SPECTROSCOPIC STUDIES

OF

AQUEOUS SOLUTIONS

A thesis submitted by

SUSAN ELIZABETH JACKSON

for the degree of

DOCTOR OF PHILOSOPHY

.

in the 👘

FACULTY OF SCIENCE

of the

UNIVERSITY OF LEICESTER

Department of Chemistry,

The University,

Leicester.

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STATEMENT

The experimental work described in this thesis was carried out by the author in the Department of Chemistry of The University of Leicester during the period between October 1974 and June 1977.

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

SE Jackson,

October 1980

Susan Elizabeth Jackson

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I would like to express my gratitude to Professor M.C.R. Symons for suggesting the field of study and for his continued interest, guidance and encouragement throughout the years spent working on this thesis.

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Thankyou also to Mrs A. Crane for drawing the diagrams.

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CHAPTER ONE

AN INTRODUCTION TO LIQUID

WATER AND AQUEOUS SOLUTIONS

1.1 Introduction

The structure and properties of water and aqueous solutions are not yet completely understood. It is the aim of this thesis to interpret evidence obtained from spectroscopic results and explain more fully the solvating properties of water.

Existing structural models for liquid water and aqueous solutions are discussed and the spectroscopic evidence analysed. This is followed by an introduction to the various spectroscopic methods employed and the reasons for using them.

1.2 Structural models for liquid water

Water as a pure liquid is far from being completely understood although many theories have been put forward. Any suggestions for structural models which hope to be taken seriously have to account for the many unusual and possibly unexpected properties of liquid water. For example, its melting point and boiling point are higher than might be predicted by comparison with other Group VI hydrides. The molar volume of the liquid is smaller than that of the solid (ice-1h, at 273) and one atmosphere). On warming, the liquid

contracts up to 277.13K, the temperature of maximum density, then expands. The molar heat capacity, C_p , is much higher for the liquid than the solid and has a minimum at 310K.

That water does have "unusual" properties is perhaps not so surprising when one considers the structure of the unassociated water molecule. It consists of approximately tetrahedrally disposed protons and 'lone pair' electrons, and this symmetry enables it to associate with other water molecules forming larger structural units. Water has the ability to 'accept' or 'donate' electrons, hence forming up to four hydrogen bonds with adjacent molecules.



Figure 1.1 Tetrahedral structure of water molecules.

A hydrogen bond is an electrostatic interaction between a partially positive hydrogen and the lone pair of a neighbouring molecule. In a hydrogen bond in ice the protons are held directly between the oxygen atoms but are asymmetric along

the line.^{1,2} In the most common configuration of ice, ice-1h, a more-or-less perfectly hydrogen bonded system occurs. As the temperature is raised and the solid melts, changes occur in the symmetry. Whether bonds between molecules actually break or are merely distorted is one of the differences between the two main classes of models for liquid water. As monomeric molecules appear in the gas phase it is reasonable to suppose that some monomers will be present in the liquid state and certainly that some molecules will be hydrogen bonded to less than four neighbours. Structural models for liquid water have been extensively covered in review articles³⁻⁶ and hence only brief details will be given here.

Models proposed are often governed by the experimental evidence they attempt to explain but an acceptable model should account for all properties. The structures for liquid water fall into two classes, 'mixture' and 'continuum'. Kell⁷ suggests the following definitions: "A mixture model is understood to describe liquid water as an equilibrium mixture (or solution) of species that are distinguishable in an instantaneous picture" and "a continuum theory describes water as having essentially complete hydrogen bonding, at least at low temperatures but as having a distribution of angles, distances and bond energies".

Continuum Model

Continuum models describe liquid water as an essentially complete hydrogen bonded network whose molecular interactions have a continuous, smooth and single peaked distribution of energies ranging from ice-like at one extreme to almost gaslike at the other. Bernal and Fowler⁸ proposed the first





Figure 1.2 Possible frameworks of hydrogen bonded water molecules continuum model in which they postulated three different intermolecular arrangements: (i) Ice-tridymite-like (four co-ordinated) below 4°C, (ii) Quartz-like (four co-ordinated) between 4 and 200°C, (iii) Ammonia-like, close packed, 200-340°C. These forms pass continuously into each other with change in temperature and the liquid remains completely homogeneous. The model proposed by Pople⁹ suggests that as ice melts no hydrogen bonds break, they merely distort and bend.

Mixture Model

The mixture model describes liquid water as an equilibrium mixture of molecular species with different numbers of hydrogen bonds per molecule. The simplest mixture models are those in which only two species are postulated. Properties of the liquid are then explained in terms of the equilibrium

 $(H_2^0)_{bulky}$ species $(H_2^0)_{dense}$ species where the bulky species is considered to be an 'ice-like' cluster of hydrogen bonded molecules, and the dense species is assumed to be more closely packed.

Interstitial models are a class of mixture models in which one of the species forms a hydrogen-bonded framework, and the other species resides in cavities within the framework. As the temperature is increased, the extent of the hydrogen-bonded structure decreases while a decrease in temperature causes an increase in structure. These temperature changes have led to the use of the terms 'structure making' and 'structure breaking'.

A closely related model proposed by Pauling^{10,11} suggests that water forms clathrate cages as do inert gases or hydrocarbons. Pauling proposes that liquid water may resemble the chlorine hydrate with twenty hydrogen-bonded water molecules forming an open pentagonal dodecahedra in which non-hydrogen-bonded water molecules reside.

An important mixture model is the cluster model proposed by Frank and Wen^{12,13}. They suggested that the formation of hydrogen bonds in water is a co-operative phenomenom.



Figure 1.3 Clusters of water molecules as proposed by Frank and Wen^{12,13}.

Association of two water molecules by hydrogen bonding stimulates association with other water molecules. Clusters of water molecules having a life time in the order of 10⁻¹¹ seconds are constantly forming and dissolving. Nemethy and Scheraga¹⁴ applied a semi-quantitative analysis to the clusters

and showed that the average cluster size decreased from 91 to 25 molecules in the 0 to 70° C temperature range.

1.3 Spectroscopic evidence

It should be possible to differentiate between the two structural models by studying the vibrational spectrum of liquid water which is a very sensitive probe of hydrogen bonding. The vibrational time-scale is of the order of 10⁻¹² seconds and can be used to probe direct molecular environments. The frequency of an OH stretching vibration decreases as the strength of the hydrogen bonding increases.

The mixture model proposes broken and unbroken hydrogen bonds and if this model is correct, each OH stretching band should consist of two sub-bands, the one due to non-hydrogenbonded OH groups being at higher frequency. This band should increase in intensity at higher temperatures.

For the continuum model to be correct, the OH stretching band should be a single broad band, moving gradually to higher frequencies as the temperature is raised.

In practise, spectroscopy does not prove either model correct as the bands which are broad and in some cases overlap, can be interpreted in different ways. Gorbunov and Naberukhin¹⁵ have explained results in terms of a continuum model which were previously suggested by the authors as evidence for a mixture model!

Falk and Ford^{16,17} studied a dilute solution of HOD in H_2^0 and D_2^0 and found that each fundamental band showed a single maximum. An increase in temperature caused a gradual shift of the entire band and there was a complete absence of

shoulders.





They concluded that their results fully support a continuum model and "are incompatible with the existence in water of any discrete molecular species differing in the extent of hydrogen bonding". Wall and Hornig¹⁸ studied the same system by Raman spectroscopy and could find no evidence to indicate the presence of distinct and distinguishable molecules in liquid water.

The alternative explanation of the Raman bands of dilute HOD in H_20 and D_20 was given by Walrafen^{19,20,21}. Karked asymmetry was observed in the bands at 3300-3700 cm⁻¹ and 2400-2700 cm⁻¹ and this was not in accord with a continuum model. Using an analogue computer, the bands were analysed into two Gaussian component bands; the peaks at 3630 cm⁻¹ and 2650 cm⁻¹ assigned to non hydrogen bonded OH groups and and the peaks at 3435 cm⁻¹ and 2520 cm⁻¹ to hydrogen bonded OH interactions. Variable temperature studies produced an isosbestic point at 2570 cm⁻¹ indicating the existence of components having opposite variations of intensity with temperature.





Thus evidence for water in two environments is provided by the experimental observation of an isosbestic point.

However this same data of Walrafen is used by Schiffer²² in claiming support for the continuum model.

 $Hartman^{23}$ observed an isosbestic frequency at 3473 cm⁻¹ from his infrared studies of HOD in D₂0.



Figure 1.6 Spectra of HOD in D₂O at various temperatures

 $(Hartman^{23})$

Senior and Verrall²⁴ claimed evidence for a mixture model with their isosbestic point at 2575 cm⁻¹ in the infrared spectra of HOD.



Overtone bands between 5000 cm^{-1} and 11 000 cm⁻¹ showing isosbestic points have been claimed as evidence for a mixture model but these bands are more difficult to assign as there are often combinations of bands which overlap.

Worley and Klotz^{25} studied the overtone spectra of 6M HOD in D_2O and reported an isosbestic point at 6812 cm⁻¹. They analysed the spectra into four bands, assigning the well resolved band at 7060 cm⁻¹ to the free OH stretch and other bands at 6550, 6425 and 6000 cm⁻¹ to various overtone modes of different hydrogen bonded species.

Buijs and Choppin²⁶ studied the water spectra at ~8330 cm⁻¹ associated with the combination $V_1 + V_2 + V_3$, and assigned three components at 8620, 8330 and 8000 cm⁻¹ to water molecules with no OH groups bonded, one OH group bonded and two OH groups bonded respectively.

The majority of spectroscopists are in agreement with the mixture model approach but disagree to a considerable extent on the estimations of the percentage of "broken hydrogen bonds" in water. Falk and Ford¹⁶ listed some of the estimates which vary from 71.5% to 0.1%.

1.4 Models for Aqueous Solvation

(i) Non-electrolytes

Non-electrolytes which do not contain a functional group are largely rejected by water and the solubilities of these solutes are low. In terms of Frank's theory, the water structure will be modified by the non-interacting non-electrolytes being accommodated within the local water structure if they can occupy one or more of the interstitial sites within the hydrogen bonded framework. Additions of small amounts of solute are accommodated by displacing water molecules from the cavities which then integrate into the $(H_2^0)_{\text{bulky species}}$ lattice. This structure promoting capacity depends on the size of the molecules.

If the solute has either acidic or basic groups it is likely to form hydrogen bonds with water and consequently modify the local structure. An excess of (OH)_{free} groups or of non-bonded lone-pairs may be generated. A molecule such as ^tbutanol will hydrogen bond to water through its OH group and the non-interacting group will be accommodated in the water framework.

Pauling's suggestion of a water hydrate model for liquid water can be extended to describe aqueous solutions. Water can buffer the structural interference of addition of solute by enclosing the molecule in a clathrate cage. The cages, which can have a variety of sizes and shapes, may become distorted or water molecules can be omitted to accommodate the larger solute molecules. The cages will be most favoured at low temperatures and will be more temperature sensitive than bulk water structure.





Figure 1.8 Examples of clathrate cages adapting to accommodate solute molecules.



(ii) Electrolytes

The most common pictorial models for ionic solvation consist of concentric regions of solvent molecules around the ions.

Horne²⁷ suggests four regions which can be identified. (See Figure 1.9) Adjacent to the ion is its 'primary hydration' shell of four strongly bound, tightly electrostricted water molecules (A). Region (B) is a Frank and Wen cluster, beyond which (C) consists of broken water structure. At some considerable distance from the ion, (D), the structure of water resumes its 'normal' fraction of hydrogen bonding.

Frank and Wen¹² suggested a similar model but omitted the region B described above.



Figure 1.10 Frank and Wen pictorial model for water

The broken down water structure of region C increases with ion size, increasing the extent of water structure breaking. For small ions, e.g. Li^+ and F^- , region C disappears completely as the ions, which are structure formers are incorporated in the water structure.

1.5 Discussion

Many models for liquid water are designed to reproduce the property of water under investigation and are then extended to fit other experimental results. In this manner the models become contrived.

Symons^{28,29} has built up a pictorial model for liquid water by first considering monomeric water molecules with two acidic and two basic sites which can interact to give dimers. A dimer, with six reactive sites will tend to scavenge monomers, certain sites being more reactive than others. As the linear polymers grow, there is a possibility of cyclization of chain-branching. Chain-branching can lead to chain-crossing and ultimately, large three dimensional polymers will be formed. Polymer-polymer interactions will occur so that pure liquid water at low temperatures could be considered as a 'single' unit.

Mis-matching will occur resulting in very bent hydrogen bonds or unusually long ones. Distortion will cause bonds to break and then new ones reform. Non-bonded OH groups (OH)_{free} will be present due to the absence of non-bonded lone pairs (LP)_{free} in the vicinity but a perpetual reforming of the groups will occur.

Any added monomer will be quickly scavenged by one of the many reactive sites and there is no reason to propose the presence of monomers in liquid water as some models do. In a survey of published infrared data³⁰, no spectroscopic evidence could be found for monomeric water.

Solvation of a solute molecule with acidic or basic groups will involve the formation of hydrogen bonds between water and solute and this will change the concentration of $(OH)_{free}$.

Cation solvation is via lone pairs, resulting in an increase in concentration of (OH)_{free}. The two lone pairs on the water oxygen may both be involved in bonding to the cation as in Figure 1.11a or alternatively as in Figure 1.11b the oxygen may also be involved in a hydrogen bond with an adjacent water molecule.



Figure 1.11 Cation and anion solvation by water.

Anion solvation is complimentary, forming hydrogen bonds with water and generating $(LP)_{free}$. These $(OH)_{free}$ and $(LP)_{free}$ groups are able to interact and the net result of electrolyte solvation will be only a small change in the concentration of each species.

Aqueous solvation involves changes in the water-water bond strengths and the formation of water-solute bonds. These bonds can be monitored spectroscopically, using nmr, ultraviolet and infrared methods. Each of the techniques has its own merits as they operate on different timescales, so giving different 'pictures'. NMR operates on a timescale of 10^{-2} seconds whereas the vibrational timescale is of the order of 10^{-12} seconds. Infrared spectroscopy probes molecular environments and can accurately 'see' the different

hydrogen bonding environments, although bands are broad and difficult to interpret. NMR peaks are sharp and well-defined but they are time averages of all the different bands contributing to the total resonance.

Room temperature infrared bands of the OH and OD fundamental stretching vibrations are broad and overlap considerably, making interpretation difficult. The frequencies of the two fundamental OH stretching vibrations, $\gamma_1 \stackrel{\sim}{}^{\star} \gamma_3$, and of the first overtone of the bending vibration, $2\gamma_2$, lie close to one another.

The situation is eased by using isotopically dilute solution. HOD in H_2O or D_2O has no intermolecular coupling of vibrations and the three fundamental bands are well separated.

More useful information can be gleaned from the spectra if the temperature of the solution is lowered, causing bands to narrow and have better resolution.

The other alternative is to study the overtone spectra of HOD. Whereas in the fundamental region the intensity of the OH_{bound} band is greater by a factor of 20 or more than the intensity of the $(OH)_{free}$ band, in the overtone regions the intensity of the $(OH)_{free}$ and $(OH)_{bound}$ bands are almost the same. Also the separation between the two bands is much larger than in the fundamental, making the spectra easier to analyse. Experimentally, the pathlength of the cells used to obtain these spectra are much more convenient.

In the second overtone region (~10 000 cm⁻¹) the intensity differences have changed to such an extent that only the $(OH)_{free}$ band is clearly detectable.³¹

Structure Making and Breaking

The terms structure making and breaking are used extensively when aqueous solutions are discussed. The terms were originally used to describe the effect of a change in temperature on the structure of water. Bernal and Fowler⁸ suggested that addition of an electrolyte to water causes either structure making or breaking to occur which to a first approximation is similar to a change in temperature. They defined the structural temperature, T_{STR}, as that temperature at which pure water would have effectively the same inner structure.

CHAPTER TWO

EXPERIMENTAL

2.1 Introduction

Vibrational spectra were recorded using several instruments. For work in the ultraviolet and near infrared regions a UNICAM SP700 was used. The infrared spectra were recorded on a UNICAM SP100 and at a later stage on a PERKIN-ELMER 580.

NMR shifts were measured on a JOEL 100mHz spectrometer.

2.2 Instrumentation

(i) Unicam SP700

The Unicam SP700 is a double beam recording spectrophotometer with a range from 54 000 to 2800 cm⁻¹. Spectra were run at various temperatures by circulating water at a desired temperature through the cell mounting block from a thermostat bath. Temperatures were measured using an electronic thermometer with its thermocouple attached to the side of the cell. Temperatures were recorded to an accuracy of ± 1 K.

Work in the ultraviolet region of the spectrum was normally carried out using stoppered silica cells of 1, 5 or 10 mm pathlength as appropriate. When shorter pathlengths were required, demountable cells, as illustrated in Figure



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(10)

(11)

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(14)

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(12)




2.1b, were used. Twenty and forty millimetre cells were used in the near infrared for work on the first and second overtones of water respectively. All cells were thoroughly cleaned before use by repeatedly washing with distilled water, rinsing with a readily volatile solvent and applying gentle heat.

(ii) Unicam SP100

Initially the Unicam SP100 infrared spectrophotometer was used for studies in the $4000 - 3000 \text{ cm}^{-1}$ region as it had been operated by previous workers for low temperature research.

Variable temperatures were obtained using a unit consisting of four main parts:- (i) Outer Jacket, (ii) Cell Holder and Refrigerant Vessel, (iii) Sample Cell with Thermocouple and (iv) a Temperature Control Unit.

The chrome plated nickel outer jacket (Figure 2.2) united the cell holder and refrigerant chamber to the spectrophotometer sample chamber and was vacuum tight. The jacket was fitted with demountable NaCl windows (1), heated to slightly above ambient temperature by an external heater (2) to prevent condensation from the atmosphere. The rectangular back plate (3) ensured the correct alignment of the sample cell.

The cell holder (4) was connected directly to the base of the stainless steel refrigerant vessel (5) (Figure 2.3). Facilities for vacuum connection (6), heaters (7) and thermocouple lead (8) were arranged on the top plate (9) of the unit. The sample cell used was the Beckman - RIIC FH-O1 type (Figure 2.1a). This was a variable pathlength vacuum tight liquid cell fitted with appropriate windows. CaF_2 windows were used in the 4000 - 2000 cm⁻¹ region and AgCl windows for lower wavenumbers. Desired pathlengths were obtained using teflon spacers (10) between the two windows (11). Filling ports (12) were sealed with stainless steel screw plugs and teflon washers. In order that the temperature of the cell could be measured, an access hole (13) in the front plate (14) was used to position a thermocouple junction adjacent to the cell windows(11).

The SPECAC 20.100 variable temperature control unit (Figure 2.4) heated both the outer windows of the jacket and the internal cell. Using the SPECAC unit, it was possible for the cell temperature to be controlled within the range 88K to 523K to an accuracy of 1K.

Low Temperature Spectra

Low temperature spectra were obtained by placing a suitable refrigerant in the refrigeration vessel. In this work, liquid nitrogen was used in all cases.

The filled sample cell was placed in the cell holder and locked in position by tightening the clamp screw (16) and the thermocouple inserted in the hole (17) in the front plate. The cell, cell holder and refrigerant vessel were placed inside the outer jacket and rotated until the locating pin (18) was in position, ensuring that the cell was aligned square to the optical beam.

A vacuum pump was connected to the outlet (6) on the top plate and the unit evacuated. With the "windows" heater



Figure 2.4 Temperature control unit

of the temperature control unit at ON, liquid nitrogen was poured into the refrigerant chamber. The pointer (19) indicated the temperature of the cell and holder and when the temperature had fallen below that required, the temperature dial (20) was set to the required temperature and the "cell" heater switched ON.

The temperature controller regulated the power supplied to the cell heater and brought the cell unit to the dial-set temperature. This was indicated by the temperature indicator showing the same temperature reading as the temperature dial. When the desired temperature was obtained, five minutes were allowed to elapse before any spectra were obtained.

(iii) Perkin Elmer 580

In the course of this research work, the Unicam SP100 broke down and being an old machine took considerable time and money to repair. In order to avert any discontinuity in the research, the low temperature attachments were transferred to another instrument. The Perkin Elmer 580 Infrared Spectrophotometer had a large cell compartment and by cutting circular holes in the roof of the cell compartment, the low temperature jackets were suspended with the cells in the correct position relative to the light beam.

This machine had several advantages over the UNICAM SP100, particularly as it was much quicker and easier to use. The absorbance spectra obtained gave a direct indication of concentration unlike the previous instrument from which only transmission spectra were obtained.

(iv) Joel 100mHz spectrometer .

The nmr spectra were recorded on a Joel PS100 NMR spectrometer fitted with a variable temperature control unit. Temperatures were measured accurately with a Comark Electronic Thermometer. The operating frequencies used were 100 mHz for ¹H and 40 mHz for ³¹P studies. Spectra were individually calibrated using side bands.

Absolute chemical shifts cannot be measured so it is usual to measure shifts from the resonance position of a suitable standard.

For the ¹H nmr of the water/base mixtures studied, a proton resonance of the added base could be used, provided that it did not shift with a change in concentration. Alternatively, a non-interacting internal reference can be added in very low concentration. The 31 P nmr shifts were measured using a capillary containing $P_{\mu}O_{6}$ as external reference.

2.3 Materials

Water was produced by distillation of deionised water from alkaline potassium permanganate under nitrogen. D_2^0 was used as obtained from Merck, Sharpe and Dohme.

Spectrograde methyl cyanide was refluxed over P_2O_5 before distillation, the fraction between 80 and 82°C being collected and stored over molecular sieves.

Spectrograde methanol was refluxed over magnesium and iodine prior to distillation, the fraction between 64 and 65°C being collected and stored over molecular sieves.

All other solvents used were analytical grade. Infrared spectra were run to detect any water present. Distillations were carried out when necessary and all solvents were stored over molecular sieves.

Deuterated solvents were used as obtained.

Salts were dried in a vacuum oven at an appropriate temperature for at least 24 hours and then stored in a dessicator over P_00_5 prior to use.

Salts to be used in near infrared spectral investigations were recrystallised from D_2^0 before drying, in order that any residual water would be D_2^0 , not H_2^0 , and hence would have no effect on the spectra.

Salts with replaceable protons were deuterated by successive recrystallisations from D₂O. The replacement process was followed by nmr and infrared techniques.

2.4 Preparation of Solutions

All solutions were prepared by weight and the values used to calculate molal concentrations for salt solutions and mole fractions for non-electrolyte solutions.

(i) for near infrared work.

A standard solution of H_2^0 in D_2^0 was prepared with the concentration such that, after dilution by D_2^0 of a fixed aliquot (1.000g) to the final volume (5cm³), the concentration was 3M H_2^0 in D_2^0 . When run against D_2^0 a standard spectrum of HOD was produced, against which all other spectra could be compared, as all the sample solutions contained the same concentration of OH oscillator.

Standard concentrated solutions of electrolytes and non-electrolytes in D_2^{0} were prepared. Solutions were prepared in sets of two 5cm³ graduated flasks by mixing suitable aliquots of electrolyte/non-electrolyte standard solution with the fixed quantity of standard HOD solution (1.000g). The same quantity of electrolyte/non-electrolyte standard solution was added to the reference flask, the HOD omitted, and both the solutions diluted to the mark with D_2^{0} .

Great care had to be taken when preparing solutions and in particular when adding the fixed quantity of standard HOD solution. The weight of this solution (1.000g) had to be accurate to three decimal places for the spectra to have reproducible baselines and isosbestic points as the spectra were so sensitive to OH oscillator concentration.

Hence considerable time and effort was spent on preparing the solutions in order that the resulting spectra were comparable and meaningful results obtained. The overtone spectra of methanol used a 1:10 ratio of $CH_3OH:CD_3OD$ versus CD_3OD with salt/solvent added in equal amounts to both solutions.

(ii) for infrared work.

Solutions were made as above but using 0.01M HOD in D_2^0 when looking at the OH stretch and 6M D_2^0 in H_2^0 when investigating the OD stretch.

(iii) for ultraviolet work.

A fixed aliquot (1.000g) of a stock I⁻/MeCN solution $(0.5 \times 10^{-3} \text{M})$ was added to each 10 cm³ sample flask, varying amounts of stock cosolvent/MeCN solution added and the flask diluted to the mark with MeCN. Reference solutions omitted the I⁻/MeCN solution.

As in the near infrared work, extreme care had to be taken when weighing out solutions. This was particularly true for the iodide component in order to obtain reproducible baselines and isosbestic points.

For the infrared work on the I /solvent systems, the solutions were prepared in a similar manner but using higher concentrations of iodide.

Spectra were recorded as soon as possible after the solutions had been prepared to decrease inaccuracies caused by deterioration of the samples. Storage, when necessary, was in the dark, to prevent tri-iodide formation.

SECTION A

AQUEOUS SOLVATION OF NON-ELECTROLYTES

Introduction

Aqueous solvation of non-electrolytes was studied by monitoring the spectral changes caused by addition of an uncharged species to water. The solvation of bases, alcohols, amines and amides was investigated mainly by looking at the near and fundamental infrared OH stretches of the water molecule. ¹H and ³¹P nmr spectroscopy (for HMPA) were used to extend the study.

A.1 Aqueous solvation of bases

A.1.1 Previous work in the infrared region

Infrared techniques are useful for studying hydrogen bonding between proton donor and acceptor molecules in 'inert' media. Mohr et.al.³² studied the infrared spectra of water plus base in carbon tetrachloride. (Figure A.1) The symmetrical water molecule exhibits coupled bands γ_1 (symmetric stretch) and γ_3 (asymmetric stretch). At low base concentration Mohr identified the 1:1 complex HOH---B having one narrow absorption near to that for OH_{free} (γ_{free}) and one broad absorption, displaced to lower frequencies, characterising



the association, (N_{bonded}) . At higher base concentrations, the species B---HOH---B was identified, for weak bases by two broad bands in the low frequency region and for stronger bases by one band, the two vibrations having the same frequency.

In a study of the same system, Saumagne³³, Glew³⁴ and others found a linear correlation between the values of V_1 ($V_{associated}$) and V_3 (V_{free}) plotted against one another for both the symmetric (B---HOH---B) and asymmetric (B---HOH) species. More recently, Bellamy et.al.³⁵ have extended the plot to include crystal hydrates where the water molecules are symmetrically hydrogen bonded to anions. (Figure A.2)



Figure A.1b The OH stretching region for CCl₄ solutions progressively richer in ethyl ether (Mohr³²)



Figure A.2 (for details see overleaf)

Figure A.2 Interdependence of y_{g} and y_{as} for water in various solvents and crystal hydrates. (Bellamy³⁵)

Line \propto correlates data for unsymmetrical water HOH---X; Line β for symmetrical water X---HOH---X and line X represents $\nu_s = \nu_{as}$ and is used for including data for HOD systems for comparative purposes.

- <u>1:1 Complexes</u> A CH_3CN/CCl_4 ; B cyclohexanone/CCl₄; C DMSO/CCl₄; D nitrobenzene/CCl₄; E trioxan/CCl₄; F $CH_3CN/$ CCl_4 ; G ethylacetate/CCl₄; H acetone/CCl₄; J dioxan/CCl₄; K ethylether/CCl₄; L n,n-dimethylformamide/CCl₄; M pyridazine/CCl₄; N pyridine/ CCl_4 ; P 4-picoline-N-oxide/CCl₄.
- 2:1 Complexes 1 H₂O vapour; 2 N₂-matrix; 3 perfluorobenzene; 4 CCl₄; 5 perchloroethylene; 6 1,1,1-trichloroethane; 7 1,2-dichloroethane; 8 ethylene oxide; 9 propylene oxide; 10 1,4 dioxane; 11 tetrahydrofuran; 12 NaClO₄.H₂O; 13 LiClO₄.3H₂O; 14 Ba(ClO₄)₂.3H₂O; 15 Ba(ClO₃)₂.H₂O; 16 Ba(BrO₃)₂.H₂O; 17 Ba(IO₃)₂.H₂O; 18 Ca(BrO₃)₂; 19 Sr(BrO₃)₂; 20 nitromethane; 21 nitrobenzene; 22 dimethylphthalate; 23 CH₃CN; 24 ethylacetate; 25 methylal; 26 acetone; 27 dioxane; 28 ethylether; 29 n,n dimethyl formamide;.

HOD Hydrate Data a
$$Sr(BrO_3)_2 \cdot H_2O$$
; b $Ba(BrO_3)_2 \cdot H_2O$;
c $Ba(ClO_3)_2 \cdot H_2O$; d $NaClO_4 \cdot H_2O$;
e $LiClO_4 \cdot LiClO_4 \cdot 3H_2O$.

Choppin and Hornung³⁶ analysed the absorption band of water in the 6600 - 7500 cm⁻¹ region for $H_2^{0/base/CCl}_4$ systems in terms of seven components. A model for water involving three species with 0, 1 and 2 hydrogens participating in hydrogen bonding, explained the resolved spectra.

Gentric et.al.³⁷ examined the bending mode, V_2 , at ~1650 cm⁻¹ of water/base mixtures. The assymetry of the peak was attributed to HOH---B and B---HOH---B complexes, the proportion of the species depending on the molecular size of the base.

Fratiello and Luongo³⁸ studied the aqueous solvation of dioxane by monitoring the shift of the CH stretch, CH deformation and C-O stretch in the infrared region across the entire mole fraction range. The shift to lower frequency of the C-O stretching mode indicated that hydrogen bond formation was at this site.

The fundamental OH stretch for water in the 3000 - 4000 $\rm cm^{-1}$ region is a broad featureless band and has proved of little use in spectroscopic studies of solvation. The spectra can be simplified using HOD but still very little information can be obtained. Cogley et.al.³⁹ studied the fundamental infrared spectra of H₂O, D₂O and HOD in propylene carbonate and concluded that the units HOH---B and B---HOH---B were formed in preference to the aggregation of water molecules. The infrared spectra of binary mixtures of water (HOD and H₂O) and four co-solvents (acetonitrile, dioxane, dimethylsulphoxide and hexamethylphosphoramide) were studied systematically by Narvor, Gentric and Saumagne⁴⁰ who found evidence for the presence of various types of hydrogen bonded complexes and confirmed the existence of 1:2 complexes of water:solvent.

A useful alternative is to study the overtone spectrum of water although the assignment of the bands is not so clear cut as in the fundamental. The water spectrum at 7000 cm⁻¹ has been assigned to $V_1 + V_3$ by Choppin⁴¹ who analysed it in terms of three spectroscopically distinguishable species with 0, 1 or 2 hydrogens bonded. The spectra of acetone/water and dioxan/water mixtures were similar, the addition of base having little effect on the component peaks. The conclusion that the weak bases interacted only slightly with the water was in opposition to work by McCabe⁴² and also Burneau and Corset⁴³ who analysed similar spectra and concluded that HOH---B and B---HOH---B units were formed, depending on concentration.

However, Choppin⁴¹ did concede that if base-water complexes are present it is probable that they would absorb at the same frequencies as the water molecules with one and two hydrogen bonds and would therefore be undetected in their analysis.

Bonner and Choi⁴⁴ utilised the $V_2 + V_3$ combination band ($\sim 5200 \text{ cm}^{-1}$) of water in organic solutes as there were no interfering water bands at adjacent wavelengths. (This band is said to be particularly useful for monitoring the effects of hydroxylic solvents as it avoids interference from the OH stretching modes in alcohols etc.) 1:1 and 1:2 water:solvent complexes were identified for various bases in studies over the entire concentration range. The positions of the bands varied with the degree of hydrogen bonding and the basicity of the solvent. Interactions between water and base were found to be weakest in nitromethane and strongest in dimethylsulphoxide.

Of course, other techniques have been widely used to study these systems. One random example is the work of Fox^{45}

who studied the $n \rightarrow \pi^*$ absorption band for aqueous acetone in the ultraviolet, plotting the shift in V_{max} as a function of concentration. An initial high frequency shift, found only at low temperatures was attributed to the enhancement of water-water interactions.

A.1.2 Near Infrared Results

This work was devised in order to attempt to gain more understanding of the structure of aqueous solutions and to produce a description which was in agreement with the data obtained. Attention was primarily focused on the water rich region of aqueous solutions of several aprotic bases.

A 3M solution of HOD in D_2^0 produced the spectrum shown in Figure A.3 in the 6000 - 7600 cm⁻¹ region. It is customary⁴⁶ to assign the peak at 7120 cm⁻¹ to free OH groups, (OH)_{free}, as the band at room temperature correlates with that at 7150 cm⁻¹ at high temperatures. The room temperature band represents the limit of weakly bound oscillators and since the limit is the free oscillator it must have a contribution from the completely free OH groups. The shift from the high temperature value does not prove the presence of weak hydrogen bonds since the water molecules responsible will still form three strong hydrogen bonds and the effect of these is to shift the band due to (OH)_{free} oscillators slightly to low frequencies.

The broad maximum at 6600 cm⁻¹ is assigned to strongly bound OH groups, $(OH)_{bound}$, and the plateau region which lies between $(OH)_{free}$ and $(OH)_{bound}$ is considered to be due to weakly hydrogen bonded OH groups, including all the bent and



stretched hydrogen bonds which exist in liquid water and are known collectively as (OH) weakly bound.

An increase in temperature, as shown in Figure A.3, results in an increase in the height of the peak at 7120 cm⁻¹ (accompanied by a slight shift in $V_{\rm max}$ towards the gas-phase value of 7150 cm⁻¹) and a decrease in height of the (OH)_{bound} peak.

The appearance of the isosbestic point at 6800 cm^{-1} suggests an equilibrium between the two species $(OH)_{\text{free}}$ and $(OH)_{\text{bound}}$ which may be represented as,



The (OH)_{free} unit and the free lone pair (LP)_{free} are completely separate from one another and are not seen as the limiting situation of very long or weak hydrogen bonds which occur in some structural models.

For pure water, an increase in temperature shifts equilibrium I to the right and will always result in an equal number of free lone pairs and free OH groups. Hence,

$$K = \frac{\left[(OH)_{free} \right] \left[(LP)_{free} \right]}{\left[(OH)_{b \text{ ound}} \right]}$$
(II)

The controversy, previously mentioned, of the concentration of $(OH)_{free}$ groups in liquid water cannot be resolved from these spectra. The entire spectrum at 25°C can

be considered as a broad envelope of many sub-bands, and at a particular wavenumber such as 7120 cm⁻¹ there will be absorptions from weakly bound OH oscillators as well as $(OH)_{free}$ groups. This is illustrated in Figure A.4 which analyses the spectrum into four components using the Dupont Curve Analyser. Subtraction of the peak due to $(OH)_{free}$ groups does not result in zero absorption at 7120 cm⁻¹.

The deconvolution shown is not unique, but several subsequent attempts to construct the HOD spectrum gave very similar residue absorptions at 7120 cm⁻¹. The reconstructions were able accurately to reproduce the temperature effect but were limited by two factors.

- (i) Only four peaks could be used although the spectrum probably consists of many more sub-bands.
- (ii) Gaussian peaks were used in the deconvolution, but in fact Lorentzian or a Gaussian-Lorentzian mixture may be more appropriate. This is particularly true in the region assigned to (OH)_{free} groups where the spectrum is very steep sided.

Addition of Base

The effect on the system of the addition of a small amount of base can be seen in Figures A.5-A.8. Results for all the bases studied are collated in Figure A.9. It is difficult to measure the exact loss of the $(OH)_{free}$ peak because of the subjective estimate of the tail in this region from the $(OH)_{bound}$ oscillators.

In the majority of cases, the peak at 7120 cm^{-1} decreases in intensity with a corresponding increase in the 6600 cm^{-1} region. This is attributed to a reduction in the concentration













of (OH) free groups by the scavenging effect of the added base.

It can be seen from Figure A.9 that for dimethylsulphoxide (DMSO), hexamethylphosphormide (HMPA), dimethylformamide (DMF), dimethylacetamide (DMA), tetrahydrofuran (THF) and triethylamine the loss of $(OH)_{free}$ is approximately the same, within the experimental error. Triethylamine is expected to behave as a monobase due to its single lone pair of electrons and therefore it is concluded that all the above act as monobases in aqueous solution.



As the base is added it forms a bond with the $(OH)_{free}$ group of a water molecule. This causes equilibrium (I) to re-adjust to compensate for the loss of $(OH)_{free}$ groups in the system and hence the observed decrease in the peak at 7120 cm⁻¹ is less than expected. As it is the loss of $(OH)_{free}$ oscillators which is observed the strength of the base does not affect the spectrum and results for the bases mentioned above are all similar.

There are exceptions in the cases of methylcyanide, acetone and trimethylphosphate, all weak bases, which show a gain, not a loss, in the intensity in the region of the (OH)_{free} peak. In these cases, it is suggested that the increase

is attributable to the OH---B peak. The position of this band is base dependant and though for strong bases the band will not interfere with the measurements, in the case of the weak bases, the OH---B peak appears coincidentally in the $(OH)_{free}$ region.

Since the completion of this work a paper has appeared by Paquette and Jolicoeur⁴⁷ which studies the effect of a range of basic aprotic solvents on one of the overtone bands of water, $(V_1 + 2V_3)$ at 10 000 cm⁻¹. The overlapping results compare favourably with those quoted here but they differ markedly in the conclusions they draw compared to those suggested in this thesis. Paquette and Jolicoeur made no allowance for absorption by the OH---B oscillators, claiming that these would be so weak in the near infrared region that they would not be visible.

While this situation may exist for strong bases it certainly will not for the weak bases such as methyl cyanide and acetone. As the base strength falls the band due to the OH---B oscillators will shift and make an increasing contribution to the 7120 cm⁻¹ peak.

For weakly basic solvents the effect is so great that there is an increase in intensity in the $(OH)_{free}$ region despite the suggestion that the $(OH)_{free}$ groups are being scavenged. However, Paquette and Jolicoeur did not recognise this and interpreted their increase in terms of a 'structure breaking' effect.

From the results obtained in this work it is not possible to prove the loss of $(OH)_{free}$ groups on addition of a weak base although the spectra obtained experimentally could be re-generated using the Dupont Curve Analyser by a decrease in

the (OH) free peak and the appearance of a new band within the same region.

The suggestion that the increase in intensity is caused by a gain in the concentration of $(OH)_{free}$ groups can be disproved using results from the fundamental OH stretching region for HOD in D_2O . On addition of a weakly basic solvent such as methyl cyanide there is no growth in the $(OH)_{free}$ region of 3660 cm⁻¹ as shown in Figure A.12. There is, however, evidence for a band intermediate between the $(OH)_{free}$ position and bulk water which confirms the conclusion that on addition of weakly basic solvents to water, weak hydrogen bonding occurs and that bands can be assigned to this OH---B unit.

A.1.3 Computer Analysis of the Results

As can be seen from the attempt to deconvolute the HOD spectrum, the height at 7120 cm⁻¹ was not due completely to $(OH)_{free}$ groups but contained a 'tail' from the $(OH)_{weakly}$ bound peaks. Even if all the $(OH)_{free}$ groups were scavenged there would be a considerable residual absorption which the curve resolver study has estimated to be 60% of the total peak height. If the remaining 40% of the peak height is considered to be equivalent to all the $(OH)_{free}$ groups, the changes on addition of bases can be re-stated in terms of 'percentage loss of $(OH)_{free}$ '.

Mention has already been made of the controversy surrounding the estimation of the concentration of $(OH)_{free}$ groups in pure water with values ranging from 71.5 - 0.1%¹⁶.

An attempt has been made to estimate this concentration from the near infrared results by computer simulation of the change in (OH) free concentration on addition of base for different concentrations of (OH) free groups in pure water.

Considering the equilibrium,

$$(OH)_{bound} \longrightarrow (OH)_{free} + (LP)_{free}$$

which leads to the equilibrium constant,

$$K = [(OH)_{free}][(LP)_{free}]$$
(II)
[(OH)_bound]

with concentrations expressed in terms of the number of OH groups involved, as distinct from the number of water groups.

x

Equilibrium concentration 1-x

Initial

$$K = \frac{x^2}{1-x}$$
(IV)

х

On introducing the base,

$$(OH)_{free}$$
 + Base $\longrightarrow OH$ ----Base (V)
(the equation is considered irreversible)

If y moles of monobase are added,

$$(OH)_{bound} \longleftrightarrow (LP)_{free} + (OH)_{free} \xrightarrow{+B} (LP)_{free} + OH --- Base$$

1-x x x-y x y

$$\therefore K = \frac{x(x-y)}{1-x}$$
 (VI)

Taking any reasonable value for the percentage of $(OH)_{free}$ present initially in the pure water, K can be calculated from equation (IV). Assuming that K does not change appreciably on addition of base, y moles of base can be added and (x-y) the new fraction of non-bonded OH groups at equilibrium can be calculated.

The computer program in Appendix 1 was used to do this by first re-arranging equation (VI).

$$K(1-x) = x^2 - xy$$

 $K - Kx = x^2 - xy$
 $x^2 - xy + Kx - K = 0$

Applying the general quadratic formula $x = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$ and

choosing the root which gives a sensible answer, x-y is calculated. The computer program allows for addition of different amounts of base and produces a plot of loss of $(OH)_{free}$ against added base concentration. This is shown in Figure A.10 when different initial concentrations of $(OH)_{free}$ for pure water are considered. The experimental loss on addition of base is also plotted and can be seen to agree with a value of about 4-5% for the concentration of $(OH)_{free}$.

This value would seem a reasonable one but it must be considered as very approximate as errors in calculating it are large. Differences in peak height on adding base are small, resulting in large errors and the estimation of the percentage of the peak at 7120 cm⁻¹ being due to $(OH)_{free}$ groups is subjective. However, a meaningful value is obtained and the results are considered to be unique and informative.

Luck and Ditter⁴⁸ estimated a value of ca.12% (OH)_{free} at 25°C from studies of HOD in D_2O in the 7120 cm⁻¹ region over



a wide temperature range. This is considerably greater than the value quoted here, but is probably an upper limit rather than a precise value. Their high temperature results relate to the molecule HOD whilst the room temperature result is for the species ---H having three hydrogen bonds.

Extinction coefficients for the two species will differ and Luck also has the problem of contributions from other bands to the absorption at 7120 cm^{-1} .

A.1.4 Infrared Results

Brink and Falk⁴⁹ conducted a typical study of HOD in D_2O with addition of DMSO, by monitoring the fundamental OH stretch in the infrared region. The spectra were very broad, making small changes difficult to detect, and as no significant changes occurred, they concluded that DMSO did not have any notable effect on the structure of water.

This work has been repeated and the same results obtained but additional information was acquired by freezing the solutions to glassy solids at low temperatures. Only solutions exhibiting no phase separation on solidification were used. Where phase separation did occur it resulted in a sudden break in a smooth band or a distorted baseline and these results have been ignored. The glassy polids were considered as infinitely viscous liquids and the view was taken that their structure resembles that of the 'static' structural features of the liquid.

Although a systematic study of several bases was impossible due to the difficulty of obtaining good glasses, some spectra were obtained which showed additional details from those obtained in the liquid state.

Figure A.11 shows a low temperature spectrum of aqueous dimethylsulphoxide which has a broad band in the 3300 cm⁻¹ region and shoulders at \sim 3230 cm⁻¹ and \sim 3420 cm⁻¹ which were not visible at room temperature.

Spectra were obtained for the water/methyl cyanide and water/hexamethylphosphoramide systems as shown in Figures A.12 and A.13 and all three bases exhibited peaks in a similar manner to one another.

Figure A.11 Infrared absorption in the OH stretching region for HOD in D_2O containing 0.18mf dimethylsulphoxide A) $25^{\circ}C$ B) $-15^{\circ}C$ C) $-125^{\circ}C$









As discussed in the preceeding section (A.1.2) the bases were thought to act according to the equation,



The major feature at $\sim 3300 \text{ cm}^{-1}$ was assigned to bulk water and appeared at higher frequencies than the pure ice band due to the inclusion of a larger range of hydrogen bond lengths and bond angles (HOD in D_2O at $-125^{\circ}C$ has a narrow band at 3280 cm⁻¹).

The shoulders at 3230 cm^{-1} and 3420 cm^{-1} appeared to be independant of base and were assigned to bonds & and β respectively. Both bonds were due to the free lone pair groups, the β bond being predicted to be weaker than an average water bond and so appearing on the high frequency side of the bulk water band, whereas the & bond will be stronger than average and could result in the band at 3230 cm^{-1} .

The band (\propto) due to water bonded to base which would be solvent-dependant was not observed and it was concluded that it was concealed beneath the broad, bulk water band on all occasions. The closeness of the two bands would explain the lack of shift observed at room temperature and the two (LP)_{free} bands merely add to the overall width of the band.

A.1.5 NMR work

Infrared and nmr techniques cannot solve all the problems individually, but must be used to complement one another. Most nmr studies of water/base systems focus attention on the water protons although some solvent nuclei can be monitored. The water protons result in a single narrow peak which is an average of all the signals from OH_{bound} to OH_{free}. On increasing the temperature, the band shifts to high field due to a general weakening of all the bonds.

Chemical shifts are measured relative to a reference signal and both this and the sample spectrum must be displayed simultaneously. In aqueous mixtures the shift of the water protons is often measured with respect to some peak in the solute spectrum but this method becomes unsatisfactory when interactions between the solute and water cause the reference signal to move. Alternatively, a third non-interacting component may be added as a reference or an external standard used, but the need for bulk susceptibility corrections may decrease the accuracy.

Glew et.al.⁵⁰ measured ¹H nmr chemical shifts for aqueous solutions of several bases and at high solute concentration observed shifts to high field arising from the formation of weak water-solute hydrogen bonds and the loss of strong waterwater hydrogen bonds. Small solute concentrations showed a low field shift in some cases indicating stronger water-water hydrogen bonds due to formation of a water-shell around the weakly interacting interstitial non-electrolytes.

Wen and Hertz⁵¹ also obtained initial downfield shifts for water/base systems which they decomposed into 'polar' and 'non-polar' contributions. They⁵¹ and Oakes⁵² concluded that
the initial downfield shift was not simply the result of a structural effect but had contributions from the basicity or acidity of the cosolvent relative to water.



OR



The base B will form hydrogen bonds with the protons of the water molecule and if the B----HOH bond is stronger than the normal water-water bond then a downfield shift will be observed. A further downfield shift will be induced if it is very strong as this will cause the oxygen lone pairs to become more basic and hence able to form stronger hydrogen bonds with neighbouring water molecules.

A solute, A, which is more acidic than water will form hydrogen bonds to the oxygen atoms of water. This will increase the acidity of the water protons and cause a slight downfield shift.

In their nmr study of binary solvent mixtures Kingston and Symons⁵³ interpreted the results in terms of the acid/base behaviour and the gain or loss of $(OH)_{free}$ groups. All solvents were found to have some contribution from both types of behaviour but in different proportions. Bulky, nearspherical groups which induce water clathrates to form, result in a scavenging of $(OH)_{free}$ groups.

A.1.6 NMR Results

The results obtained in the water rich region are summarised in Figure A.14. With the exception of a few very weak bases there is an initial plateau region and in some cases a shift to low field before the subsequent linear trend to high field. The results are in agreement with those obtained by other workers^{50,51} and can be interpreted in terms of the loss of $(OH)_{free}$ groups which was previously detected in the near infrared.

NMR 'sees' the protons of the (OH)_{free} groups as similar to the protons in the water monomer and they must make a considerable upfield contribution to the normal water resonance. If they are removed by a base the water resonance will be shifted downfield.

The low temperature infrared results suggested that while protons hydrogen bonded to strongly basic cosolvents experienced very little shift, those associated with the (LP)_{free} 'groups' were shifted up and possibly also down field.



There are twice as many β protons causing an upfield shift as there are δ protons causing a downfield shift so the resulting shift of the protons associated with the (LP)_{free} groups should be upfield.

In the case of the weak bases such as methylcyanide the $B---\underline{H}OH$ protons are shifted upfield and this together with the upfield shift from the $(LP)_{free}$ protons outway the loss



Figure A.14 Proton resonance shift for water as a function

of the mole fraction of added base.

of $(OH)_{free}$ groups causing an immediate upfield shift with no plateau region being observed. In all cases the loss of $(OH)_{free}$ will not be as large as expected due to the readjustment of equilibrium (I).

Kingston and Symons⁵³ studied the effect of base on methanol by monitoring the shift in the methanol OH resonance. The addition of base causes a rapid upfield shift with no initial plateau region. In this instance there is no downfield contribution associated, as it was in the water case, with an initial loss of $(OH)_{free}$ groups and is in agreement with the suggestion (see Section B.2) that there are no $(OH)_{free}$ groups in methanol at room temperature.

A.1.7 Computer simulation

The nmr resonance for water contains contributions from protons in environments ranging from bonded to completely free. If the shift for $(OH)_{free}$ protons is A_1 and for $(OH)_{bound}$ protons is A_3 then the observed shift for pure water is given as,

Observed shift =
$$(OH)_{free} x A_1 + (OH)_{bound} x A_3$$

total (OH) total (OH)

To predict a shift for water with added monobase, an OH---Base shift must be chosen, then

Observed shift =
$$\frac{(OH)_{free} \mathbf{x} \mathbf{A}_1}{total} + \frac{(OH)_{bound} \mathbf{x} \mathbf{A}_3}{total}$$

+ $\frac{(OH---B) \mathbf{x} shift OH---B}{total}$

The computer program of Appendix Two predicts the shift on successive additions of base and plots the results as shown in Figure A.15 for values of 2, 4, 6 and $8\% (OH)_{free}$ in pure water. The different curves on each plot arise from taking different values for the OH---Base shift, as will occur for bases of differing strengths.

The following assumptions have to be made.

- 1. The OH_{bound} resonance position does not change over the $0.8 \rightarrow 1.0$ mf of water studied.
- 2. The OH---Base resonance position does not change over the $0.8 \rightarrow 1.0$ mf of water studied.
- 3. The equilibrium constant, K, does not change.

The shifts show a reasonable similarity with the experimental curves with an initial dip or plateau region before an upfield shift. This is, however, a very simple approach and can be made more sophisticated by deeper consideration of various hydrogen bond strengths.



Strength of bonds: n=normal, s=strong, w=weak.

Bulk shift = $z \times shift (OH)_{free} + 2z \times shift (OH)_{w} + z \times shift (OH)_{s} + 2z \times shift (OH)_{w} + z \times shift (OH)_{s} + (1-z-6z) \times shift (OH)_{n}$

On addition of y moles of monobase,



Observed shift = $(z-y) \times \text{shift (OH)}_{free} + y \times \text{shift (OH---B)}$ + $2(z-y) \times \text{shift (OH)}_{W} + (z-y) \times \text{shift (OH)}_{S}$ + $2z \times \text{shift (OH)}_{W} + z \times \text{shift (OH)}_{S} + (1-z-3(z-y)-3z) \times \text{shift (OH)}_{D}$

The computer plots shown in Figure A.16 are a result of this more sophisticated approach being employed in the computer program of Appendix Three for various concentrations of $(OH)_{free}$ groups in pure water. The experimental results, also plotted, show that a 4% concentration of $(OH)_{free}$ groups gives the best fit for DMSO, THF and MeCN. The agreement is good considering the simplistic approach used and the assumptions which are made. Figure A.15 Computer simulation of proton resonance shifts for water as a function of the mole fraction of added base, for various concentrations of (OH) free:







Figure A.17 Computer simulation of Figure A.16 for a 4% concentration of (OH) free with the addition of experimental plots.



A.2 Aqueous solvation of alcohols

A.2.1 Previous nmr and infrared work

The study of water-alcohol mixtures by nmr techniques has been limited by the fast rate of hydroxyl proton exchange on the nmr timescale in the water-rich region. The shift of the coalesced peak is generally assigned to the water protons although this is not established experimentally.

Glew et.al.⁵⁰, studying the effects of t-butanol on water using nmr spectroscopy, found an initial downfield shift of the averaged hydroxyl resonance followed by an upfield shift at higher alcohol concentrations.

Subsequent workers^{51,54} found that those alcohols which are soluble in water in all proportions exhibit a minimum in the plot of nmr shift versus mole fraction which was attributed to an initial structuring followed by a structure breakdown as the alcohol concentration increased. ^tButanol produced the largest downfield shift in the alcohol series and the ^tbutanol molecule was assumed to fit snugly within the water lattice and at the same time 'tighten up' the hydrogen bonding or increase the amount of it around the alcohol molecule resulting in an initial downfield shift. There is a limit to the amount of structuring possible within the water lattice and once this is reached no further increase is possible. As more alcohol is added there are insufficient water molecules available to form hydrogen bonded units and a net breakdown of structure results and hence a subsequent upfield shift.

This explanation is less compelling in the case of methanol which also causes a shift to low field but does not



contain a bulky group. Contributions to the shift may come from the acid/base effect discussed earlier in Section A.1.5 and this possibility was studied by Kingston and Symons⁵³ by monitoring the effect of temperature. They concluded that the ^tbutanol effect was almost entirely structural in nature but that the methanol/water system had a large acid/base contribution and a small structural interaction.

Studies of water and ^tbutanol using the first overtone infrared region⁵⁵ showed a clear loss of (OH)_{free} groups on initially adding the alcohol, followed by a region of insensitivity. The alcohol was assigned the role of structure maker as its action paralleled that caused by a decrease in temperature.

Despite Bonner's claim⁴⁴ that the $V_2 + V_3$ combination band of water was particularly useful for studying the effect of addition of alcohols as there was no interference from the alcoholic OH groups, he looked at only one alcohol, 1-pentanol, and identified 1:1 and 1:2 water:alcohol complexes.

Waddington⁵⁶ studied the effects of four alcohols on the OD stretch of D_2O in H_2O in the infrared, but found little or no shift in the band position. This was because the oxygen atom of water bonded to the OD oscillator was replaced by an oxygen atom of alcohol and this was unlikely to have any dramatic effect on the OD oscillator frequency.





A.2.2 Near infrared results

Figures A.19 and A.20 show the effect of the addition of alcohols on the OH overtone spectrum of HOD in the near infrared. Addition of the alcohols causes a marked decrease in the band at 7120 cm⁻¹ assigned to $(OH)_{free}$ oscillators. Although the drop varies slightly between alcohols, (see Figure A.21) it is within the rather large experimental error and is not considered to be important. The loss is comparable to that caused by addition of base, reported in Section A.1.2, and suggests that the alcohols are acting as mono-bases.



added alcohol.

Water has an equivalent number of OH groups and lone pairs and can be considered as dibasic and diacidic but the alcohols differ markedly in that they have only one OH group and two lone pairs. Whilst water at room temperature contains a percentage of $(OH)_{free}$ groups, methanol has only a negligible concentration, as is shown in the near infrared region where water exhibits a peak due to $(OH)_{free}$ but no such absorbance is visible for methanol. Each molecule of alcohol has two lone pairs for every OH group so that any $(OH)_{free}$ group can immediately be scavenged by the huge excess of $(LP)_{free}$ groups to give units such as VII.



Normally, in the pure liquid, alcohols act as mono proton donors and acceptors and the effects roughly cancel but dilute alcohols in water can act as di-proton acceptors on demand, because of their second lone pair group and the molecule then appears to be acting as a mono base.

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VII

A.2.3 NMR Results

The problem of the rate of OH proton exchange for aqueous solutions of alcohols has recently been overcome⁵⁷ by using low temperatures and largely deuterated solvents. The results for some simple alcohols are shown in Figure A.22 which displays the low field shifts of the water protons. Figure A.23 shows both the water proton resonance and the methanol proton resonance as a function of the mole fraction of methanol. Thus, although previously, the initial downfield shift on addition of alcohol had been assigned to the water protons⁵¹⁻⁴, it had not been established experimentally.

In all cases the ROH resonance is to low field of the water resonance and this can be understood if the alcohols are considered to be more acidic than water and hence form stronger hydrogen bonds to a given base. This would also explain the observation that both resonances shift overall to high field on going from water to alcohol. The water protons in an alcoholic environment are more basic and are therefore to highfield of those in water and the alcohol OH protons in an aqueous mixture are more acidic and therefore are shifted to low fields. There is however no clear agreement on the relative basicities of water and alcohols and in fact Taft et.al.⁵⁸ have reached the opposite conclusion.

It is important to note that the initial downfield shift of the water proton resonance observed on addition of ^tbutanol is also present on addition of methanol but no initial shift is observed for the alcohol OH resonance. Previously the low field shift of ^tbutanol had been assigned to the formation of 'clathrate cages' as at higher temperatures this shift was reduced to zero, but it is unlikely that methanol





molecules encourage cage formation.

The explanation used for the near infrared results can also be used to understand the nmr results. If the alcohol is considered to be dibasic and if the effects of mono-donating and accepting roughly cancel, then the alcohols can be considered as mono-bases.



Hence the initial downfield nmr shift can be explained by the loss of (OH) free groups as alcohol is added.

The position of the alcohol resonance downfield of that of the water resonance can partly be explained since the alcohol molecules acting as dibases will have increased acidity, resulting in a downfield shift of their OH proton resonance. Initially all the alcohols will behave in this way, scavenging (OH)_{free} groups, but as the alcohol concentration increases they will act as monobases. A.3 Aqueous solvation of amines and amides

A.3.1 Previous work

a) Amines

Strait and Hreroff⁵⁹ used the combination bands of NH_2 in the near infrared to study association of the NH_2 group of primary amines with recognized donor and acceptor solvents. A ratio, R, of the absorbances of the two band peaks due to $(NH)_{free}$ and $(NH)_{bound}$ was used to indicate the changes taking place upon association. The R value was high for protic donors, e.g. isopropyl alcohol, which interacts with the amine as the base and was much lower when the amine acted as a proton donor to solvents with π -electrons or lone-pair electrons to donate.

In nmr studies of hydrogen bonding relatively little has been done to investigate the influence of hydrogen bonding on the nmr shift of the atom which donates the electron pair in forming the hydrogen bond. Litchman et.al. 60 , 61 studied nitrogen-15 nmr for 15 NH₃ and 15 NMe₃-solvent mixtures and assumed the shifts had contributions from two types of interactions. 1) The interaction of the nitrogen lone pair electrons with solvent molecule protons and 2) interaction of solvent molecule unshared electron pairs with the amine protons. It was concluded that interactions of the first type made much larger contributions to the shifts than did the second type.

A single crystal X-ray study of solid ammonia by Olovsson and Templeton⁶² suggested that each ammonia molecule was involved in six hydrogen bonds. Each hydrogen of the ammonia molecule forms a hydrogen bond and the free electron pair forms three.

In the infrared region, hydrogen bonding of primary and secondary aliphatic amines has been studied 63,64 using the NH stretching vibration. Hydrogen bonded and free NH groups are observed for the amines in CCl₄ whereas the overtone spectra only contains an absorbtion due to free NH groups except at the lowest temperatures.

Falk⁶⁵ studied the infrared spectrum of dilute HOD in the solid and liquid trimethylamine hydrate, $Me_3N.10\frac{1}{4}H_2O$. The OD band differed only slightly from that in liquid water, showing the same distributions of hydrogen bond strengths in the two media.

Hydrogen bonding between amines and alcohols in the gas phase was studied by Hussein and Millen⁶⁶ as it had the advantage of being free of lattice vibrations or solvent interactions and provides the possibility of observing fine structure. Frequency displacements of the OH stretching vibration provided a measure of the relative electron donating abilities of the free amines in the order $\text{Et}_3\text{N} > \text{Et}_2\text{NH} \simeq \text{Me}_3\text{N} > \text{Me}_2\text{NH} > \text{Et}\text{NH}_2 >$ MeNH₂ > NH₃.

b) Amides

Hinton and coworkers⁶⁷⁻⁷⁰ have undertaken extensive studies of aqueous amide solutions using nmr spectroscopy. With the exception of formamide, the first addition of amide to water produces a low field shift in the water resonance position, indicative of structure promotion or a 'tightening' of water hydrogen bonds. Following the model of Glew⁵⁰ used to explain the structure promotion observed with dilute aqueous nonelectrolyte solutions, the enhanced hydrogen bonding between water molecules was explained by solute molecules stabilizing adjacent water into ordered, hydrogen bonded shells. Also competing is a high field shift caused by amide molecules hydrogen bonded to water since it is assumed that the wateramide hydrogen bond is not as strong as the water-water hydrogen bond.

The shifts measured are the weighted average of these two effects and the results would suggest that the interstitial effect dominates on first adding the amide followed by a net structure breaking effect with increased amide concentration. Although the data for the formamide system do not indicate the presence of interstitial formamide molecules this does not mean they do not exist. Because of its small size it is possible that no water expansion has to take place and therefore only structure breaking is observed.

For all systems except N-methylformamide, N-methylacetamide and N-ethylformamide the high field shift was continuous on addition of amide. However, for the above three amides a dramatic low field shift was observed at low field concentration which would indicate well-ordered, tightly bonded water molecules, but was not explained by Hinton.

A difference was also noted in the shifts for the cis and trans NH protons of formamide, acetamide and propionamide in aqueous solutions. (The designation is relative to the hydrogen or alkyl groups on carbon.) The shift of the trans proton is affected most and although both cis and trans protons shift to high field, the difference would suggest stronger hydrogen bonding at the cis position.

Hydrogen bonding at the carbonyl oxygen was suggested by the resonance position of the carbon nucleus shifting to low field in aqueous formamide relative to pure formamide.

A.3.2 NIR results for amines and amides

Figures A.24-26 show the effect of the addition of amines and amides on the OH overtone spectrum of HOD in the near infrared. Of the three amines studied, triethylamine has already been mentioned in Section A.1.2, as showing a loss of $(OH)_{free}$ groups consistent with the other mono-bases. Diethylamine produced a similar loss in the $(OH)_{free}$ peak but also a gain at ~6550cm⁻¹ which is probably due to $(NH)_{free}$ groups as diethylamine dilute in CCl₄ gives a peak at 6530cm⁻¹. The addition of n-butylamine also showed a loss in the $(OH)_{free}$ region and the growth of a new peak at 6600cm⁻¹. The results suggested the three amines were acting as mono-bases and the NH groups were not involved with bonding to the water.

Formamide, n-methylformamide, dimethylformamide, acetamide, n-methylacetamide and dimethylacetamide were the amides used in this study. Dimethylacetamide (DMA) and dimethylformamide (DMF) have already been mentioned (Section A.1.2) as acting as monobases. Formamide produces a loss of $(OH)_{free}$ consistent with a mono-base but also shows a gain of a peak at ~6800 cm⁻¹. Similar spectra were obtained for n-methylformamide, acetamide and n-methylacetamide which showed losses in the $(OH)_{free}$ region and the growth of new peaks in the 6400 - 6800 cm⁻¹ region.

The C=0 group is presumed to act as a base and bond to $(OH)_{free}$ groups but it could be acting as a mono-base or as a di-base in different circumstances depending upon concentration and steric hindrance.

An explanation of the spectra can be obtained by considering the amides to act as mono-bases with the $\sum C=0$ bonding to $(OH)_{free}$ groups and the NH groups remaining free







and producing peaks in the $6400 - 6800 \text{ cm}^{-1}$ regon. However, the NH groups would be expected to bond to the lone pairs of the oxygen of the water molecule, generated by the OH groups bonding at the carbonyl group.

In the case of formamide and acetamide, if just one NH group bonds there will still be a NH group free and responsible for the peaks appearing in the spectrum. In the cases of n-methylacetamide and n-methylformamide where there are growths in the (NH)_{free} region it is possible that the (LP)_{free} groups of water are not able to bond with the NH groups on the amides due to steric hindrance by the adjoining methyl group.

However, for the spectra to show a loss of (OH) free groups consistent with the monobase line, formamide and acetamide must be acting as di-bases, although why they should do this, is not obvious.



It is possible that the lone pair of the nitrogen could be bonded to OH groups and this is more likely for formamide and acetamide which do not have methyl groups bonded to the nitrogen and this would relieve the C=0 group of being di-basic.



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A.4 Aqueous Urea Solutions

A.4.1 Previous work

It has been recognized for some time that aqueous solutions of urea possess remarkable properties, e.g.enhancing the solubility of hydrocarbons⁷¹, affecting the conformational properties of a wide range of water-soluble polymers.^{72,73} Urea is extensively hydrogen bonded in the solid state⁷⁴, and has a suprisingly high solubility in water (>20M at 25°)⁷⁵ with which it forms almost ideal solutions^{76,77}.

The interest in aqueous urea solutions stems from the ability of urea to 'denature' biologically active molecules notably proteins. Kauzmann recognised the tendancy of non-polar side chains of proteins to adhere to one another in aqueous solutions, i.e. form hydrophobic bonds, and suggested that this could be an important factor in the stabilisation of particular conformations of polypeptide chains⁷². The denaturation of proteins by urea is thought to be brought about by the destruction of hydrophobic bonds caused by urea destabilising the water structure.

Two different approaches have been used to account for the observed physical properties of urea-water mixtures. Stokes⁷⁶ used the idea of urea association, which in dilute solutions postulates urea dimerization as the dominant process, and at higher concentration the stepwise addition of urea occurs.

MacDonald⁷⁸ studied the effect of urea on the fluidity of water, concluding that urea acts as a structure breaker, and that the concentration dependance of the results suggested clustering of urea at 2 Molar and above. This agrees with the work of Vold et.al.⁷⁹ who studied acid- and basecatalysed protolysis in urea solutions by nmr techniques and found evidence for aggregates of urea at 2-3 molar concentrations.

X-ray diffraction studies by Adams⁸⁰ of aqueous solutions of urea indicated urea-urea interactions at large urea concentrations but association was considered extremely unlikely at low concentrations.

The second model is that of Frank and Franks⁷¹ who assume water to be described as a mixture of distinguishable species, co-existing in equilibrium and mixing ideally. $(H_2 0)_{bulky} \longleftrightarrow (H_2 0)_{dense}$ Because of its geometry, urea is unable to be incorporated into the tetrahedrally hydrogen bonded bulky species but is allowed to mix with the dense species. It acts as a diluent and the effect is counteracted by a shift in the equilibrium from left to right. Urea has reduced the degree of water-water bonding without replacing it by any urea-water hydrogen bonds.

Finer et.al.⁸¹ used their nmr shift and relaxation results to try and distinguish between the two models. The upfield shift of the water proton and slight downfield shift of the urea proton resonance on increasing the urea concentration were evidence for slight long range structure breaking tendancies and negligible self-association of urea. The upfield shift of the urea resonance on increasing the temperature suggests the existence of some urea-water interactions but these are probably short-range and short-lived. The conclusions fit the model of Frank and Franks with urea displacing the water equilibrium from a bulky species with

long range order to a dense species with only short range structure. Urea closely resembles water in its ability to form hydrogen bonds but has the wrong geometry to take part in extended water structures.

Subramanian et.al.⁸² studied urea/water solutions by nmr spectroscopy and found that relative to pure water, the water proton resonance shows no shift up to an urea concentration of 7M. Addition of urea to water causes neither promotion nor destruction of the solvent structure and the urea molecules may simply be accommodated in the bulk water clusters via urea-water hydrogen bonds.

Vold⁸⁴ used nmr spectroscopy to measure the chemical shifts of the water proton resonance in a variety of aqueous solutions of urea-related compounds. The results are displayed in Figure A.27.

Wen and Hertz⁸⁵ added urea to the $H_2O/^tBuOH$ system being studied by nmr spectroscopy. The downfield shift of the proton resonance was enhanced by addition of urea. Kingston⁸⁶ examined the system further and concluded that addition of the urea causes the water structure to be broken down and the ^tbutanol can have a greater effect on forming new structure.

Barone et.al.⁸⁷ extended the work of Finer⁸¹ to include alkyl ureas. In all the cases studied the water signal was initially shifted downfield before moving back towards the value for pure water and then upfield.

Although a large amount of work has been carried out on aqueous urea systems the effect of the solute on the hydrogen bonding in water, often expressed as 'structure making' or 'structure breaking' is still subject to a great



deal of controversy. Support for urea as a 'structure breaker' is given by the raman studies of Walrafen⁸⁸ and the near infrared work of Barone, Rizzo and Vitagliano⁸⁹. The majority of workers would agree with this view but Abu-Hamdiyyah⁷⁵ favours structure making although his paper and the whole concept of structure making and breaking has been seriously questioned by Holtzer and Emerson⁹⁰.

James and Frost^{91,92} studied the effect of urea on the librational band of water and suggested urea bonded to water through its four hydrogen atoms and carbonyl oxygen and is suited by symmetry to fit into the water structure although its size is rather larger than that of water.

Swenson⁹³ studied the effect of urea and related compounds on the OD stretch of HOD in the infrared, but found only minor shifts in the band position. This indicated that the strength of the hydrogen tond interactions between solute and water molecules are similar to those between molecules in pure water.

A.4.2 NIR results for urea and two derivatives

Figures A.28 and A.29 show the effects of 1,3 dimethylurea and tetramethylurea on the OH overtone spectrum of HOD in the near infrared. Of the three urea derivatives studied, urea gives a slight increase in the $(OH)_{free}$ peak, 1,3-dimethylurea gives a loss consistent with a mono-base and tetramethylurea gives a greater loss. The first two compounds also show a peak growing at ~6800 cm⁻¹. Urea is presumed to behave as a base at the c=0 group and bond to either one or two $(OH)_{free}$ groups. The NH groups are also available for bonding to lone




pairs on the oxygen of the water molecule. The following scheme is suggested,



to explain the overall loss or gain in the $(OH)_{free}$ peak and the appearance of the $(NH)_{free}$ peak.

SECTION B

AQUEOUS SOLVATION OF ELECTROLYTES

Introduction

Aqueous solvation of electrolytes was studied by monitoring the spectral changes caused on their addition to water. Investigation of the near infrared OH stretch of water was the main technique used but results from other branches of spectroscopy were considered when drawing conclusions.

B.1 Infrared Studies

B.1.1 Previous work

As in the study of non-electrolytes, inert media can be used for studying solvation by a single solvent molecule but it is difficult to extend the results to bulk solvents. Kuntz and Cheng⁹⁴ have studied ionic solvation using dilute solutions of water in aprotic solvents. Infrared bands were detected for OH---anion and cation---OH---solvent interactions and association constants calculated.

Unfortunately the infrared spectra of electrolytes in bulk water are not very informative as the bands are very broad envelopes and no definite conclusions can be drawn.





Isotopic dilution by D₂O does simplify the spectra, but except in one or two special cases, addition of electrolytes does not produce any dramatic effect.

The information available has been summarised in a recent review⁹⁵ and Hartman's²³ study of HOD/D₂O/salt systems produced a shift in V_{max} of the OH oscillator for a large number of different salt solutions. The plot of shift of band maxima against concentration shows, in general, a shift to high frequency by alkali halides, the largest by NaClO₃, whereas sodium acetate produced a low frequency shift. (See Figure B.1) The general conclusion was that anions have a much greater effect than the cations and I <Br <Cl <F for order of increasing average hydrogen bond strength in solution.

While some workers believed that addition of an electrolyte caused the water structure to be broken, others suggested that the ions form new bonds to water and become hydrated.

Walrafen⁹⁶⁻⁸ studied several different bands in the Raman spectra of aqueous solutions and concluded that electrolytes caused the breakage of OH---O bonds, the bromide ion being the most effective and the cations having very little effect.

In a Raman study of electrolyte solutions, Wall and Hornig⁹⁹ found large intensity and bandwidth changes in the order $F^{+}H_{2}O^{-}I^{-}$. They concluded that there was no indication of any ion-water association leading to the changes, as would be implied by the rigid hydration model.

Wyss and Falk¹⁰⁰ studied NaCl in HOD and could find no evidence for shoulders or sub-bands in the OH peak, even at





(a) -120°C (b) room temperature.

-30° C. This indicated that the OH---Cl⁻ bond has a similar distribution of frequencies to OH---O. The large bandwidths suggest OH---Cl⁻ has a variety of energies due to the water molecules around Cl⁻ having a variety of orientations with no strong preference for any single well defined configuration.

Recent work¹⁰¹ has shown that these broad and relatively uninformative infrared spectra narrow sufficiently to give reasonable resolution on freezing to the glassy state. Generally, the OH groups bonded directly to the anions give rise to narrow components usually on the high frequency side of the band for pure solvent (Figure B.2). The cation effects are generally smaller and result in an apparent shift of the main solvent band.

Important exceptions to the uninformative, room temperature spectra mentioned above are those obtained from solutions of perchlorates and fluoroborates. These show a resolved CH stretching component on the high frequency side of the main infrared and raman band. Solutions of perchlorate with different cations give the same effect and the band increases in intensity as the perchlorate concentration is increased. The perchlorate and fluoroborate solutions show a difference of 16 cm^{-1} in the resolved peak position suggesting that the bond strength is dependant upon the anion. The peak has been assigned to $(OH)_{\text{free}}$ groups, 102,103to OH groups weakly bonded to the anions, 104,105 and to both 106.

Walrafen¹⁰² suggested the peak was due to $(OH)_{free}$ groups because HOD solutions exhibit a band in nearly the same region that grows strongly on warming and is assigned to $(OH)_{free}$ groups. Walrafen thus concluded that perchlorate

ions are 'structure breakers'.

However other workers have favoured the suggestion that the high frequency band is associated with water solvating perchlorate ions. This is supported by crystallographic data for $\text{LiClO}_4.3\text{H}_20$ which points to a weak hydrogen bond between water and the perchlorate ions.

Brink and Falk¹⁰⁷ found almost identical stretching frequencies for HOD for the hydrates and aqueous solutions of NaCl0₄.H₂0 and LiCl0₄.3H₂0 which pointed to a weak hydrogen bond between water and perchlorate ion.

In an attempt to distinguish between the two hypotheses, recent work¹⁰⁶ has been carried out on the low temperature infrared spectra of perchlorate ions in methanol and water. For methanolic solutions at 120K there was no sign of the band at 3540 cm⁻¹ and it was concluded that the room temperature band was not due to $(OH)_{free}$ groups. The aqueous solutions retained the high frequency peak at low temperatures although the area under the peak was reduced by ~50%. This suggested that at room temperature the high frequency band has contributions from $(OH)_{free}$ groups and from water solvating perchlorate ions.

Worley and Klotz^{25} studied the effect of electrolytes on the near infrared spectra of HOD in D_2O . The sharp peak at 7 062 cm⁻¹ was attributed to all non-bonded OH species and the absorbance at 6 427cm⁻¹ to all OH groups in a bonded state. They expressed their results in terms of a quantity R, given by the ratio <u>Absorbance at 6 427cm⁻¹</u>. <u>Absorbance at 7 062cm⁻¹</u>.

When the temperature increased, R decreased and the ratio R was seen as a measure of water-water interaction at each temperature. When various salts were added to the HOD the ratio R changed. Worley and Klotz compared these changes with those associated with a change in temperature and produced "structural temperatures", as proposed by Bernal and Fowler⁸. If on addition of salt, R increased, the salt was called a 'structure maker', if R decreased, it was called a 'structure breaker'.

Bunzl¹⁰⁸ studied the effect of tetra-n-alkyl ammonium bromides on the water band at 10 000cm⁻¹, concluding that $(C_{4}H_{9})_{4}NBr$ and $(C_{3}H_{7})_{4}NBr$ were structure makers, $(CH_{3})_{4}NBr$ a structure breaker, and $(C_{2}H_{5})_{4}NBr$ has little overall effect.

The sensitivity of the overtone infrared spectra to added electrolytes increases with temperature and Luck¹⁰⁹ utilised this with temperatures up to 140°C, discussing the results in terms of structural temperatures.

Difference spectra are obtained by placing an aqueous solution in the sample cell and pure water in the reference cell. The mis-match in the concentration of water in each beam is corrected by using a variable pathlength cell and adjusting accordingly.

Jolicoeur et.al.¹¹⁰ used difference spectra to study aqueous solution of organic salts in the overtone region. $Bu_{\downarrow}NBr$ showed a loss in the $(OH)_{free}$ region, while NaBPh₄ showed a gain. Using the concept of Bernal and Fowler, $Bu_{\downarrow}N^{+}$ was assigned a structure maker and BPh_{\downarrow}^{-} a structure breaker. A further study¹¹¹ assigned $R_{\downarrow}N^{+}$ (R = Me to nBu) as a structure maker and noted that $T_{structural}$ decreased as the solution temperature increased.

McCabe and Fisher¹¹² used difference spectra of aqueous solutions of alkali halides versus water in the 7 000cm⁻¹ region $(\nu_1 + \nu_3)$. The spectra were resolved into

two components, one representing the hydration of the solute and the second the volume of the hydrated solute, and from these, hydration numbers were calculated.

Bonner and co-workers¹¹³⁻⁵ have investigated the $v_1 + v_2 + v_3$ band at 8 000 - 9 000 cm⁻¹ for aqueous solutions of several electrolytes and observed all cations as 'structuremakers' in the order H⁺>Li⁺>Cs⁺>Rb⁺>K⁺>Na⁺ and all anions as 'structure-breakers' in the order PF₆⁻ = Cl0₄⁻ = N0₃⁻>I>Br⁻ >Cl⁻>F⁻.

B.1.2 Near Infrared Results

The effect of various electrolytes on the near infrared spectrum of HOD in D_2O at $25^{\circ}C$ can be seen in Figures B.3-11. Isosbestic points appear at 6 $800cm^{-1}$ and are accompanied by a gain or loss in the $(OH)_{free}$ peak at 7 $120cm^{-1}$. The results can be displayed, as in Figure B.12, with the change in peak height versus concentration for many different salts. From these graphs, the change on addition of 1 molal of salt can be found and these are tabulated for all the salts studied in Table One. The value for CIO_{4}^{-} salts is not included because, as was discussed previously for the infrared data, this change is not thought to be simply a measure of $(OH)_{free}$ groups but to have a contribution from a weak bond between CIO_{4}^{-} and water which appears coincidentally in this area.

A simple model for the solvation of electrolytes can be























considered in which the cation bonding to the oxygen of water via its lone pairs will produce $(OH)_{free}$ groups and the anion bonding to the hydrogen will cause a loss of $(OH)_{free}$ groups. When an electrolyte is dissolved in water the nett effect will be either a gain or a loss in the $(OH)_{free}$ peak.

The present work began with the observation that the effect of sodium tetraphenylboride was opposite to that for the tetra-alkylammonium salts¹¹⁶. Sodium tetraphenylboride greatly enhances the $(OH)_{free}$ concentration and to a first approximation, the reason for this is that only the cations are solvated and these bond to lone pairs, generating an excess of $(OH)_{free}$ groups.



On addition of tetrabutylammonium bromide to water the anions are strongly solvated and they bond to OH groups.



The BPh₄ and $R_4 N^+$ ions are considered to have only a small effect on the concentration of $(OH)_{free}$.

This is in complete contrast with the conclusions of other workers^{111,114} who have attributed the loss of $(OH)_{free}$ to a structure-making effect of the R_4N^+ ion and have ignored the role of the anions. The results presented here disagree as they show a clear anion effect with the 1:1 electrolytes but no trend with the size of the alkyl group, R.

When measuring the change in concentration of $(OH)_{free}$ groups the same problems arise as in Section A, as a complete loss of $(OH)_{free}$ does not correspond with zero absorption at 7 120cm⁻¹. Hence the change in peak height has been measured in arbitrary units and no attempt has been made to estimate absolute values for the concentration of $(OH)_{free}$. Some of the changes measured are small, therefore errors are large and it has been necessary to use concentrations of greater than 1 molal for most salts in order to obtain reliable data.

If the changes are additive, as is suggested, then the salt shifts can be separated into contributions from each ion. With the arbitrary assumption that BPh_4^- and R_4N^+ both have slight structure breaking effects at 25°C, individual ion shifts are calculated and displayed in Table Two. The values reproduce all the salt shift data recorded, within experimental error.

It is possible to obtain rough values for solvation numbers for these ions if the spectral change is related to the first solvation shell of the ions. Using this crude approximation, it is solely the primary solvation number that controls the $(OH)_{free}$ concentration and not the strength of the bonds. Ions such as Li⁺ and F⁻ are both expected to have

TABLE ONE

Experimental changes in the peak height at 7 120cm⁻¹ of HOD

in D_2^0 at 25°C on addition of salts

Salt	Experimental char	nge Predicted char	ige Error
	for 1M solution ((cm)	
NaBPh ₄	+ 1.9	+ 1.9	
NaN03	+ 0.5	+ 0.7	- 0.2
NaF	+ 0.1	+ 0.1	
NaCl	+ 0.2	+ 0.2	
NaI	+ 0.9	+ 0.65	+ 0.25
KN03	+ 0.9	+ 0.9	
KF	+ 0.1	+ 0.3	- 0.2
KCl	+ 0.4	+ 0.4	
KBr	+ 0.5	+ 0.5	
ΚI	+ 0.8	+ 0.85	+ 0.05
CsN03	+ 0.8	+ 0.8	
CsCl	+ 0.3	+ 0.3	
CsBr	+ 0.5	+ 0.4	+ 0.1
LiCl	+ 0.1	+ 0.15	- 0.05
LiBr	+ 0.3	+ 0.25	+ 0.05
KMn04	0.0	0.0	
MeuNCl	- 0.8)		
Et ₄ NCl	- 1.0 } -	- 0.85 - 0.75	+ 0.1
Mo NBR	- 0.75)		
Et, NBr	- 0.6	- 0.48 - 0.65	- 0.17
Bu ₄ NBr	- 0.5		
MgSO4	- 1.1	- 1.13	- 0.03

Table One contd.

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<u>Salt</u>	Experimental change for 1M solution (cm)	Predicted change	Error
к ₂ so ₄	+ 0.87	+ 0.87	
Na2CO3	+ 0.35	+ 0.35	
Rb I	+ 0.95	+ 0.95	
AgN03	+ 0.65	+ 0.65	
снзсоок	- 0.05	- 0.05	
снзсооті	- 0.2	- 0.2	
KCNO	+ 0.8	+ 0.8	
KCN	+ 0.5	+ 0.5	
NaNO3	+ 0.4	+ 0.4	
K ₂ Cr0 ₄	+ 0.6	+ 0.6	

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TABLE TWO

	Ion	Individual	<u>Ion Shift(cm)</u>	Solvation Number
a)	Na ⁺	+	1.4	4.7
	к+	+	1.6	5.3
	Cs ⁺	+	1.5	5.0
	Li ⁺	+	1.35	4.5
	r ₄ n⁺	+	0.45	
	BPh4	+	0.5	
	F ⁻	-	1.3	4.3
	C1 ⁻	-	1.2	4.0
	Br ⁻	-	1.1	3.7
	I_	-	0.75	2.5
	N03-	-	0.7	2.3
ъ)	Mg ²⁺	+	1.2	4.0
	Ag ⁺	+	1.35	4.5
	Rb ⁺	+	1.7	5.7
	ті+	+	1.45	4.8
	so ₄ 2-	-	2.33	7.7
	co ₃ -	-	2.45	8.1
	CN ⁻	-	1.1	3.7
	CNO ⁻	-	0.8	2.7
	NO2	-	1.0	. 3.3
	Mn0 ₄ 2-	-	1.6	5.3
	Cr04 ²⁻	-	2.6	8.7
	CH3COO-	-	1.65	5.5

•

-

solvation numbers close to four, so if a value of +3 units is assigned to the gain or loss of one $(OH)_{free}$ group then the solvation numbers of Table Two are derived.

These results are in agreement with the studies of non-electrolytes in Section A, as the loss of (OH)_{free} calculated for the chlorine ion is four times that previously noted for the mono-bases. Considering the simplistic approach used, reasonable solvation numbers have been obtained which bear comparison with the results of other workers.

A more sophisticated approach would consider the possibility of a cation such as Mg^{2+} bonding to both lone pairs of the oxygen, hence liberating double the number of $(OH)_{free}$ groups.



Previous workers¹¹⁷ have found the nitrate ion to be assymmetrically bonded. The oxygens may be bonded to none, one or two OH groups and the value of 2.3 quoted here suggests some combination of these different possibilities.



Many of the workers quoted previously in this Section do not calculate solvation numbers from their spectroscopic studies but are content merely to quote changes in 'structural temperature' or to classify salts as structure-makers or breakers.

However, comparisons can be made with results obtained in other areas of chemistry. The neutron diffraction studies of Soper et.al.¹¹⁸ produced a solvation number for chlorine of between five and six. The X-ray diffraction results of Licheri et.al.¹¹⁹ suggest that six water molecules are octahedrally displaced about the bromine ion and Maeda et.al.¹²⁰ suggest solvation numbers of four and six for sodium and iodide ions respectively. Narten and coworkers¹²¹ suggest solvation numbers of six for chlorine and four for iodide whilst Licheri et.al.^{122,123} give values of six or eight for calcium, six for chlorine and six for bromine.

The results quoted here are comparable with those found by other workers and it would appear therefore that this method does have some contribution to make to furthering the study of the solvation of electrolytes, despite the many potential sources of error and the very simplistic approach used.

B.2 Near Infrared Spectra for Methanolic Solutions

The overtone region for methanol solutions is less useful to study because of the absence of any resolved peaks assignable to (OH)_{free} groups. This is because of the scavenging of potentially free OH groups by the huge excess of 'free' lone pairs to give structures such as

Figure B.13 shows the effect of temperature on the OH stretching overtone of CH_3OH in CD_3OD . No clearly defined $(OH)_{free}$ peak is visible (cf. the peak at 7 120cm⁻¹ for $(OH)_{free}$ in HOD), merely a plateau region (6 800 \rightarrow 7 200cm⁻¹) similar to that associated with $(OH)_{weakly bound}$ in the water spectrum.

Addition of NaBPh₄ results in a broad peak at 7 010cm^{-1} . It seems unlikely that BPh₄ would form hydrogen bonds with methanol, but Na⁺ can bond to the methanol lone pair, thus creating an excess of OH groups. These can bond to the methanol chains as shown (\vee III) and the 7 010cm^{-1} band is assigned to the OH groups marked \ll .

Addition of sodium perchlorate to methanol produces a relatively narrow band at 7 050 cm⁻¹ which is assigned to OH groups bonded to ClO_4^{-} ions. This is weaker, but better defined than the \propto band probably because the negative charge helps to make the bonding more precise.



On Structure Making and Breaking

Since Bernal and Fowler⁸ introduced the term 'structural temperature' the effects of electrolytes and non-electrolytes on the properties of water have often been discussed in terms of 'structure-making' and 'structure-breaking' which correspond to a fall or rise in temperature. The results presented here are not expressed in terms of equivalent temperatures as the concept is believed to be unsatisfactory and incorrect conclusions can be drawn.

'Structure-making' is generally defined by vibrational and nmr spectroscopists as causing a loss of (OH)_{free} groups and a 'structure-breaker' as a generator of (OH)_{free} groups.

When water is heated the structure is genuinely broken as the increase of $(OH)_{free}$ groups is equal to the increase in $(LP)_{free}$ groups. However, on addition of a base the $(OH)_{free}$ groups are scavenged, producing an excess of $(LP)_{free}$. Infrared techniques studying the concentration of $(OH)_{free}$ groups would deduce that 'structure-making' had occurred, but had attention been focused on $(LP)_{free}$, 'structure-breaking' would have been declared.

Similarly on dissolving an electrolyte in water, cations scavenge $(LP)_{free}$ groups and anions scavenge $(OH)_{free}$ groups, the nett effect depending on the solvation number of the ions. On dissolving R_4 NCl salts in water there is a marked fall in $(OH)_{free}$ concentration compared to an increase for NaBPh₄. The overall reason to a first approximation is that for R_4 NCl only the anions are strongly solvated and bond to OH groups while for NaBPh₄ only the cations are solvated, bonding to lone pairs and generating $(OH)_{free}$. Obviously the terms 'structuremaking' and 'structure-breaking' are misleading, as, if attention had been focused on (LP)_{free} the signs of the equivalent temperatures would be reversed.

SECTION C

SOLVATION OF IODIDE IONS

Introduction

The solvation of iodide ions has been studied using ultraviolet and infrared spectroscopy.

Addition of a protic solvent to iodide ions in methyl cyanide was monitored using the OH oscillator of the cosolvent in the infrared and the charge transfer to solvent spectra of the iodide ions in the ultraviolet region.

Attempts have been made to calculate equilibrium constants from the spectra and the two methods are consistent within experimental error.

The addition of certain solvents to aqueous iodide was investigated and attempts made to understand the causes of solvent and salt shifts.

C.1 Ultraviolet Studies

C.1.1 Previous work

Although early spectroscopic studies of solvation were mainly in this area, ultraviolet spectroscopy has not been very widely or significantly applied to the study of aqueous solutions. Probably the most studied system is that of aqueous iodide ions.

The ultraviolet absorption spectrum of iodide in solution

contains a well resolved doublet which has been shown¹²⁴ to be due to transfer of an electron from the ion to the surrounding solvent. Hence the spectrum belongs to the general group known as charge transfer to solvent (C.T.T.S.) spectra.

Since the ground state is the solvated ion, it is considerably influenced by the solvent as is the excited state in which the solvent plays an integral part. Thus, C.T.T.S. transitions are unusually environment-sensitive and consequently are useful to probe changes in solvent structure with temperature, pressure and on addition of solvent or solute.

An important advantage of C.T.T.S. spectra is that information is obtained for a single ionic species, in contrast with many studies of salt solutions in which problems arise when assigning contributions from cations and anions.

A review of experimental findings and theoretical models for C.T.T.S. transitions was published by Blandamer and Fox¹²⁵ and although a large amount of data is available the proposed models are only moderately successful. The two main classes of models used in quantitative treatments will be only briefly mentioned. All models have the common concept of the excitation of an electron originally on the ion into a new orbit extending over a region of solvent molecules. Both classes of models use the same cycle as their starting point and assume that the arrangement of solvent molecules around the ion is the same in both the ground and excited states.

$$I^{-}(H_{2}O)_{x} \xrightarrow{E_{1}} (H_{2}O)_{x} + I^{-}_{gas} \xrightarrow{E_{2}} (H_{2}O)_{x} + I^{-}_{gas} + e^{-}_{gas}$$

$$\downarrow E_{max} \qquad \qquad \downarrow E_{3} \qquad \qquad \downarrow E_{3}$$

$$(I^{-} + e^{-})(H_{2}O)_{x} \xleftarrow{E_{4}} - I(H_{2}O)_{x} + e^{-}_{gas}$$

From the cycle it follows that,

 $E_{max} = E_1 + E_2 + E_3 + E_4$

The <u>diffuse</u> model proposed by Stein and Treinin¹²⁶ produces the following equation for an aqueous solution at $25^{\circ}C$.

$$E_{max}$$
 (eV) = I.P. $-\Delta H_s^0(I) + (17.8e^2/R_d) - 36.4$

where I.P. = ionisation potential of the iodide ion.

 $\Delta H_{S}^{O}(I)$ = Enthalpy of solvation.

 R_d = radius of solvent cavity.

The important term is the third one which contains a radius parameter defining the ionic cavity, this being characteristic of the ground state.

The <u>confined</u> model proposed by Smith and Symons¹²⁷⁻⁸ produces an equation of the same form but much simpler.

$$E_{max} = I.P. + \frac{h^2}{8mr_0^2}$$

where I.P. = ionisation potential of the iodide ion.

h = Planck's constant.

m = mass of the electron.

 \mathbf{r}_{o} = radius of the potential energy well.

The excited electron was placed within a potential energy well with infinitely steep walls. Thus in this case E_{max} depends



on the radius of the potential energy well defining the excited state and on the ionisation potential. The expression for E_{max} contains no terms which relate to the ground state.

The two models differ as to whether alterations in E_{max} can be attributed to changes in the ground or excited state and as to the extent to which the excited state is localised. R_d in the diffuse model is the distance between the ion-centre and the inside edge of the solvent molecules whilst r_o is the distance between the ion centre and the inner surface of the potential energy well.

Quantitative treatments of C.T.T.S. spectra have, mainly, attempted to correlate the variation of E_{max} with changes in temperature, pressure and solvent. Little attention has been given to bandwidth and intensity.

Bandwidth is governed by the range of ion-solvent structures present and can be taken as a measure of precision of solvation, the narrower the band, the more precise the solvation. Widths increase with temperature in parallel with the shift in E_{max} as hydrogen bonds become longer and the number of different units increases.

Dependance of E on solvent

E_{max} for iodide shows extreme sensitivity to solvent as shown in Figure C.1. In general, ions in protic solvents exhibit high energy bands compared to aprotic solvents.

Dependance of E on temperature

The sensitivity of the absorption maxima to temperature is the most notable feature of C.T.T.S. spectra. E_{max} shifts to lower energies with an increase in temperature. Shifts are linear and C.T.T.S. spectra for a given ion in a given solvent can be characterized by the slope in dE_{max}/dT . Figure C.2 shows that solvents giving a low E_{max} have a large dE_{max}/dT and vice versa. This can be explained using a model in which ion-solvent separation varies with temperature and controls the energy of the transition. The proton donating solvents form short hydrogen bonds to iodide which are only slightly affected by temperature whereas solvents forming only weak hydrogen bonds can move further away from the ion at high temperatures.

Dependance of E on Pressure

Changes in pressure at constant temperature produce linear shifts with the exception of aqueous solutions¹²⁹. The shifts are to high energies as the pressure increases and can be interpreted simply as a compression of the solvent cage surrounding the ion.

For aqueous solutions, after an initial 'normal' shift the pressure effect is reduced. The iodide ion seems to be buffered against more pressure changes in an unusual manner, possibly due to the three dimensional structure of water.

Effect of added co-solvent

The absorption spectra in mixed solvents show a gradual transition between the values of E_{max} for the two pure solvents¹³⁰. A plot of E_{max} against mole fraction is not a straight line and suggests that generally, iodide prefers an


environment having a different composition from that of the bulk mixture.

The behaviour of aqueous solutions is more complex¹³¹ as shown in Figure C.1. The sharp initial high energy shift caused by the addition of dioxan has been interpreted as an increased precision in the way water surrounds each ion as the iodide is forced into a special type of water lattice and also as a loss of one water molecule from the solvation shell causing the remaining hydrogen bonds to become stronger.

Addition of low concentrations of ^tbutyl alcohol shifts the absorption band to high energies¹³² and narrows it in a way which closely resembles that of lowering the temperature. A limit is reached at ca. 0.05 mole fraction of alcohol and no further changes occur until there is an excess of alcohol. This has been interpreted as a tightening of the iodidehydrogen bonds as solvation becomes more specific.

The causes of these, and other, solvent shifts will be discussed later in more detail.

C.1.2 Ultraviolet work and results

The system chosen to probe the causes of solvent shifts was iodide in methyl cyanide (MeCN) with added protic solvent. Methyl cyanide was considered suitable as it is a basic, aprotic solvent which is transparent in the ultraviolet. Methanol, water and ethylene glycol were used as the protic solvents and methylene chloride was used as a nearly inert aprotic solvent for comparative purposes.

When a solute is dissolved in two solvents the spectra of the solute gradually changes from that observed in one pure

Figure C.3 Effect of added methanol on the first CTTS band of I⁻ ions in methyl cyanide. (Mole fraction of added methanol a) 0 b)0.005 c) 0.01 d) 0.02 e) 0.05 f) 0.06 g) 0.12 h) 0.17)







solvent to the other. There are two limiting ways in which this change may occur. Firstly, the absorption spectrum may gradually shift from its position in one pure solvent to its position in the other without any sudden changes in band shape or position and is described as a "band shift". Secondly, the initial absorption spectrum may be seen to decrease at the expense of a new band and an isosbestic point will be generated suggesting an equilibrium between the two species responsible for the two bands.

The C.T.T.S. spectrum for iodide (0.5×10^{-5} M KI) in methyl cyanide at 25°C is a Gaussian band with a maximum at 40 700cm⁻¹ as shown in Figure C.3. (E_{max} for the low energy component of the doublet was monitored, it being assumed that E_{max} for the high energy band behaves in a similar manner.) Great care had to be taken when running these spectra as they are so susceptible to minute changes in solvent composition and temperature. The weighing of the stock and sample solutions was accurate to 0.001g and reference solutions were prepared with equal accuracy and to the same composition as the sample solution but omitting the iodide. Each set of spectra were run using the same stock solution to try to eliminate inaccuracies.

Addition of low concentrations of protic solvent resulted in a loss of the band at 40 700 cm⁻¹ and the growth of new bands at higher energies, with the generation of isosbestic points. The results can be seen in Figures C.3-C.5. Further additions of the protic solvents resulted in shifts to higher energies as shown in Figure C.6.



Mole fraction of cosolvent

C.1.3 Discussion

The MeCN and MeOH system

The C.T.T.S. band for iodide in methyl cyanide at 40 700cm⁻¹ at 25°C was rapidly lost on addition of small concentrations of methanol and a new band was generated at 41 900cm⁻¹. Even before this second band was fully developed, a further band began to appear at ca. 43 000cm⁻¹ but was never very well defined as further additions of methanol shifted the peak to higher energies.

The band at 41 900cm⁻¹ was assigned to an iodide ion hydrogen bonded to one methanol molecule and the second band at ca. 43 000cm⁻¹ to an iodide ion hydrogen bonded to two methanol molecules. After 0.3 mole fraction of methanol the shift became linear and no evidence could be found for the gain or loss of individual bands.

The initial shift of $1 \ 200 \text{cm}^{-1}$ and the overall shift of $4 \ 700 \text{cm}^{-1}$ tempts one to suggest a solvation number of four for iodide. This is however, too simple a situation and one has to consider that secondary and tertiary solvation must have an effect on the strengths of the hydrogen bonds formed to iodide.



Evidence for this comes from recent work on the low temperature infrared spectra of electrolytes in methanol¹³³⁻⁴. The OH peak for a single methanol molecule bonded to a halide ion was in a different position from the OH peak due to methanol bonded to the same ion in bulk methanol. Also in a very concentrated solution a number of bands were found on either side of that obtained from dilute solutions. It was inferred from these results that as primary solvation increased, the hydrogen bonds became weaker, whereas an increase in secondary solvation caused stronger hydrogen bonding by methanol molecules directly bound to the ion. It is likely therefore that successive additions of primary solvent molecules will produce progressively smaller shifts but these will be increased by the addition of secondary methanol molecules. There is also no reason to suppose that primary solvation has to be complete before secondary solvation commences.

Hence the trend to high energies between 0.3 and 1.0 mole fraction of methanol is attributed to successive additions of primary, secondary and even tertiary methanol molecules.

The MeCN and H₂O system

Addition of small concentrations of water produced a similar effect to the addition of methanol although the presence of a second new band was less convincing. The first new band appeared at 41 500cm⁻¹ which was less than the initial shift for methanol. This suggests that water forms a weaker hydrogen bond to iodide than does methanol but one has to consider that the water molecule also forms a bond to the methyl cyanide which will weaken the bond to the iodide ion. That is to say that MeCN---HOH---I⁻ appears weaker than MeOH---I⁻ but this does not mean that HOH---I⁻ and MeOH---I⁻ would be so different.

The values for the C.T.T.S. peak positions of iodide in bulk methanol (45 350 cm⁻¹) and bulk water (44 300 cm⁻¹) also suggest that iodide forms a stronger bond with bulk methanol than with bulk water but this may arise because of a smaller primary solvation number.

The initial shift of 800cm^{-1} compared with the total shift of 3 600cm^{-1} would suggest a solvation number of 4.5 but here again secondary and tertiary solvation affects the shift by increasing the strength of the hydrogen bonds to iodide.



The linear shift between 0.3 and 1.0 mole fraction of methanol was not observed for water. In the 0.8 to 1.0 mole fraction of water region, no shift was observed except for a slight shift to high energy in the region close to pure water. This was in agreement with previous results for other aqueous systems and will be discussed later.

The MeCN and (CH₂OH)₂ system

The addition of ethylene glycol was studied because of the possibility of finding evidence for chelation. As the initial amounts of glycol were added an isosbestic point was observed but the initial shift in band maxima was far more rapid than for methanol or water (Figure C.5 and C.6)

The new band at \sim 42 550cm⁻¹ with a shift of 1 850cm⁻¹. from the methyl cyanide value was assigned to structure (a) with a small contribution from structure (b).



The initial rapid shift, almost complete by 0.5 mole fraction was was thought to be caused by the chelate effect. The interaction of iodide with one molecule of glycol will produce two hydrogen bonds giving a greater shift. Loss of a glycol molecule is much less likely because both hydrogen bonds have to be broken.

The CH₂Cl₂ and MeOH system

This system was studied to provide a contrast with the previous ones as methylene chloride probably forms weak hydrogen bonds with iodide but methanol forms clusters in preference to bonding with methylene chloride.

The iodide peak at 40 800cm^{-1} in pure CH_2Cl_2 disappeared rapidly on addition of methanol and the high energy shift gave no suggestion of an isosbestic point. This suggests that the iodide ion interacts with a methanol cluster rather than individual molecules. The overall shift behaviour is shown in Figure C.7.





C.2 Infrared Studies

C.2.1 Infrared work and results

Infrared spectra were run of the system studied above in order to confirm the proposed assignments. Different solutions were used as the iodide concentration had to be increased and isotopic dilution of water was necessary for reasonable spectra to be obtained.

The OH stretching bands for water, methanol and ethylene glycol in MeCN are shown in Figure C.8. The two hydrogen bonds of the MeCN---HOH---NCMe unit (3570 cm^{-1}) are seen to be weaker than the single hydrogen bond of the MeOH---NCMe unit (3540 cm^{-1}) . On addition of $R_4 \text{ N}^+\text{I}^-$ new bands appear at 3440 cm^{-1} for water and 3380 cm^{-1} for methanol, indicating a stronger bond between iodide and methanol than between iodide and water and confirming the C.T.T.S. results, although it is recalled that the comparison is between MeOH---I⁻ and MeCN---HOH---I⁻.

Ethylene glycol in MeCN has a band at 3530cm⁻¹ which on addition of iodide ion shifts to 3450cm⁻¹, a much smaller shift than the other two systems. This is more evidence for chelation, since when an anion forms hydrogen bonds with two solvent molecules the strength of each hydrogen bond will be reduced.

C.2.2 Equilibrium constants

Attempts were made to calculate equilibrium constants from the ultraviolet and infrared spectra for the reaction,

 $I^{(MeCN)}_{x}$ + ROH \leftarrow $I^{(MeCN)}_{x-1}$ (ROH) + MeCN

Figure C.8 Infrared spectra of methyl cyanide/ protic solvent systems on addition of iodide ions.

a) MeCN/H₂0
 b) MeCN/H₂0/I⁻





Using the method of Ryall¹³⁵, and assuming that the concentration of methylcyanide is effectively constant,

$$K = [I^{-}(ROH)]$$
$$[I^{-}][ROH]$$

From the ultraviolet spectra, the loss of intensity of the $I^{-}(MeCN)_{x}$ band and the gain in intensity of the $I^{-}(MeCN)_{x-1}(ROH)$ band were used to calculate K. In the infrared the loss of intensity of the ROH---NCMe band and the gain in intensity of the ROH---I⁻ band were used. But due unfortunately to overlapping bands the intensities of these peaks could not be read directly from the spectra and Dupont Curve Analyser had to be used to obtain bands which when increased or decreased, combined to reproduce the experimental spectra. It was the intensities of the deconvoluted peaks which were used in the calculations.

In all cases several different spectra were used to calculate the equilibrium constants and it is the average value for each system which appears in Table 3. (More details of the calculations are to be found in Appendix 3).

Using the procedure followed by Ryall it was extremely difficult to obtain reasonable results and great care was taken. The deconvolution of the spectra was likely to cause many errors and other overlapping bands added to the problems. For the methanol systems, the ultraviolet and infrared results were in good agreement but it was found impossible to obtain consistent and meaningful results from the infrared spectra obtained for the H_00 and ethylene glycol systems.

However, the ultraviolet data does provide us with equilibrium constants which in the case of methanol is TABLE THREE

Ultraviolet and infrared spectral data for solutions of iodide in methyl cyanide

		MeCN + MeOH	$MeCN + H_2O$	<u> MeCN + Ethylene Glycol</u>
UV Data	E [*] max/cm ⁻¹	41 800	41 500	42 550
	ΔE _{max} /cm ⁻¹	1 100	800	1 850
	** *	10	8	23
IR Data	E [*] max/cm ⁻¹	3 380	3 440	3 450
·	ΔE _{max} /cm ⁻¹	1 60	130	80
	К *	Ø	I	1

* For the band formed on the addition of a single protic solvent molecule. ** Equilibrium constant for the addition of one protic solvent to iodide.

supported by the infrared data all of which is presented in Table Three.

The results for water and methanol are similar and well within the experimental error. That the result for ethylene glycol is so much greater supports the suggestion that it forms two bonds to iodide.

It has previously been shown that $K(25^{\circ}C)$ for the formation of I⁻---HOMe in CCl_4 is ~19.0¹³⁶. This value is much larger than that quoted here due to competition from the competing hydrogen bond to methyl cyanide (MeOH---NCMe) whereas in CCl_4 the alcohol molecules are virtually free and readily available to bond to iodide. Kuntz and Cheng calculated K≈2 for I⁻ and water or methanol in MeCN using Bu_4NI but a higher value of ~9 when using LiI. The difference is probably due in part to the solvating of the Li⁺ ion.

 $Li^{(MeCN)}_{x}$ + ROH \longrightarrow $Li^{(ROH)}(MeCN)_{x-1}$ + MeCN

For the ultraviolet results presented here the salt concentration was so low (0.5 x 10^{-3} M) that the cation would have a negligible effect.

C.2.3 Water rich studies

At the water rich end of the mole fraction range the ultraviolet results for MeOH and H_2O differ, as shown in Figure C.6. As MeCN is added to I⁻ in water, there is a small initial shift to high energy before the rapid trend to low energy. In the methanol case there is an immediate low energy shift. This initial high energy shift has been observed previously for aqueous solutions with alcohols, particularly ^tbutyl alcohol¹³² and for aprotic solvents such as dioxan,

but not for the corresponding methanol solution.

Previously⁵³ the ^tbutyl alcohol result was explained using the clathrate effect as the introduction of the I⁻ ion into a well defined cage structure would produce a higher and better defined solvation shell of water molecules. However this is hardly likely to be the case with MeCN and so it is suggested that the addition of the basic cosolvent scavenges the (OH)_{free} groups in water.

 $(OH)_{bound} \longleftrightarrow (LP)_{free} + (OH)_{free}$ OH---B

so the equilibrium

$$I^{(H_2^0)}_{x} \xleftarrow{} I^{(H_2^0)}_{x-1} + (OH)_{free} IX$$

moves to the right. The loss of one molecule of water from the solvation shell will result in the remaining molecules bonding more strongly and forming a better defined shell, which will give rise to a narrower absorption at higher energy. Further additions of cosolvent gives direct solvation which results in a rapid low energy shift.

This explanation can also be used to account for the small high energy shifts in the C.T.T.S. band of iodide on addition of electrolytes¹²⁶. Tetra-alkylammonium chlorides cause a much larger shift to high energy than LiCl or NaCl. The major part of the shift is a dehydration of the I⁻ ions caused by the Cl⁻ ions. The overtone infrared studies (Section B.1.2) showed a rapid loss of $(OH)_{free}$ when tetra-alkyl-

ammonium halides were added to water as did the addition of basic solvents, generating an excess of (LP)_{free} and pushing equilibrium IX to the right. When LiCl or NaCl are used the effect of the cations interacting with the lone pair groups almost cancels the effect of the anions and hence the tetra-alkylammonium halides show a much larger effect.

APPENDIX ONE

This program calculates the change in $\% OH_{free}$ on addition of base and plots the result as the % of the initial value.

00100 /JOB

00110 JMH2, T20, CM36000.

00120 USER, JMH, JMH.

00130 CHARGE, CHEM, CHEM.

00140 FTN,L=0.

00150 ATTACH, CGHOST/UN=LIBS.

00160 LDSET, LIB=CGHOST.

00170 LGO.

00180 RETURN, CGHOST.

00190 REWIND, GRIDFL.

00200 REPLACE, GRIDFL=JMHGRID.

00210 GOT0,77.

00220 EXIT.

00230 77, DAYFILE, JMHDAY1.

00240 REPLACE, JMHDAY1.

00250 /EOR

00260	PROGRAM PLOT (INPUT, OUTPUT, TAPE1, TAPE2)
00270	DIMENSION Y(100), XJ(100), X(100)
00280	CALL PAPER(1)
00290	XMIN=1.0
00300	XMAX=0.8
00310	YMIN=0.0
00320	YMAX=100.0
00330	CALL MAP(XMIN, XMAX, YMIN, YMAX)
00340	CALL BLKPEN
00350	M=7

00360	DO 20 I=1,M
00370	F0=2.*I/100.
00380	FK=FO*FO/(1FO)
00390	NP=100
00400	DO 10 J=1,NP
00410	X(J)=1(J-1.)/500.
00420	YJ=.5/X(J)5
00424	Z=0.0*YJ
00430	A=1 .
00440	B=FK-YJ-Z
00450	C=YJ*Z-FK
00460	XJ(J) = (-B + SQRT(B * B - 4 . * A * C))/(2 . * A)
00470	Y(J)=100.*(XJ(J)-YJ)/FO
00480 · 10	CONTINUE
00490	CALL PTPLOT(X,Y,1NP,-2)
00500 20	CONTINUE
00510	CALL GRNPEN
00520	CALL GRATIC
00530	CALL BLKPEN
00540	CALL CTRMAG(10)
00550	CALL AXES
00560	CALL GREND
00570	STOP
00580	END

APPENDIX TWO

This program calculates the predicted shift of the OH proton of water on introducing a monobase.

00100 /JOB

00110 JMH2, T100, CM36000.

00120 USER, JMH, JMH.

00130 CHARGE, CHEM, CHEM.

00140 FTN,L=0.

00150 ATTACH, CGHOST/UN=LIBS.

00160 LDSET, LIB=CGHOST.

00170 LGO.

00180 RETURN, CGHOST.

00182 EXEC, LPPROC.

00184 EXEC, CCPROC.

00190 REWIND, GRIDFL.

00200 REPLACE, GRIDFL=JMHGRID.

00210 GOT0,77.

00220 EXIT.

00230 77, DAYFILE, JMHDAY1.

00240 REPLACE, JMHDAY1.

00250 /EOR

· · · · · · · · · · · · · · · · · · ·	00260	PROGRAM	PLOT(INPUT,	OUTPUT	, TAPE1	,TAPE2)	
---------------------------------------	-------	---------	-------	--------	--------	---------	---------	--

00270 DIMENSION Y(100), XJ(100), X(100)

00280 A1=1.

00290 A2=3.67

00300 A3=5.5

00310 A4=5.78

00320 A5=5.0

00330 CALL PAPER(1)

00340 XMIN=1.0

00350		XMAX=0.8
00360		YMIN=5.3
00370		YMAX=4.6
00380	20	CALL MAP(XMIN,XMAX,YMIN,YMAX)
00390		M=10
00400		F0=.04
00410		FK=F0*F0/(1F0)
00420		CALL BLKPEN
00430		NP=100
00440		DO 10 J=1,NP
00450		X(J)=1(J-1.)/500.
00460		YJ=.5/X(J)5
00470		A=1.
00480 -		B=FK-YJ
00490		C=-FK
00500		XJ(J)=(-B+SQRT(B*B-4.*A*C))/(2.*A)
00510	10	CONTINUE
00520		DO 11 I=1,M
00530		A2=13.12
00535		A5=5.55*I
00540		A3=(5F0*A1)/(1F0)
00550		DO 12 J=1,NP
00560		YJ=.5/X(J)5
00570		X1 = XJ(J)
00580		H=X1-YJ
00590		Y(J)=H*A1+YJ*A5+(1X1)*A3
00600	12	CONTINUE
00610		CALL PTPLOT(X,Y,1.NP,-2)
00611	11	CONTINUE
00620		CALL REOPEN
00621		DO 32 J=1,3

00622		READ(1,403) N
00623		DO 30 I=1,N
00624		READ(1,404) X(I),Y(I)
00625	30	CONTINUE
00626		CALL PTPLOT(X,Y,1,N,-2)
00627	32	CONTINUE
00630		CALL GRNPEN
00640		CALL GRATIC
00650		CALL BLKPEN
00660		CALL CTRMAG(10)
00670		CALL AXES
00675		CALL PLACE(1,1)
0067 6		CALL TYPECS(31 HNMR H20 PROTON SHIFT SIMULATION, 31)
00677.		CALL PLACE(1,2)
00678		CALL TYPECS(25HFOR WATER-MONOBASE SYSTEM, 25)
00688		CALL GREND
00690	401	FORMAT(20A4)
00700	403	FORMAT(1615)
00710	404	FORMAT(4F10.5)
00720		STOP
00730		END

APPENDIX THREE

The method used for calculating the equilibrium constants was that of $Ryall^{135}$.

MeOH---NCMe + I - MeOH---I + MeCN

$$K = \underline{[MeOH---I][MeCN]}$$
$$\underline{[I][MeOH---NCMe]}$$

Let $[I^-]_{total} = x = Fixed amount.$ $[MeOH]_{total} = y = Range of values.$ [MeCN] = Constant.

At equilibrium,

MeOHNCMe	+	I_	 MeOHI	+	MeCN
y – 🕶		X-X	ĸ		

$$K = \frac{\propto [MeCN]}{(x-\alpha)(y-\alpha)}$$

From the optical density of I,

$$0.D.(I^{-})^{=} \epsilon_{1} c_{(I^{-})}^{1}$$

From the optical density of MeOH---I

$$0.D_{(\alpha)} = \mathcal{E}_2 c_{\alpha} 1$$

where ξ = extinction coefficient, c=concentration, l=length of cell Assuming that the extinction coefficients are equal,

•

$$\frac{c^{(1_-)}}{c^{(1_-)}} = \frac{c^{\alpha}}{c^{\alpha}}$$

$$c_{(I^-)} = x - \alpha, \text{ and } c_{\alpha} = \alpha$$

$$\vdots$$
$$\frac{O.D.(I^-)}{x - \alpha} = \frac{O.D.(\alpha)}{\alpha}$$

Rearranging gives,

$$\propto = \underbrace{0.D.(\alpha) \cdot \mathbf{X}}_{0.D.(\mathbf{I}^{-}) + 0.D.(\alpha)}$$

For the ultraviolet work, x was constant at 0.5 x 10^{-3} M, the optical density for iodide ions was taken from the spectra and the optical density for MeOH---I was obtained for a series of solutions as methanol was added in increasing concentration. A typical calculation for a solution containing 1.56M of methanol and 18.54M MeCN for which the 0.D.(\propto) was 0.53, gives

$$\propto = \underbrace{0.53 \times 0.5 \times 10^{-3}}_{0.53 + 0.61} = 0.23 \times 10^{-3} \\ = 0.23 \times 10^{-3} - 0.23 \times 10^{-3} \\ = 0.27 \times 10^{-3} \\ y - \propto = 1.56 - 0.23 \times 10^{-3} \\ = 1.55977$$

: K = $\underbrace{0.23 \times 10^{-3} \times 18.54}_{1.55977 \times 0.27 \times 10^{-3}} = 10.15$

Hence, on addition of successive amounts of methanol, equilibrium constants could be calculated and the average found.

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Spectroscopic Studies of Aqueous Solutions

Susan E. Jackson

The work of this thesis was carried out in order to try to understand more fully the structure and solvating properties of water. Several forms of spectroscopy were used to gain information on the effect of non-electrolyte and electrolytes on the structure of water.

The spectra of water and aqueous solutions are generally regarded as being uninformative as the bands are broad and insensitive to additives. However, the work in this thesis overcomes the problem by isotopic dilution of H_2O by D_2O and

by greatly lowering the temperature of the solutions to form 'glassy solids'. The bands become better resolved and information can be obtained from the appearance of sub-bands. A water molecule is capable of forming four hydrogen-

A water molecule is capable of forming four hydrogenbonds, tetrahedrally disposed, but this ideal situation does not exist in liquid water and hydrogen-bonds will be constantly breaking to give OH free and Lone Pair groups. The presence of the OH free groups was monitored in the near infrared as a function of temperature and added electrolytes and nonelectrolytes. In the infrared, at low temperatures, bands can be identified due to OH groups bonded to additives. Using these results, this thesis attempts to explain

the manner in which water solvates and also to calculate the percentage of OH_{free} groups which are present in pure water at

room temperature. Results compare favourably with those of other workers although conclusions often differ.

Ultraviolet spectroscopy was used to study the CTTS spectrum of the iodide ion in methyl cyanide when solvated by water, methanol and ethylene glycol. Equilibrium constants were obtained from the spectra which gave good agreement with those of other workers.