By using a weighted mean calculation it is possible to calculate what the downfield shift in the δ(H₂O) position should be if all the [(OH)\text{\text{free}}] in water is removed, i.e. by base.

$$\delta H₂O = \frac{a va + b vb + c vc}{a + b + c}$$

where:

- $a = [(OH)\text{\text{free}}]$ = Zero (i.e. all removed by Base)
- $b = [(IP)\text{\text{free}}] = 8\% \times 111.11 = 8.888$ mols
- $c = [\text{bulk}] = 84\% \times 111.11 = 93.33$ mols

$a + b + c = [H₂O] = 111.11$ mols

- $va = Zero$ (i.e. taken as reference point)
- $vb = -1.443$ ppm δ(IP)\text{\text{free}} from δ(OH)\text{\text{free}}
- $vc = -4.325$ ppm δ(bulk) from δ(OH)\text{\text{free}}

If all the [(OH)\text{\text{free}}] is scavenged by base, the [(IP)\text{\text{free}}] concentration is approximately doubled.

$$\therefore \delta H₂O \times 111.11 = 2(8.888) \times -1.443 + (93.33 \times -4.325)$$

$$\therefore \delta H₂O = -3.864$$ ppm from δ(OH)\text{\text{free}}

This is equivalent to a downfield shift of -11.38 Hz from the usual δ(H₂O) position, which ties in well with the experimentally extrapolated value, i.e. -9 Hz (Figure 9.3). Thus indicating further that the correlation plot slope is a good one and that 8% (OH)\text{\text{free}} in water is a good estimate.

### 9.4.7 Solvation Numbers

Solvation numbers can be calculated for anions, by using the model described in Section 9.4.1. Values for most of the terms in the model are either known or can be estimated after the analysis of δ(OH)\text{\text{free}}, δ(IP)\text{\text{free}} and δ(bulk) terms in the previous sections. Tetraalkylammonium salts are studied since the large R₄N⁺ cations are thought to undergo negligible solvation relative to the anion. Hence, overall the cation
term \( \nu^+ \cdot S^+ \) in the model is expected to tend to zero contribution to the molal solution shift at 25°C. However, in the limit of the \( R_4N^+ \) cation having a low solvation number, i.e. 1, the \( \nu^+ \cdot S^+ \) term can be accounted for in the model by using individual \( R_4N^+ \) ion shifts (\( \nu^+ \)), determined by Symons et al. [12]. In this section, solvation numbers are determined for anions by both accounting for the \( R_4N^+ \) contribution and also ignoring it, to see if there is any significant difference. A worked example is shown below for the calculation of an anion solvation number using the model:

Consider \( Et_2NBr \) in Water at 25°C

\( ^1H \) NMR molal shift in HOD = 0.05 ppm
\( \nu_{OH} \) shift = 17 cm\(^{-1}\) (\( \equiv 0.25 \) ppm from correlation plot for Br\(^-\))
\( Et_2N^+ \) shift = -0.023 ppm from [12].

\[ (111.1 \times 0.05) = 0.25 \times S^- + (-0.023 \times S^+) + (3.75 \times \Delta[OH]) + (2.3 \times \Delta[LP]) + (-0.575 \times -\Delta[bulk]) \]

In this case, \( Et_2N^+ \) is allowed a solvation number = 1. The final solvation number is arrived at using this model, consequent upon an iterative process whereby the concentrations of \((OH)_{\text{free}}\) and \((LP)_{\text{free}}\) are varied within the range of zero to hexabase. Hence, if \( Et_2NBr \) is assumed to be approximately a hexabase in water, then the theoretical change in \([OH)_{\text{free}}\) and \([LP)_{\text{free}}\) is thus:

\[ \Delta[(OH)_{\text{free}}] = (111.11 \times 0.041) - (111.11 \times 0.08) = -4.333 \text{ mols} \]

\[ \Delta[(LP)_{\text{free}}] = (111.11 \times 0.1486) - (111.11 \times 0.08) = 7.623 \text{ mols} \]

\[ -\Delta[\text{bulk}] \equiv \text{Solvation number of the anion} \]

\[ 5.55 = 0.25 \times S^- - 0.023 + (3.75 \times -4.33) + (2.307 \times 7.623) - S^-(-0.575) \]

\[ \therefore S^- = 5.12 \]
This result ties in well with literature values for halide ion solvation numbers in water (see Chapter 4), which are thought to be hexabasic. The model would seem to be finely tuned to the use of strict parameters and works well using the data available. The same treatment applied to Et₄NI in H₂O, produced a solvation number of 6.3 for I⁻. In the case of Et₄NCl, it proved difficult to establish the ν₀[HCl⁻] IR shift, so in this case a solvation number of 6 was used in the model for Cl⁻, since 6 is a firm number from the literature and the ν₀[H] shift calculated. A value of ν⁻ = -0.14 ppm w.r.t. δ(H₂O) was calculated which ties in with about a 9 cm⁻¹ shift for Cl⁻ obtained from the correlation plot. Listed below in Table 4 are NMR/IR parameters for individual anions:

<table>
<thead>
<tr>
<th>Anion</th>
<th>NMR shift from correlation plot</th>
<th>IR shift relative to H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>-0.14 ppm</td>
<td>ca. 9 cm⁻¹</td>
</tr>
<tr>
<td>Br⁻</td>
<td>0.25 ppm</td>
<td>17</td>
</tr>
<tr>
<td>I⁻</td>
<td>0.65 ppm</td>
<td>38</td>
</tr>
<tr>
<td>OCN⁻</td>
<td>0.15 ppm</td>
<td>8</td>
</tr>
<tr>
<td>CN⁻</td>
<td>0.17 ppm</td>
<td>10</td>
</tr>
</tbody>
</table>

Using the same method a solvation number of ca. 4 was obtained for CN⁻ and OCN⁻ in water. By adopting a similar approach it is possible to estimate metal cation NMR shifts, i.e. ν⁺ terms in the model.

Consider NaCl

\[ ^1H \text{ NMR molal shift in HOD} = 0.11 \text{ ppm} \]
\[ \nu_{0[H]} \text{ Cl}^- \text{ shift} = \approx 9 \text{ cm}^-1 \quad (\equiv -0.14 \text{ ppm on the correlation plot}) \]

\[ 111.11 \times 0.11 = -0.14.S^- + \nu^+.S^+ + (3.75 \times \Delta[OH_f]) + (2.307 \times \Delta[LP_f]) \]
\[ S^- (-0.575) \]

The net acidity of NaCl is estimated at a monoacid (from 3ν₀[H] results), i.e. Na⁺ scavenges 6 or 7 (LP)free groups; Cl⁻ scavenges 6 (OH)free groups.
\[ \Delta[\text{OH}_f] = (111.11 \times 0.0887) - (111.11 \times 0.08) = 0.967 \text{ mols} \]
\[ \Delta[\text{LP}_f] = (111.11 \times 0.0707) - (111.11 \times 0.08) = -1.033 \text{ mols} \]

\[ 12.222 = -0.14 \times 6 + v^+ \cdot 6 + (3.75 \times 0.967) + (2.307 \times -1.033) - S^- (-0.575) \]

**NB:** The bulk term, \( S^- \), is estimated at -12 moles due to \( \text{Na}^+ \) removing 6 \( \text{LP}_{\text{free}} \) and \( \text{Cl}^- 6 \) \( \text{OH}_{\text{free}} \) groups.

\[ 12.222 = -0.84 + v^+ \cdot 6 + 3.626 - 2.383 + 6.9 \]

\[ V_{\text{Na}^+} = 0.81 \text{ ppm w.r.t. } \delta(\text{H}_2\text{O}) \text{ at } 25^\circ\text{C} \]

The same method when applied to \( \text{NaI} \) produced a value of +0.81 ppm for \( V_{\text{Na}^+} \) shift w.r.t. \( \delta(\text{H}_2\text{O}) \). Thus an average value of \( V_{\text{Na}^+} = 0.81 \text{ ppm} \) can be taken. Now that a value for \( V_{\text{Na}^+} \) has been calculated it is possible to calculate a solvation number for \( \text{ClO}_4^- \) using the same procedure as before.

\( \text{NaClO}_4 \)

\[ ^1\text{H NMR molal shift in HOD} = +0.15 \text{ ppm} \]
\[ \text{ClO}_4^- \text{ shift} = 40 \text{ cm}^{-1} \text{ (i.e. 0.65 ppm on the correlation plot)} \]
\[ V_{\text{Na}^+} = +0.81 \]

**NB:** For the purpose of calculating \( \Delta[\text{OH}_f] \) and \( \Delta[\text{LP}_f] \) terms in the model, \( \text{NaClO}_4 \) is estimated to be a di-acid in water, since the \( 3\nu_{\text{OH}} \) work (Chapter 4) showed \( \text{Na}^+ \) to scavenge on average 6 \( \text{LP}_{\text{free}} \) groups and \( \text{ClO}_4^- 4 \) \( \text{OH}_{\text{free}} \) groups.

\[ \Delta[\text{OH}_{\text{free}}] = (111.11 \times 0.099) - (111.11 \times 0.08) = +2.124 \text{ mols} \]
\[ \Delta[\text{LP}_{\text{free}}] = (111.11 \times 0.063) - (111.11 \times 0.08) = -1.889 \text{ mols} \]

\[ 111.11 \times 0.15 = 6 \times 0.81 + 0.65 \times S^- + (3.75 \times 2.12) + (2.307 \times -1.88) - 10(-0.575) \]
Thus the ClO$_4^-$ solvation number is calculated at ca. 3.8 using the model which, regarding the errors involved, ties in well with literature values and the result obtained for ClO$_4^-$ in Chapter 4. Listed in Table 5 are anion solvation numbers calculated in this work, (a) accounting for the R$_n$N$^+$ contribution and (b) neglecting the R$_n$N$^+$ term due to negligible cation solvation.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Solvation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>ca. 6</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>(a) 5.12</td>
</tr>
<tr>
<td></td>
<td>(b) 5.09</td>
</tr>
<tr>
<td>I$^-$</td>
<td>(a) 6.3</td>
</tr>
<tr>
<td></td>
<td>(b) 6.26</td>
</tr>
<tr>
<td>CN$^-$</td>
<td>(a) 4.1</td>
</tr>
<tr>
<td></td>
<td>(b) 4.06</td>
</tr>
<tr>
<td>CN$^-$</td>
<td>(a) 4.0</td>
</tr>
<tr>
<td></td>
<td>(b) 3.95</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>3.8</td>
</tr>
</tbody>
</table>

The figures show that the R$_n$N$^+$ term does not significantly effect the final solvation numbers.

9.5 CONCLUSION

A model has been proposed to explain aqueous solution shifts for salts in water. It accounts for the anion and cation hydration terms in the weighted average observed shift, as well as changes in [(OH)$_{\text{free}}$], [(LP)$_{\text{free}}$] and [bulk] terms. It makes use of a novel IR/NMR correlation plot which can be used to convert $\nu$$_{\text{OH}}$ ion shifts into previously unknown cation and anion NMR shifts w.r.t. $\delta$(H$_2$O) position. The slope used to define the correlation plot is crucial for using the model to calculate ion solvation numbers since to a large extent the slope determines the
δ(bulk) and δ(LP)_{free} shift contributions to the δ(H_2O) weighted average resonance. The δ(OH)_{free} term is known by experiment. Using the slope, values for δ(LP)_{free} and δ(bulk) are estimated, which when applied to the model, give a value of ca. 8% (OH)_{free} in water. This result adds validity to the gradient of the slope, since 8% is a good literature value. Also calculations of solvation numbers reveal reasonable numbers and show the model to be finely tuned, accepting only rigid parameters to give acceptable numbers.
REFERENCES FOR CHAPTER 9

REFERENCES FOR CHAPTER 9 (Continued)

Appendix A
A DIFFERENCE SPECTRA STUDY OF WATER + SALT SYSTEMS

Introduction

Difference spectra were used to study the effects of added salts on the Second Overtone water spectrum. Difference spectra are obtained by placing an aqueous solution in the sample cell and pure water in the reference cell. The imbalance of OH oscillator concentration is corrected using a density correction method. The spectra were recorded to see if trends appeared which are similar to the Second Overtone results in Chapter 3.

Previous Work

Jolicoeur et al. [1] studied the Near-Infrared spectrum of water at various temperatures and in aqueous solutions of organic salts in the Second Overtone region using $\text{H}_2\text{O}$. The spectra were recorded differentially with respect to water by varying the cell pathlength to allow for density changes or the volume occupied by the solutes. Jolicoeur et al. [1] observed the qualitative similarity between the effects of the $\text{Bu}^+\text{N}^+$ ion and that of reducing temperature on the spectrum of water. In a latter study Philip and Jolicoeur [2] interpreted the difference spectra for pure water at various temperatures in terms of an equilibrium between two states for the OH oscillators of the water molecules - non-bonded and bonded. They note that $\text{R}_4\text{N}^+$ ions shift the hydrogen bonding equilibrium in favour of bonded species and discuss results in terms of structure breaking and making abilities of ions.

Experimental

All spectra were recorded on a Perkin-Elmer 340 UV/VIS/NIR spectrophotometer at $25^\circ\text{C} \pm 0.1$, using a 3-minute time scan, $\lambda$ expansion $\times 5$ and a photometric scale of 0.02-0.02. Quartz cells of 1 cm pathlength were
used. Any absorbance due to the cells was recorded into the baseline correction before each series of runs. Spectra were corrected for density changes by calculating the % moles of OH oscillator concentration in each sample and multiplying up the absorbance accordingly, hence allowing for loss of OH concentration by added salt. Samples were made up to 5 ml volumes by adding a weighed amount of salt to a weighed amount of water.

Results

The effect of added electrolytes on the water Second Overtone spectrum at 25°C are shown in Fig. C. Examples of the spectral changes for adding NaClO₄ and Et₄NCl are shown in Figs. A and B. The greatest effect can be seen for NaClO₄ and tetraalkylammonium salts which produce contrasting results. Trends observed on a qualitative scale, show great similarity to results obtained in the Second Overtone HOD study in Chapter 3. However, in this difference study, a change in absorbance as the spectra changes is being observed. Hence as salt is added we are looking at a change of a change and not a true peak. The maxima or minima of the change varies its position throughout the series of systems studied, so results cannot be directly related to those obtained for HOD work. The 3νOH band maximum for HOD occurs at 960 nm, however the apparent peak ranges from 980 nm - 948 nm in this work.
FIGURE A
Second overtone Difference spectra showing the effect of NaClO₄ on 30% of water.
Temperature = 25°C ± 0.1.
Et$_4$NCl molefraction
1. 0.0055
2. 0.0110
3. 0.0165
4. 0.0220
5. 0.0275

FIGURE B
Second Overtone Difference spectra showing the effect of Et$_4$NCl on 3vOH of water.
Temperature = 25°C ± 0.1
FIGURE C
Effect of electrolytes on H$_2$O, Difference Spectra  
Second Overtone.  
Temperature = 25°C ± 0.1
<table>
<thead>
<tr>
<th>Salt</th>
<th>Initial Gradient</th>
<th>Peak maxima (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₄</td>
<td>651</td>
<td>964</td>
</tr>
<tr>
<td>NaI</td>
<td>303</td>
<td>977</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>288</td>
<td>970</td>
</tr>
<tr>
<td>NaBr</td>
<td>124</td>
<td>975</td>
</tr>
<tr>
<td>KI</td>
<td>238</td>
<td>970</td>
</tr>
<tr>
<td>KBr</td>
<td>113</td>
<td>975</td>
</tr>
<tr>
<td>KCl</td>
<td>075</td>
<td>978</td>
</tr>
<tr>
<td>NaCl</td>
<td>051</td>
<td>980</td>
</tr>
<tr>
<td>LiF</td>
<td>012</td>
<td>980</td>
</tr>
<tr>
<td>LiBr</td>
<td>-005</td>
<td>980</td>
</tr>
<tr>
<td>NaF</td>
<td>-103</td>
<td>960 ±10</td>
</tr>
<tr>
<td>LiCl</td>
<td>-133</td>
<td>956</td>
</tr>
<tr>
<td>Me₄NCl</td>
<td>-302</td>
<td>958</td>
</tr>
<tr>
<td>Me₄NBr</td>
<td>-403</td>
<td>958</td>
</tr>
<tr>
<td>Et₄NBr</td>
<td>-872</td>
<td>960</td>
</tr>
<tr>
<td>Bu₄NBr</td>
<td>-925</td>
<td>960</td>
</tr>
<tr>
<td>Et₄NCl</td>
<td>-875</td>
<td>958</td>
</tr>
</tbody>
</table>

A characteristic absorbance at 893 nm which appears in all the $R_n^+N^-X^-$ systems is assigned to CH₃ coupling.

**Concluding Remarks**

A qualitative analysis of the results shows trends for anions and cations which are similar to those obtained in the HOD study in Chapter 3. Regarding group I metal cations, the trend, $Na^+ > K^+ > Li^+$ for relative solvation numbers in water is noted in accordance with HOD results. Likewise the trend for anion solvation numbers for halide ions: $F^- > Cl^- > Br^- > I^-$ correlates well with HOD work. The tetraalkylammonium salts show the characteristic decrease in OH absorption, the cation trend being: $Me_4N^+ > Et_4N^+ > Bu^+_4N^+$ indicating that the relatively smaller $Me_4N^+$ undergoes some solvation whereas it is thought the larger $Et_4N^+$, $Bu^+_4N^+$ undergo negligible solvation.

We have not attempted any qualitative study of these results nor have we derived any solvation numbers therefrom. We consider that the procedure detailed in Chapter 3 using HOD is more satisfactory and gives a more direct indication of the changes involved.
REFERENCES

1971.

Appendix B
SYMOS THEORY FOR ACID SALTS IN WATER

Add acid:

assume Zn moles of (LP)\textsubscript{f} bond to n moles of acid, Z = acidity

at equilibrium:

\[ \text{no. of moles} = 2n(H_2O) + n(OH) + n(LP) + n(A) + Zn(LP-A) \]

at start

\[ n_T \text{ moles of water} + n(A) \text{ moles of acid} \]

\[ \therefore \text{total no. of moles} \quad n_s = n_T + n(A) \]

at equilibrium:

\[ n_s = 2n(H_2O) + n(OH) + n(LP) + n(A) + Zn(LP-A) \]

\[ n(LP) = n(OH) + Zn(LP-A) \]

\[ \therefore n_s = 2n(H_2O) + 2n(OH) + n(A) \]

\[ K = \frac{X(OH)}{n_s} \left[ \frac{n(OH) - Zn(LP-A)}{n - 2n(OH) - n(A)} \right] \]

\[ K = \frac{X(OH)}{1 - 2X(OH) - X(A)} \]

\[ K = \frac{a(a - nb)}{1 - 2a - b} \]

where:

\[ a = X(OH) \]

\[ b = X(LP-A) \]

\[ n = Z \]
BLANDAMER'S THEORY FOR ACID SALTS IN WATER

Add acid:

 assume each mole of acid bonds to \( Z \) moles of \((LP)f\), \( Z = \) acidity.

at equilibrium:

\[
\text{no. of moles} = 2\tilde{n}(H_2O)b + \tilde{n}(OH)f + \tilde{n}(LP)f + \tilde{n}[A(LP)]
\]

at start \( n_i \) moles of water + \( n(A) \) moles of acid

\[
\therefore \text{at equilibrium} \quad n_s = 2\tilde{n}(H_2O)b + \tilde{n}(OH)f + \tilde{n}(LP)f + \tilde{n}[A(LP)]
\]
\[
\tilde{n}(LP)f = \tilde{n}(OH)f - 2\tilde{n}[A(LP)]
\]
\[
\therefore n_s = 2\tilde{n}(H_2O)b + \tilde{n}(OH)f + \tilde{n}(OH)f - 2\tilde{n}[A(LP)] + \tilde{n}[A(LP)]
\]
\[
\therefore n_s = 2\tilde{n}(H_2O)b + 2\tilde{n}(OH)f + (1-Z)\tilde{n}[A(LP)]
\]
\[
\therefore 2\tilde{n}(H_2O)b = n_s - 2\tilde{n}(OH)f - (1-Z)\tilde{n}[A(LP)]
\]
\[
\therefore K = \tilde{x}(OH)f \left[ \frac{\tilde{n}(OH)f - 2\tilde{n}[A(LP)]}{n_s} \right]
\]
\[
\left[ \frac{\tilde{n} - 2\tilde{n}(OH)f - (1-Z)\tilde{n}[A(LP)]}{n_s} \right]
\]
\[
\therefore K = \tilde{x}(OH)f \left[ \frac{\tilde{x}(OH)f - 2\tilde{x}[A(LP)]}{1 - 2\tilde{x}(OH)f - (1-Z)\tilde{x}[A(LP)]} \right]
\]
\[
\therefore K = \frac{\alpha(x - nb)}{1 - 2\alpha - b + nb}
\]

where: \( \alpha = \tilde{x}(OH) \)
\( b = \tilde{x}[A(LP)] \)
\( n = Z \)
SPECTROSCOPIC STUDIES OF SOLVATION IN AQUEOUS AND ALCOHOLIC MEDIA

Howard L. Robinson

ABSTRACT

This work is concerned with a study into hydrogen bond formation in alcohol and water systems using Infrared spectroscopy and NMR. In the former case, the first overtone region is investigated for the alcoholic systems and the second overtone region used in the aqueous work. Additional information is gleaned from fundamental studies, however emphasis is attached to the overtone work which amplifies changes in weakly hydrogen bonded entities and non-bonded $\text{(OH)}$ and $\text{(LP)}$ free groups in the methanol study.

The loss of water/alcohol $\text{(OH)}_{\text{free}}$ groups due to added base is determined by using computer graphics to curve analyse the overtone spectra. It was found that the originally labelled "$\text{(OH)}_{\text{free}}$" peak is only about 50% $\text{(OH)}_{\text{free}}$, the remainder being weakly hydrogen bonded species. A good correlation is found between experimental and a theoretical consideration of loss of $\text{(OH)}_{\text{free}}$ groups, using a Law of Mass Action approach. This allows an accurate classification of solvation numbers for solutes studied.

The two-dimensional structure and bifunctionality of methanol presents a simpler picture to interpret than does water. The methanol work can ultimately be related to the aqueous results which clearly shows that water brings out the maximum solvation numbers for solutes compared to methanol, t-BuOH and fluoroalcohols. A rise in absorbance is observed in the methanol overtone spectrum in the $\text{(LP)}_{\text{free}}$ region on adding base or increasing temperature. Curve analysis has been used to monitor changes in $\text{[(LP)}_{\text{free}}$ which leads to a determination of solute basicities in methanol.

The NMR work examines the change in hydrogen bonded environments for water and also t-BuOH on adding solutes or cosolvents. Aqueous solution shifts are explained using a proposed model which accounts for anion and cation hydration terms and changes in $\text{[(OH)}_{\text{free}}$, $\text{[(LP)}_{\text{free}}$, all of which contribute to the time averaged water resonance. The model makes use of a novel NMR/IR correlation plot which allows IR shifts to be converted into previously unknown NMR shifts for H-bonded species. A similar plot has been constructed in the t-BuOH study.