Structure in Solvents and Solutions—NMR and Vibrational Spectroscopic Studies*

By Martyn C. R. Symons
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF LEICESTER,
LEICESTER LE1 7RH

1 Introduction

Some 30 years ago, when many chemists were engulfed in S_N1 and S_N2 reactions, I decided to direct my research towards trying to obtain direct evidence for intermediate species such as carbonium ions that were invoked by chemists with such success in interpreting mechanism. Part of this effort, which started with carbonium ions, quickly moved into the realm of free-radicals with the advent of e.s.r. spectroscopy. Another popular area in which direct evidence for the presence of postulated solution species had not been forthcoming was that of conductivity. It was clearly necessary to invoke ion-pair formation, but the structure and concentrations of ion-pairs was a matter of intense debate. We therefore set out to obtain direct structural information about solutions using spectroscopy, in the hope of obtaining evidence for ion-pairs, in addition to learning generally about structure in the liquid-phase. Although this is a popular and successful approach today, it was quite novel at that time.

The accent in this review is therefore on *structure*: obviously, structure and dynamics are intimately linked in fluid systems, as is nicely illustrated by the fact that, whilst infra-red spectroscopy 'sees' a largely static system, very much on the slow-exchange side, n.m.r. spectroscopy detects a largely dynamic system, almost always on the fast-exchange side. A great deal of effort has been, and is being, directed towards understanding the dynamic information derivable from such studies, especially using n.m.r. data, but surprisingly little attention is given to the structural information contained therein. I have long maintained that a proper understanding of structure should precede detailed analysis of dynamic factors, and this Review reports our recent attempts at probing structural aspects of solvents and their solutions.

Water is, for obvious reasons, the solvent that takes our major interest.[1,2] However, being a three-dimensional cross-linked polymer, it is more difficult to understand than its near relative, methanol. For this reason, we have studied methanolic systems quite extensively in the hope of shedding some light on the

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* This Review is based upon a lecture given at the Faraday Division Symposium held at Aston in April 1982. I was asked to review work at Leicester and this bias is carried through herein.

[1] M. C. R. Symons, *Philos. Trans. R. Soc. London, Ser. B*, 1975, **272**, 13.

[2] M. C. R. Symons, *Acc. Chem. Res.*, 1981, **14**, 179.

problems encountered with water. Incidentally, in these studies, pertinent information regarding the structural properties of other solvents has been forthcoming. For convenience, the Review is divided into two parts—*Methanol* and *Water*.

2 Methanol

A. Methanol + Bases in Inert Solvents.—Very dilute solutions of methanol (or water) in fairly inert solvents such as tetrachloromethane are monomeric. This is nicely established by infra-red spectroscopy (Figure 1). We use this narrow 'free OH' band as the origin from which shifts are measured, as indicated in Figure 1. We could have used the gas-phase value, but since going from the gas-phase to *any* medium, however inert, invariably results in a significant spectral shift, and since the factors causing such shifts (which are not our present concern) apply to all condensed solvent systems, I feel that it is more self-consistent to use an inert solvent system as our 'origin'.

Addition of any basic solute (B) results in hydrogen bonding:

$$\mathrm{MeOH} + \mathrm{B} \rightleftharpoons \mathrm{MeOH} \cdots \mathrm{B}, \qquad (1)$$

the resulting O—H absorption band being shifted to low-frequencies, the shift $\Delta\nu/\mathrm{cm}^{-1}$ being a useful measure of the strength of the bond (Figure 1). The band

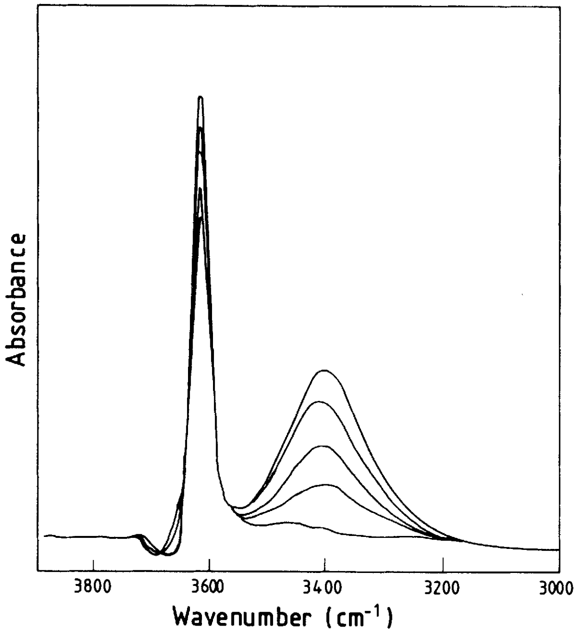

Figure 1 *Infra-red absorption spectrum in the* O—H *stretch region of methanol in dichloromethane, with increasing concentration of dimethylsulphoxide*

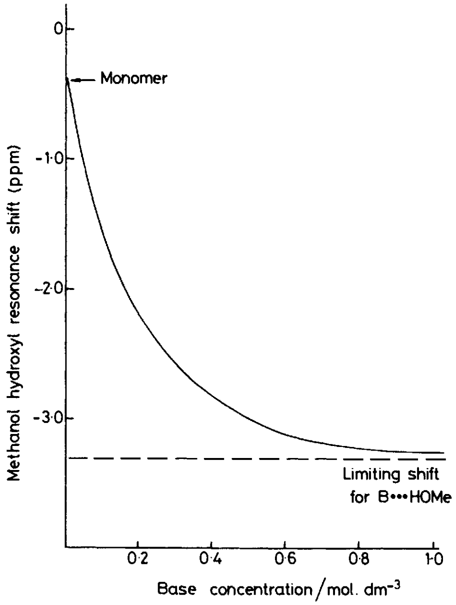

Figure 2 *Trend in the OH proton resonance for methanol in tetrachloromethane on the addition of dimethylsulphoxide*

is also broadened and, in the fundamental region, the oscillator strength increases markedly. [In the first overtone region, the oscillator strength of the $(OH)_f$ (f = free) band is, relatively, much greater, and in the second overtone region, this band dominates.]

The (OH) proton resonance spectra of such systems comprise rapid time-averaged features, even at low temperatures. However, limiting shifts for MeOH monomers and for MeOH $\cdots$ B units can readily be deduced in most cases (Figure 2). Intermediate values are simply the weighted mean values for MeOH and MeOH $\cdots$ B and hence equilibrium constants can be calculated. These simple systems link together satisfactorily. The problem with proton resonance studies arises when there are more than two significant components in fast exchange, and limiting shifts for at least some of the components cannot be derived by direct measurements.

We have therefore obtained plots connecting infra-red shifts of the type shown in Figure 1 ($\Delta\nu$/cm^{-1}) and n.m.r. shifts ($\Delta\nu'$/p.p.m.) of the type shown in Figure 2. Such a plot, for methanolic systems, is shown in Figure 3. Others are discussed elsewhere.[3] In this plot, the correlating line has been constrained to pass through the origin,[3] since this is a necessary requirement. This plot need not be linear,

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[3] M. C. R. Symons and V. K. Thomas, *J. Chem. Soc., Faraday Trans. 1*, 1981, 77, 1891.

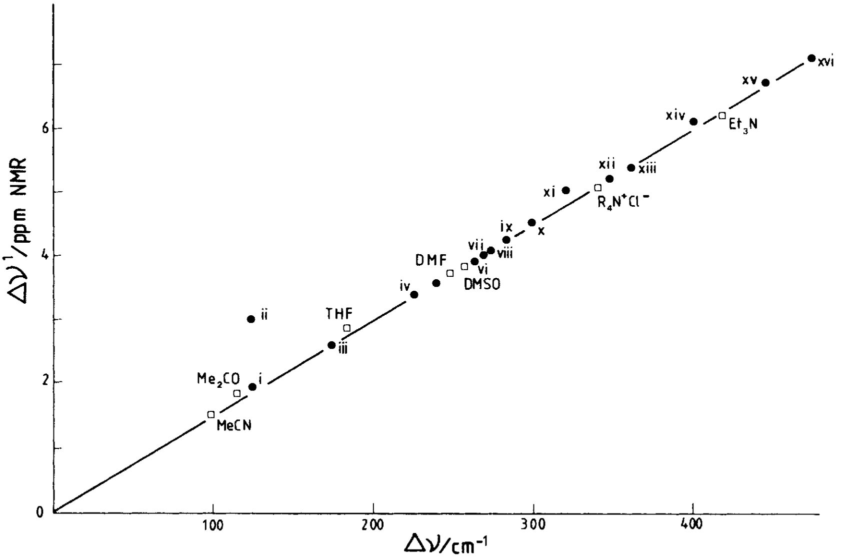

Figure 3 *Correlation between infra-red shifts, ν*(OH)*, and proton resonance shifts, ν'*(OH) *for methanol in* CCl_4 + *added bases, indicated on the graph.* (*The key, given in Table 2, relates to estimated values for salts in pure* MeOH, *discussed in section* 2.D)

but there seems to be little gain in introducing curvature. I stress that all the points on this plot are good, in the sense that there are no overt approximations used in their derivation. We use the plot to obtain n.m.r. shifts for species whose infra-red shift is known but for which no n.m.r. shift can be obtained.

It is noteworthy that the points for bulk liquid methanol fit well onto this line over a range of temperatures below 25 °C. This is significant since the infra-red spectral maximum covers only the majority species, whereas the n.m.r. line is a weighted average of *all* species. Had entities such as terminal methanol molecules been of importance, we would have needed to allow for their presence in this correlation. This confirms our conclusion from infra-red spectroscopy that they are not of major significance in the low-temperature region.

B. Methanol–Aprotic Solvent Binary Systems.— (i) *Methanol + Tetrachloromethane and Dichloromethane.* As the concentration of methanol in tetrachloromethane increases one might have expected to detect well-defined infra-red features for the dimer. In fact, in addition to a shoulder possibly assignable thereto (Figure 4), a broad feature in the region for bulk methanol grows in. At low temperatures in methylene chloride the intermediate feature is hardly detectable. This result is, in fact, to be expected. Taking the view that the dimer is 'linear' (1) rather than cyclic (2),[4] it should be both more basic and more

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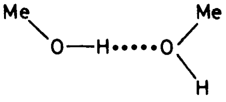
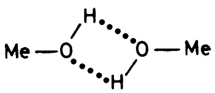
[4] M. C. R. Symons and V. K. Thomas, *J. Chem. Soc., Faraday Trans. 1*, 1981, 77, 1883.

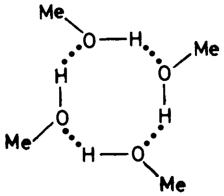


(1)



(2)

acidic than the monomer.[1] Thus it should react more strongly with monomers than do other monomers. This will lead to a loss of dimers and a gain of oligomers. Since this represents high organization, it will be most marked at low temperatures. Once tetramers or pentamers have been formed, cyclization should ensue, as in (3). This gives fully, and strongly bonded methanol molecules that are



(3)

spectroscopically almost indistinguishable from bulk methanol, which is itself expected to contain many such cyclic structures.

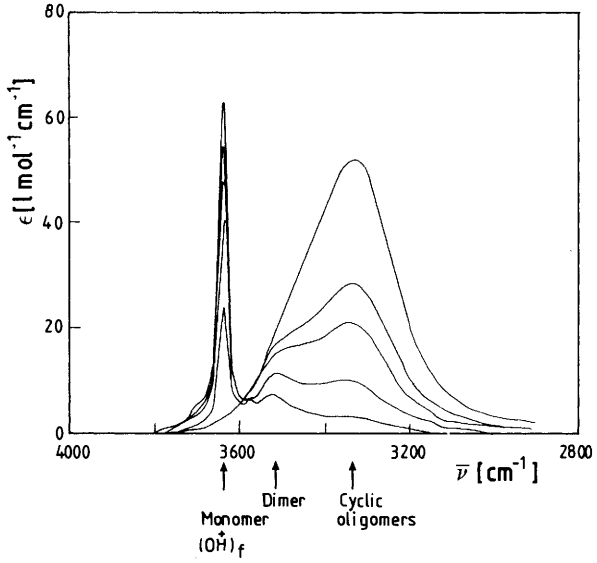


Figure 4 *Infra-red spectrum [(OH) stretch] of increasing concentrations of methanol in tetrachloromethane showing growth of features assigned to hydrogen-bonded dimers and oligomers, with loss of the monomer and* $(OH)_f$ *band*

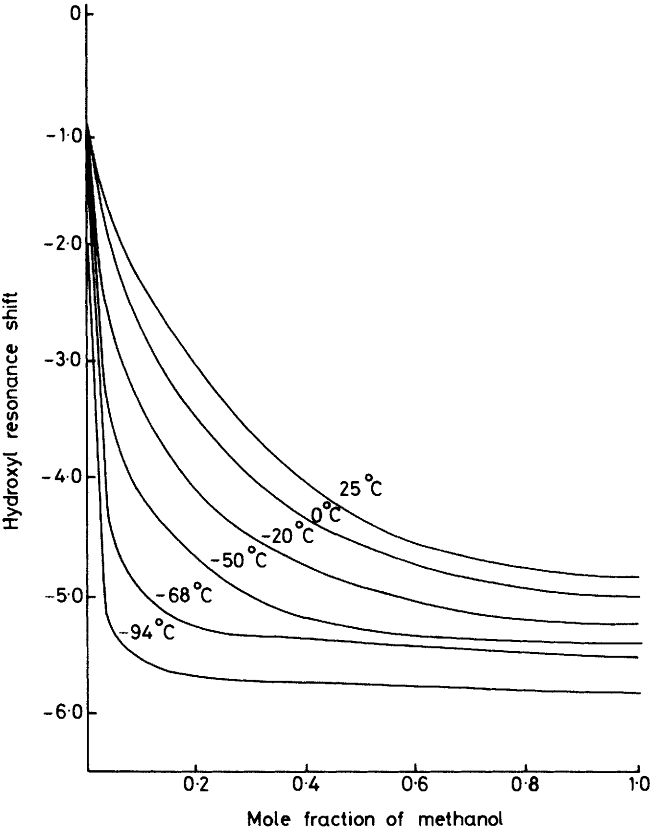
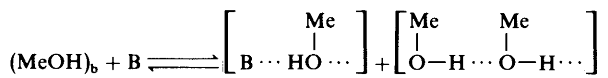


Figure 5 *Hydroxyl proton resonance shifts for methanol*–CH_2Cl_2 *solutions at various temperatures*

These considerations nicely explain the n.m.r. results shown in Figure 5. Thus, from the n.m.r. and infra-red viewpoints, methanol remains effectively unchanged in the 0—0.9 MF (CH_2Cl_2) range. From then on $(OH)_f$ groups in monomers and dimers begin to form, which induce a drastic shift to high fields. Using the infra-red data and the correlation of Figure 3 we have been able to reproduce curves such as that in Figure 5 quite satisfactorily.[4] Interchange between these entities must be very rapid on the n.m.r. time-scale since, even at the lowest temperatures available, no marked exchange-broadening was detected.

(ii) *Methanol + Basic Co-solvents.* Most common aprotic solvents (B) contain a basic function (*e.g.* oxygen in ketones and amides, nitrogen in amines and cyanides, *etc.*). This leads to the reaction (2):



$$(\mathrm{MeOH})_b + \mathrm{B} \rightleftharpoons \left[\mathrm{B}\cdots\mathrm{H}\overset{\mathrm{Me}}{\mathrm{O}}\cdots\right] + \left[\overset{\mathrm{Me}}{\mathrm{O}}-\mathrm{H}\cdots\overset{\mathrm{Me}}{\mathrm{O}}-\mathrm{H}\cdots\right] \qquad (2)$$

Here $(\mathrm{MeOH})_b$ stands for fully H-bonded 'bulk' solvent, the base is represented as being mono-basic (see below), and the terminal methanol in the unit $\left[\overset{\mathrm{Me}}{\mathrm{O}}-\mathrm{H}\cdots\overset{\mathrm{Me}}{\mathrm{O}}-\mathrm{H}\cdots\right]$ is described as a free 'lone-pair' molecule $(\mathrm{LP})_f$. This reaction can be envisaged as involving chain-breaking to give an $(\mathrm{OH})_f$ and an $(\mathrm{LP})_f$ unit, with $(\mathrm{OH})_f$ bonding to B. The remaining methanol molecules are largely unmodified unless B is either much more or much less basic than bulk methanol. We seem to have been the first to consider the importance of such terminal $(\mathrm{LP})_f$ molecules, and they are still normally ignored. Nevertheless, they seem to me to be of prime importance both from a chemical and spectroscopic viewpoint.

Spectroscopically, $(\mathrm{LP})_f$ terminal molecules should be readily distinguishable from bulk molecules because their hydrogen bonds must be markedly weaker, as is found for the dimer, and as expected because of the co-operative effect.[1] This is indeed the case.[5,6] We have recently shown that a band in the 3470 cm^{-1} region can be assigned to this unit. This band is found, for a range of basic co-solvents, strong or weak, and comes in the region expected for such molecules (Figure 6). It is also observed for concentrated solutions of tetra-alkylammonium halides at low temperatures.[7] This entity, which is of equal importance to the obvious species, $\left[\mathrm{B}\cdots\mathrm{H}\overset{\mathrm{Me}}{\mathrm{O}}\cdots\right]$, also contributes significantly to the weighted average proton shifts for mixed solvent systems.[6]

From such spectra, using both the O—H fundamental and overtone bands, we have obtained at least approximate band positions for a range of $\left[\mathrm{B}\cdots\mathrm{H}\overset{\mathrm{Me}}{\mathrm{O}}\cdots\right]$ adducts (Table 1). From these, and the correlation of Figure 3, we have obtained approximate absolute n.m.r. shift values for these entities (Table 1).

When one examines mole-fraction plots of the proton resonance shifts for methanol in a range of binary solvent systems, a variety of curves are obtained, which on first sight seem somewhat random (Figure 7). To these must be added the shifts obtained for dichloromethane systems (Figure 5). It might seem surprising, for example, that the initial up-field shift on adding $\mathrm{MeNO_2}$ is less than that for cyanomethane, as is the shift for acetone, yet the order of basic strength is $\mathrm{MeNO_2} < \mathrm{MeCN} < \mathrm{Me_2CO}$. Equally, it may seem surprising that hexamethylphosphoramide (HMPA) appears to have no more effect than $\mathrm{CH_2Cl_2}$, despite its very high basic strength, except in the 0.9—1.0 mole-fraction region.

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[5] M. C. R. Symons, N. J. Fletcher, and V. K. Thomas, *Chem. Phys. Lett.*, 1979, **60**, 323.

[6] M. C. R. Symons, V. K. Thomas, N. J. Fletcher, and N. G. M. Pay, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1899.

[7] I. M. Strauss and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2146.

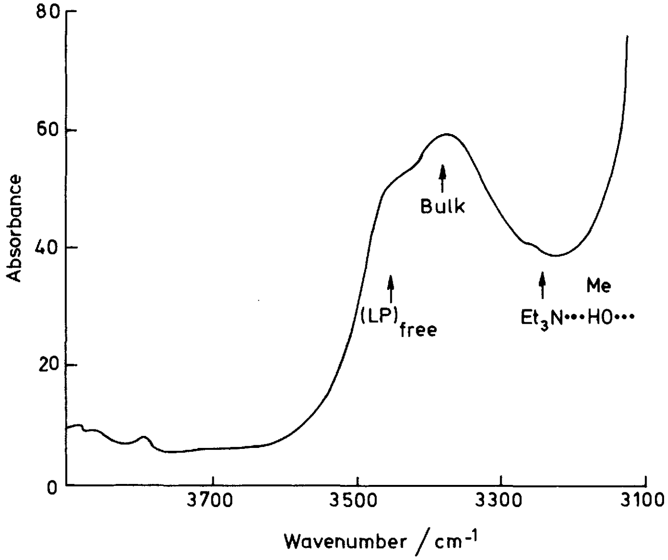


Figure 6 *Infra-red spectrum for methanol + triethylamine in the* (OH) *stretch region, showing the band in the* 3440 cm^{-1} *region assigned to* $(LP)_f$ *or 'terminal' methanol molecules*

Table 1 *Proton resonance shifts* [A, *from* $(OH)_f$; B, *from bulk methanol at* 25 °C] *for various types of methanol molecules, discussed in the text, estimated from their infra-red spectra*

[(Bulk) represents methanol H-bonded as in the pure solvents: $(OH)_f$ and $(LP)_f$ are defined in the text]

	Infra-red maxima/cm^{-1}		*N.m.r. shift*/p.p.m.	
Structure	ν_{OH} (±10)	$2\nu_{OH}$ (±20)	A (±0.15)	B (±0.15)
MeOH $(OH)_f$	3640	7120	0.0	+4.5
MeOH (bulk)	3340	6590	+4.5	0.0
MeOH $(LP)_f$	3440	6790	+3.1	+1.4
$Me_2CO \cdots$ HOMe	3530	6920	+2.0	+2.5
$Me_2CO \cdots$ (bulk)	3415	6700	+3.8	+0.7
DMSO ··· HOMe	3400	6690	+3.7	+0.8
DMSO ··· (bulk)^a	3280	~6500	+4.6	−0.1
DMF ··· HOMe	3410	6690	+3.7	+0.8
DMF ··· (bulk)^a	3300	~6500	+4.8	−0.3
HMPA ··· HOMe	3340	6580	+4.5	0.0
HMPA ··· (bulk)	3240	~6400	+5.2	−0.7
$Et_3N \cdots$ HOMe	3180	6240	+5.7	−1.2

(*a*) Approximate value estimated from the shift in the bulk methanol band

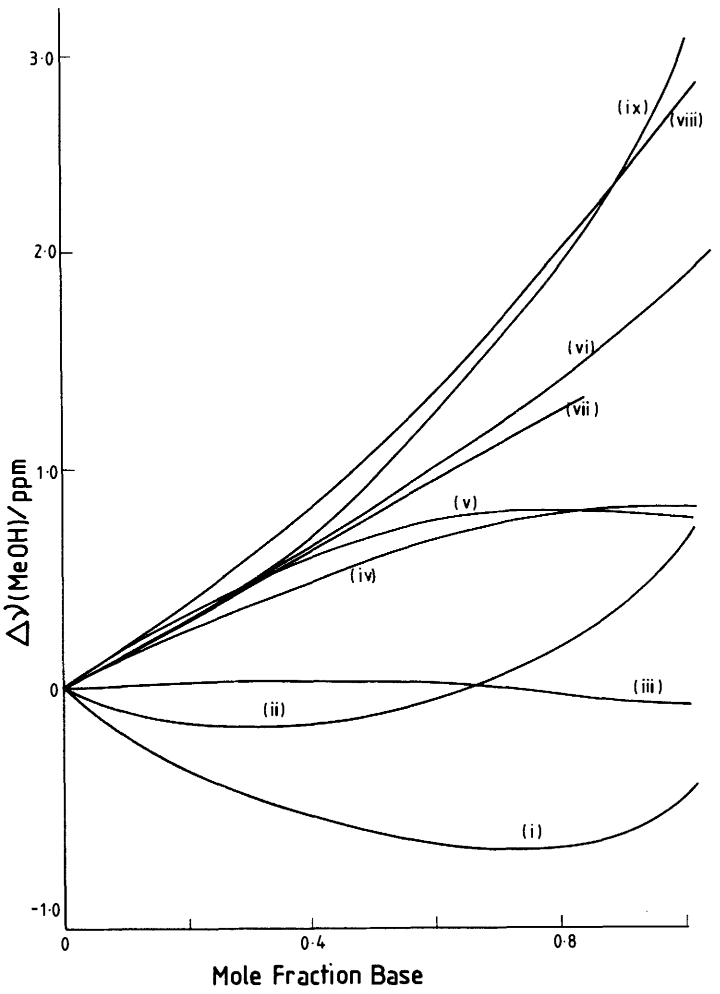
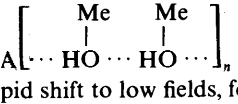


Figure 7 *Hydroxyl proton resonance shifts for methanol + a range of aprotic solvents at* 25 °C: (i) *pyridine,* (ii) *triethylamine,* (iii) *hexamethylphosphoramide,* (iv) *DMF,* (v) *DMSO,* (vi) *acetone,* (vii) *THF,* (viii) MeCN, (ix) $MeNO_2$



My point is that the hydrogen bonds in $\text{HMPA}\left[\cdots\overset{\text{Me}}{\overset{|}{\text{HO}}}\cdots\overset{\text{Me}}{\overset{|}{\text{HO}}}\cdots\right]_n$ units must be strong. Hence one would expect an initial rapid shift to low fields, followed by an up-field shift as the final unit, (HMPA ··· HOMe), dominates. In my view, the only way to rationalize these trends is *via* the use of equation (2), taking due note of the shift for $(LP)_f$ units.

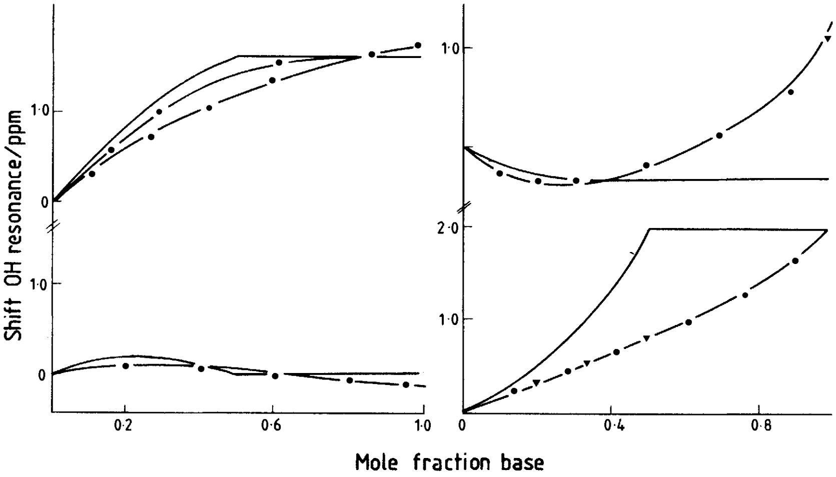
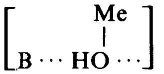


Figure 8 *Reconstructed hydroxyl proton resonance shifts for methanol for the systems shown in Figure 7, using the data of Table* 1

Using the approximation that equilibrium in equation (2) lies largely to the right, and that the solvation numbers for the co-solvents are all equal to one, we have been able to reconstruct some of these n.m.r. shifts, as indicated in Figure 8. I stress that the accuracy of our infra-red data is not high, but nevertheless for part of the triethylamine plot, and for those for HMPA, dimethylsulphoxide (DMSO), and dimethylformamide (DMF) there is fair agreement. In some of these cases, we know from direct infra-red studies that these molecules are monobasic in methanol (see below), and that equilibrium for equation (2) does indeed lie to the right.

This approach clearly fails for acetone and all less basic co-solvents. This is undoubtedly because equilibrium for equation (2) now lies increasingly to the left, as the base concentration increases. We have established this semi-quantitatively for acetone + MeOH systems using the C=O stretching frequency as a guide.[8] Hence we have obtained a reasonable fit for the n.m.r. plot for acetone in Figure 7, as shown in Figure 8. Similar results have been obtained for cyanomethane + methanol systems.

In summary, the initial shift in the methanol-rich region is due to a constant up-field component from $(\mathrm{LP})_f$ units, and a down-field or up-field component from  $\left[\mathrm{B}\cdots\overset{\mathrm{Me}}{\overset{|}{\mathrm{HO}}}\cdots\right]$ units. As the base-strength gets less the resultant is an increasingly up-field shift. However, when equilibrium in equation (2) becomes significantly reversible, the base is less and less bound and the upward trend falls once more to the limit of zero slope for dichloromethane or tetrachloromethane.

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[8] M. C. R. Symons, G. Eaton, T. A. Shippey, and J. M. Harvey, *Chem. Phys. Lett.*, 1980, **69**, 344.

For most strong bases, once [MeOH $\cdots$ B] units dominate (MF base >0.5) further changes are minor. However, in the special case of triethylamine, there is a marked up-field shift in this region (Figure 7). Once again, infra-red spectroscopy helps: dilute solutions of methanol in Et_3N, in contrast with the other bases, exhibit a clear feature for unbound MeOH molecules. If one makes allowance for the powerful up-field contribution made by these monomers to the averaged shift, good agreement with experiment results (Figure 8).

We suggest that this is purely a steric effect since the cone of approach for successful bonding is small. This result helps to explain why on Gutmann's scale[9] Et_3N is a very strong base, whilst on Taft's scale[10] it has about the same strength as that of DMSO. It all depends on the information required: the bonds, once formed, are very strong, but there is an entropy factor working against their formation.

These results enable us to state the nature of species present in a given binary solvent system to a fair degree of accuracy. Hence we can interpret previously uninterpretable n.m.r. shifts. Hopefully, these results will prove to be useful in the interpretation of relaxation and even thermodynamic phenomena.

Before turning to the more complicated systems of electrolytes in methanol, I consider results obtained for binary solvent systems to which low concentrations of a 'probe' molecule have been added.

C. The Use of Probes.—By a probe, I mean any species, in minimum concentration, that can be monitored spectroscopically in a range of solvent systems. When dissolved in pure solvents, such probes have frequently been utilized to provide so-called empirical solvent scales, such as Z-values[11] or E_t-values.[12] They are perhaps even more useful for studying mixed solvent systems. When n.m.r. shifts are measured, weighted-average information results, whereas infra-red or ultra-violet spectroscopy provides, in favourable cases, separate pieces of information for all the different solvates formed by the probe. So long as this is borne in mind, one cannot say which measurement is the most useful. However, for mixed solvent work, averaged shift measurements alone are very hard to interpret correctly.

An example is our work on the hyperfine coupling (A_{iso}, ^{14}N) for R_2NO radicals in mixed solvent systems.[13,14] The trends observed were interpreted, but we now know, from concomitant ultra-violet spectroscopic studies, that some of these interpretations were in error. We therefore decided to use infra-red and n.m.r. studies in tandem, as in the work outlined above. We have studied a range of probes, including acetone (C=O stretch),[8] amides (C=O), DMSO (S—O), and triethylphosphine oxide (Et_3PO) (P—O).[15] I outline the results for Et_3PO

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[9] V. Gutmann and R. Schmid, *Coord. Chem. Rev.*, 1974, **12**, 263.

[10] M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377.

[11] E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3253; 3261; 3267.

[12] K. Dimroth, C. Reichardt, T. Siepmann, and R. Bohlmann, *Justus Liebigs Ann. Chem.*, 1963, **661**, 1.

[13] Y. Y. Lim, E. A. Smith, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1976, 2876.

[14] S. E. Jackson, E. A. Smith, and M. C. R. Symons, *Faraday Discuss. Chem. Soc.*, 1978, **64**, 173.

[15] M. C. R. Symons and G. Eaton, *J. Chem. Soc., Faraday Trans. 1*, 1982, in press.

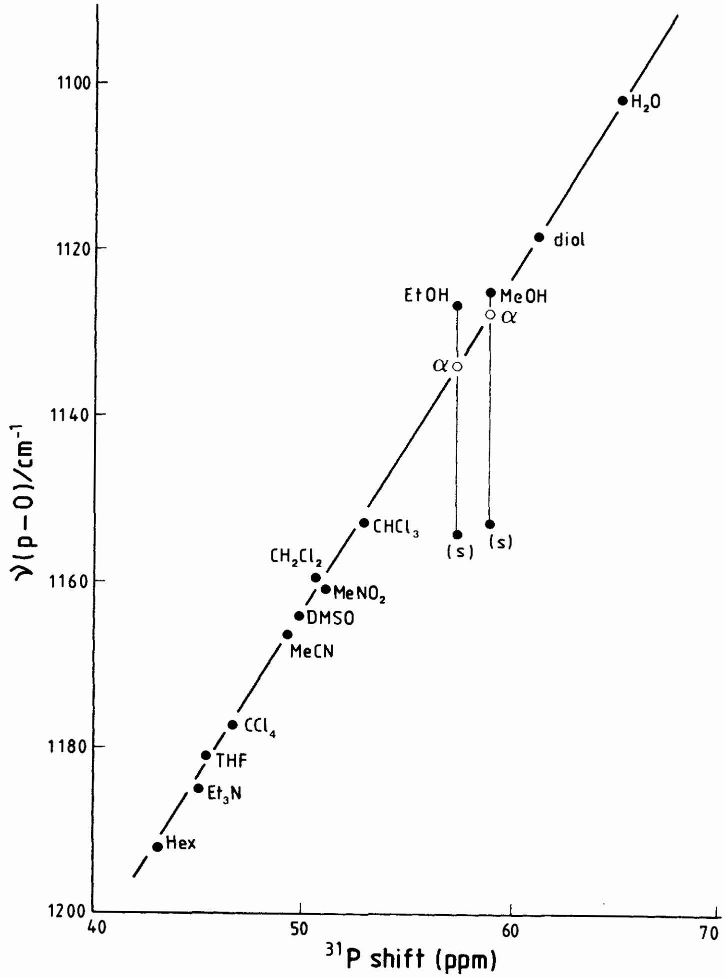

Figure 9 *Correlation between the shifts of the* P—O *stretching mode* ($\Delta\nu$) *for* Et_3PO *in a range of solvents and the shifts of the* ^{31}P *resonance in these solvents* (Et_3N = *triethylamine, THF = tetrahydrofuran, Hex = hexane, diol = ethane* 1,2-*diol*)

herein, because they are characteristic, and the shifts ($\Delta\nu$ and $\Delta\nu'$) are large and hence reasonably accurate.

Triethylphosphine Oxide. This probe is of particular significance since the ^{31}P resonance shift ($\Delta\nu'$, from the inert solvent value) was taken by Gutmann as his 'acceptor number' for solvents.[16] We were pleased to find that there is a good

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[16] V. Gutmann, 'Donor–Acceptor Approach to Molecular Interactions,' Plenum Press, New York, 1978.

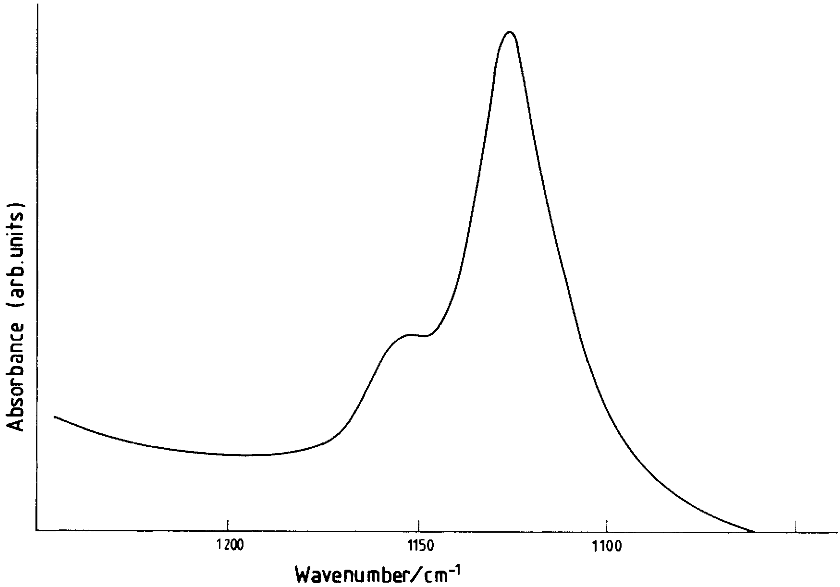
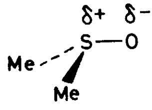


Figure 10 *Infra-red spectrum of* Et_3PO (P—O *stretch) in methanol, showing the presence of two solvates*

linear correlation between the shift ($\Delta\nu$) in the infra-red spectrum (P—O stretch), and $\Delta\nu'$ (Figure 9). The alcohols are unusual in that infra-red spectroscopy establishes the presence of two distinct solvates, as illustrated in Figure 10. If these bands are used to estimate ^{31}P shifts for the individual solvates, the weighted-mean shifts lie nicely on the correlating line (Figure 9).

How should we interpret this plot? We suggest that, for the aprotic solvents, dipole–dipole interactions dominate, the more 'exposed' the solvent dipole, the bigger the interaction. Thus DMSO, with a very large charge separation and an exposed dipole (4) induces a large shift, whilst Et_3N with a submerged dipole, is apparently almost inert. Trichloromethane probably forms a single hydrogen bond to oxygen whilst the alcohols probably form both mono-$\left[\mathrm{Et_3PO}\cdots\overset{\mathrm{Me}}{\overset{|}{\mathrm{HO}}}\cdots\right]$ and di-$\left[\mathrm{Et_3PO}(\cdots\overset{\mathrm{Me}}{\overset{|}{\mathrm{HO}}}\cdots)_2\right]$ solvates. It might appear that water forms stronger



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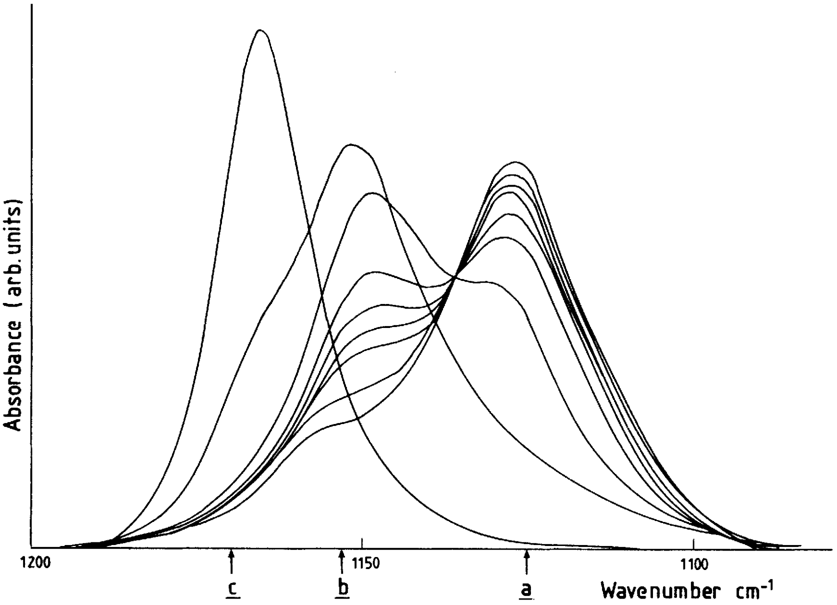

Figure 11 *Infra-red spectra for* Et_3PO (P—O *stretch*) *in the solvent system* MeOH + MeCN, *showing features for the di-hydrogen bonded* (a), *mono-hydrogen bonded* (b), *and non-hydrogen bonded* (c) *species*

hydrogen bonds than methanol, from its very large shift (Figure 9), but, as I show below, this large shift in fact arises because Et_3PO forms a trihydrate in pure water. The shift for the dihydrate is actually almost equal to that for methanol (see below), confirming that these two solvents are very similar proton-donors, as are the monomers,[17] despite suggestions to the contrary.[18] I consider later why the solvation number is higher in water than in alcohols.

This linear correlation can now be used to predict ^{31}P shift values in cases where direct measurements cannot be made. This situation has already been illustrated for solutions in alcohols, and I now consider some mixed solvent systems.

Consider first the effect of adding basic co-solvents to Et_3PO in methanol. Some resulting infra-red spectra are shown in Figure 11. These curves have been deconvoluted and normalized, some resulting intensity trends being shown in Figure 12. Although the errors involved are quite large, nevertheless these curves give, possibly for the first time, a good idea of the composition of the probe solvates in a range of different environments. Note the relatively slow loss of the

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[17] M. C. R. Symons, T. A. Shippey, and P. P. Rastogi, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 2251.

[18] A. Le Narvor, E. Gentric, J. Lauransan, and P. Saumagne, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 1329.

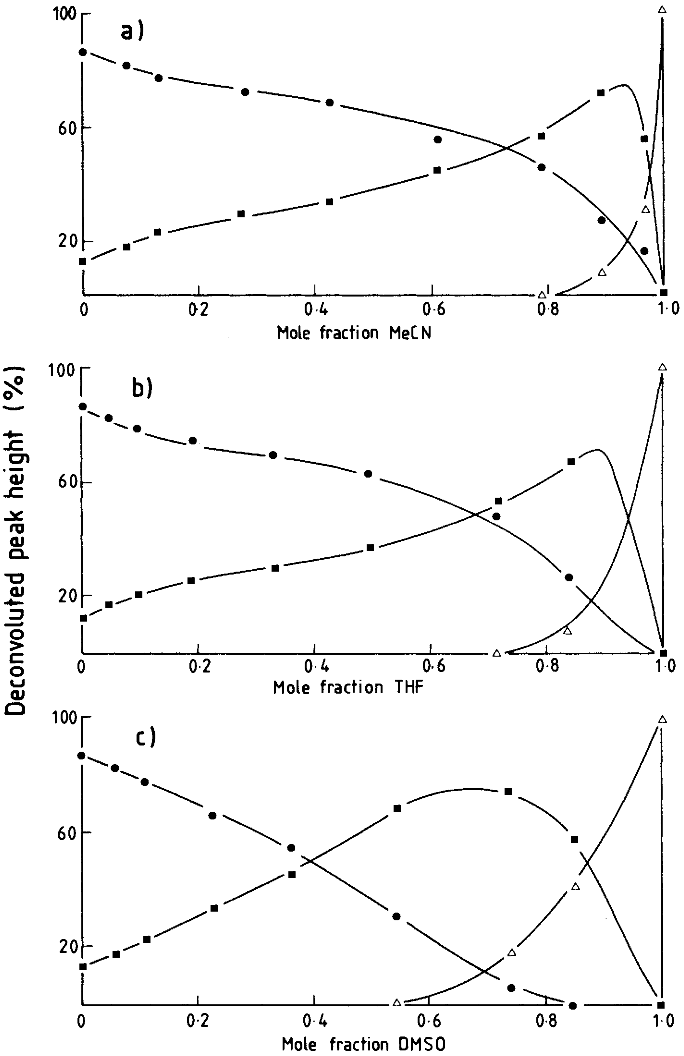

Figure 12 *Trends in the intensities of the bands shown in Figure* 11 *obtained by deconvolution into the three separate components,* (a) MeCN, (b) *THF,* (c) *DMSO*

dimethanolate as MeCN is added, with, of course, the concomitant growth of the monosolvate. Only in the 0.9 MF (MeCN) region does the MeCN solvate become significant. In the high MF (MeCN) range a direct competition for MeOH molecules is being studied (reaction 3):

$$Et_3PO \cdot (\cdot HOMe)_x + MeCN \rightleftharpoons Et_3PO \cdots (HOMe)_{x-1} + MeOH \cdots NCMe \quad (3)$$

As might be expected, the basic strength of Et_3PO is so high that these molecules are favoured even when MeCN is in large excess. In contrast, DMSO is far more efficacious, there being significant concentrations of non-hydrogen bonded Et_3PO in the 0.8 MF (DMSO) region. It is interesting that the non-hydrogen bonded P—O band frequencies are strongly dependent on the nature of the base in pure aprotic solvents (Figure 9), but when MeOH is attached this dependence is only minor. That the two solvents (DMSO or MeOH) should be almost self-excluding is not a structural necessity so far as I can tell, but the results seem to suggest that the presence of MeOH bound to Et_3PO inhibits effective dipolar interaction between Et_3PO and DMSO.

A knowledge of the structures of the probe solvates in these solutions should help in the interpretation of the ^{31}P chemical shifts which form the basis of acceptor numbers. Such shifts, for methanol + aprotic solvent systems, are shown in Figure 13. Whilst these shifts can be discussed in terms of preferential solvation by methanol in the case of MeCN and THF (but not for DMSO or HMPA), the infra-red results give a far more detailed picture. These have been used to give reconstructions for three of these solvents, making use of the i.r.–n.m.r. correlation (Figure 9) and the compositions (Figure 12). These reconstructed ^{31}P shifts are also shown in Figure 13, and, considering the inaccuracies inherent in the method, the agreement is good.

Ultimately, we can extend this method to binary MeOH + B systems, but this is more difficult because of the need to use very short path-length cells, with consequent errors in intensity measurements.

D. Methanol + Salts.—The problems outlined above are intensified for salts since we now have two independent entities to consider. Indeed, more than two when ion-pairs are important.

For reasons given below, n.m.r. spectroscopic studies originally seemed more fruitful than infra-red studies. Well-defined salt shifts were observed which were often linear through the origin so that initial slopes could be derived with confidence. The task of dividing these shifts into contributions from cations and anions was accomplished empirically, for example by setting the shift for NH_4^+ equal to zero (a curious choice since these ions are strongly solvated) or by equating the shifts for K^+ and Cl^-.

Some years ago,[19,20] we tried to separate proton resonance shifts for methanol ($O\underline{H}$) into average shifts from cations and anions, using solutions of magnesium salts at low temperatures, under conditions such that the protons for $Mg^{2+}(MeO\underline{H})_6$ units were resolved separately from the main resonance.[21,22] We argued that the residual shift of the bulk methanol resonance was due largely

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[19] R. N. Butler and M. C. R. Symons, *Trans. Faraday Soc.*, 1969, **65**, 945.

[20] R. N. Butler and M. C. R. Symons, *Trans. Faraday Soc.*, 1969, **65**, 2559.

[21] J. H. Swinehart and H. Taube, *J. Chem. Phys.*, 1962, **37**, 1579.

[22] Z. Luz and S. Meiboom, *J. Chem. Phys.*, 1964, **40**, 1058; 1066.

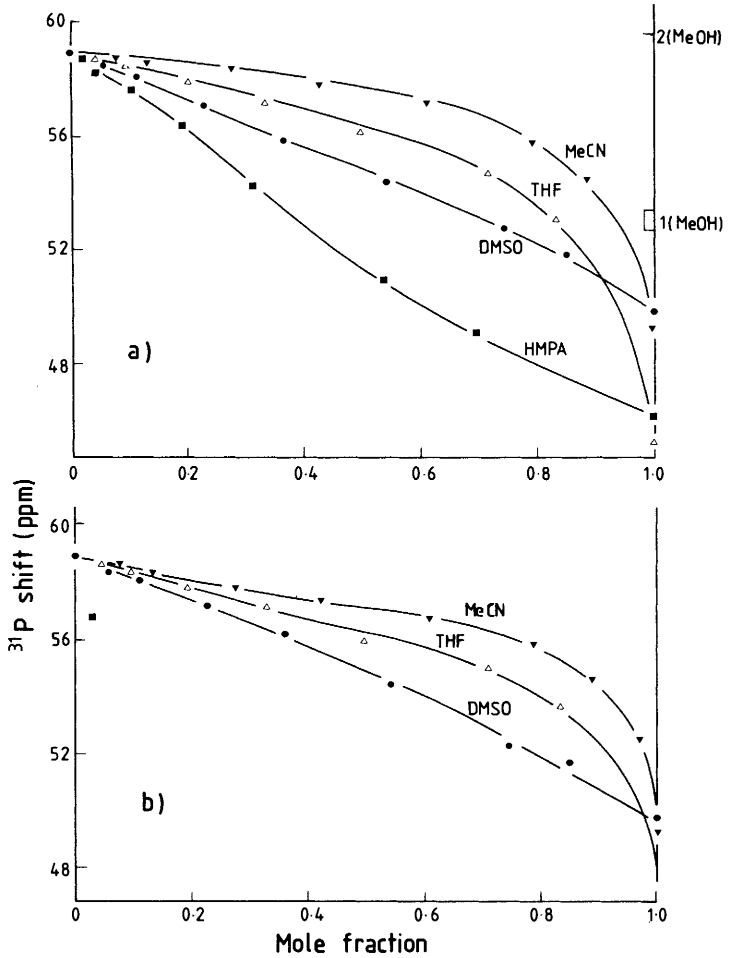

Figure 13 *Trend in the* ^{31}P *resonance for* Et_3PO *for solutions in* MeOH + *aprotic solvent systems* (a), *together with reconstructions based on infra-red data* (b)

to the anions. Hence separate shifts were derived, which have been widely quoted in subsequent years.[23,24]

More recently, we studied the infra-red spectra of a range of electrolytes in methanol to see if we could obtain separate features for the species involved. There had been many such studies, using both infra-red and Raman spectroscopy

[23] A. K. Covington and K. F. Newman in 'Modern Aspects of Electrochemistry,' ed. J. O'M. Bockris and B. E. Conway, Plenum Press, New York, 1977, p. 41.

[24] B. E. Conway, 'Ionic Hydration in Chemistry and Biophysics,' Elsevier, Amsterdam, 1981, p. 158.

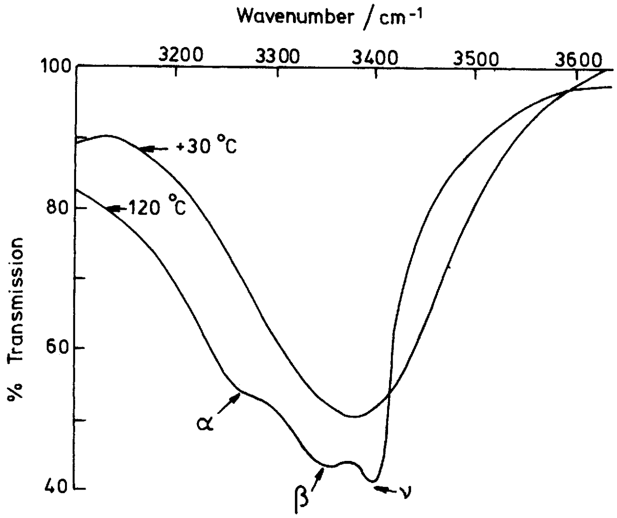

Figure 14 *The* OH *stretching bands for a solution of* LiI *in methanol at different temperatures, showing resolution into separate bands on cooling* [*α is bulk methanol, β is for* I^- $(HOMe)_n$ *solvates, and γ is for* MeOH *in solvent-shared ion-pairs*]

at room temperature.[25–30] However, only for solutions containing ClO_4^-, BF_4^-, or PF_6^- ions were separate bands obtained. For these salts, the bands were strongly shifted to high frequencies, and there has been much argument regarding their significance. One school of thought assigns the band to free OH groups,[25,26] another to OH groups weakly bound to ClO_4^- ions,[27,28] and yet another to OH groups in $M^+ \cdots ClO_4^-$ ion-pairs.[29,30] I return to this problem later.

It is possible to gain some idea of anion shifts ($\Delta\nu$ for $\left[A^- \cdots \underline{H}\overset{\text{Me}}{\overset{|}{\underline{O}}} \cdots\right]$ units) using tetra-alkyl ammonium salts and the concept that these cations do not greatly modify methanol structures.[31] Also, we have measured limiting cation shifts using a range of perchlorates, arguing that residual shifts of the bulk $Me\underline{OH}$ band must be largely due to the cations.[32] The most important development, however, was our discovery that, at low temperatures, the broad $\underline{OH}$ stretch bands are often resolved into at least two components, as exemplified in Figure 14. These extra bands are readily assignable to anion solvates,

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[25] G. E. Walrafen, *J. Chem. Phys.*, 1970, **52**, 4176.

[26] T. T. Wall and D. F. Hornig, *J. Chem. Phys.*, 1967, **47**, 784.

[27] D. M. Adams, M. J. Blandamer, M. C. R. Symons, and D. Waddington, *Trans. Faraday Soc.*, 1971, **67**, 611.

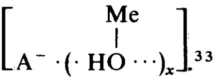
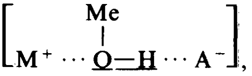
[28] G. Brink and M. Falk, *Can. J. Chem.*, 1970, **48**, 2096.

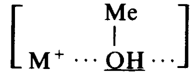
[29] Z. Kecki, P. Dryjanski, and E. Kozlowska, *Roczniki Chem.*, 1968, **42**, 1749.

[30] P. Dryjanski and Z. Kecki, *Roczniki Chem.*, 1970, **44**, 1141.

[31] I. M. Strauss, Ph.D. Thesis, Leicester University, 1981.

[32] M. C. R. Symons and D. Waddington, *Chem. Phys. Lett.*, 1975, **32**, 133.

 $\left[\mathrm{A^- \cdot (\cdot H\overset{Me}{\overset{|}{O}} \cdots)_x}\right]$.[33] At high salt concentrations, for alkali-metal salts, extra very narrow bands grew in, which we have assigned to solvent-shared ion-pairs,  $\left[\mathrm{M^+ \cdots \underline{\overset{Me}{\overset{|}{O}}{-}H} \cdots A^-}\right]$, *i.e.* to methanol molecules bound to both cations and anions. Evidently the methanol molecules in these units are very precisely bound relative to MeOH in bulk methanol, so the bands are sharp. This extra resolution arises for two main reasons, one being the fact that the envelope of the bulk Me$\underline{\mathrm{OH}}$ band is more temperature sensitive than those for $[\mathrm{A^-\ HOMe}]$ units, the other being that all bands narrow on cooling. (In this work, dilute solutions of MeOH in MeOD were used to eliminate intermolecular coupling.)

It is interesting that bands due to most cation solvates  $\left[\mathrm{M^+ \cdots \underline{\overset{Me}{\overset{|}{O}}H} \cdots}\right]$ were not well defined, and hence were never far removed from the bulk solvent band. Nevertheless, limiting shifts due to cations could be measured in some cases. For $\mathrm{Mg^{2+}}$ there were indications of a broad extra feature on the low-frequency side of the bulk solvent band. This was also seen at room temperature.

I take these results to mean (*a*) that hydrogen-bonds to most anions are apparently weaker than bulk solvent hydrogen-bonds, (*b*) that they are sensitive to the nature of the anion because the O—H oscillator is *directly* bound to the anion and, (*c*) that the major factor governing the shift of the 'cation band' is the fact that the oscillators remain bound to other methanol molecules, this hydrogen-bond being the controlling factor. Evidently, replacing methanol by $\mathrm{Na^+}$ slightly weakens this bond giving a high-frequency shift whilst $\mathrm{Mg^{2+}}$ ions strengthen it, giving a low-frequency shift. The temperature dependences of these bands seem to be close to that for bulk solvent bands.[33]

I now consider how these ideas impinge upon the problems involved in proton-shift studies. We are satisfied that $\mathrm{R_4N^+}$ ions [R = Bu or greater] have no more effect on methanol structure than $\mathrm{CCl_4}$, $\mathrm{CH_2Cl_2}$, or $\mathrm{SnMe_4}$ in the 0—0.1 mole-fraction range, all of which give rise to zero shift in the proton resonance,[34] or in the infra-red absorption. In that case, the responsibility for shifts by $\mathrm{R_4N^+A^-}$ salts is entirely that of the anions. However, it must be remembered that $(\mathrm{LP})_\mathrm{f}$ groups will be formed as in equation (4):

$$\mathrm{A^-} + (\mathrm{MeOH})_\mathrm{b} \rightleftharpoons \mathrm{A^-(HOMe)}_x + x(\mathrm{LP})_\mathrm{f} \qquad (4)$$

Unfortunately, resonances for bulk methanol, anion solvates, and $(\mathrm{LP})_\mathrm{f}$ groups are in the fast-exchange limit, giving a single narrow feature: no-one has yet succeeded in detecting anion solvates in slow exchange. The measured molal shift is due to $x(\mathrm{LP})_\mathrm{f}$ units together with x units of MeOH bound to the anions. The predicted unaveraged shifts come from our infra-red n.m.r. correlation

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[33] I. M. Strauss and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1977, 1796.
[34] M. Krell, unpublished results.

Table 2 *Proton resonance shifts for various salts and individual ions in methanol, together with solvation numbers required to fit the correlation of Figure* 3

Key	*Salt/ion*	*Shift*/p.p.m.[a,b]	*Solvation number*
—	Bu_4N I	0.272[d]	—
—	Bu_4N Br	0.172[d]	—
—	$Bu_4N\ ClO_4$	0.240[d]	—
i	ClO_4^-	2.0	2
ii	ClO_4^{-}[e]	3.0	3
iii	ClO_4^{-}[c]	2.6	2
iv	$(LP)_f$	3.1	
v	I^-	3.6	4
vi	Br^-	3.9	4
vii	$(LP)_f$[c]	4.0	—
viii	I^-[c]	4.1	4
ix	Br^-[c]	4.3	4
x	MeOH bulk	4.5	—
xi	Cl^-	4.5	4
xii	Li^+	5.0	4
xiii	Na^+[c]	5.2	5
xiv	MeOH bulk[c]	5.4	—
xv	Li^+[c]	6.1	4
xvi	Mg^{2+}	6.75	6
	Mg^{2+}[c]	7.1	6

(*a*) From the value for MeOH monomers in CCl_4. (*b*) at 25 °C unless otherwise stated. (*c*) at −70 °C. (*d*) from ref. 17. (*e*) this datum does not fit the correlation.

(Figure 9). This enables us to calculate approximate values of x, using standard procedures.

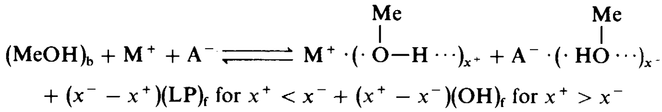
These calculations give reasonable values of x for anions (Table 2). It is particularly interesting that $x \approx 4$ for Cl^-. In aqueous solutions, it seems clear that Cl^- has a solvation number of 6.[35] The fall from 6 to 4 on going from water to methanol is in line with the fall from 3 to 2 for Et_3PO, discussed below. Water brings out a maximum solvation number, in our view, because of the large concentration of $(OH)_f$ groups in water (see below). The low solvation number for ClO_4^- ions is also in line with its low basicity.

The way in which these results are linked is shown in Table 2 and Figure 3 (p. 4). The solvation numbers are chosen so that the correlation is obeyed most satisfactorily. In particular, I show how firmly the solvation number is fixed: calculations for $x = 3$ for ClO_4^-, for example, give points well removed from the correlating line. (I should stress that by 'solvation number', I mean the number of molecules bound directly to the ion: in my view, for hydrogen-bonded systems, other definitions have little significance. However, this is not the only view.[24,36])

[35] G. W. Neilson and J. E. Enderby, *Ann. Rep. Prog. Chem.*, 1979, **76**, 185.

[36] B. E. Conway, in ref. 24, p. 582.

For cations, a similar method can be used. We need to consider two alternatives. If the solvation number of the cation (x^+) is greater than that of the anion (x^-) there will be an excess of '$(\mathrm{OH})_f$' groups. (As stressed above, these are weakly bound rather than free.) If (x^+) is $<(x^-)$ however, there will be an excess of $(\mathrm{LP})_f$ groups (equation 5):



$$(\mathrm{MeOH})_b + \mathrm{M}^+ + \mathrm{A}^- \rightleftharpoons \mathrm{M}^+ \cdot(\cdot \overset{\overset{\mathrm{Me}}{|}}{\mathrm{O}}\text{—}\mathrm{H}\cdots)_{x^+} + \mathrm{A}^- \cdot(\cdot \mathrm{H}\overset{\overset{\mathrm{Me}}{|}}{\mathrm{O}}\cdots)_{x^-}$$
$$+ (x^- - x^+)(\mathrm{LP})_f \text{ for } x^+ < x^- + (x^+ - x^-)(\mathrm{OH})_f \text{ for } x^+ > x^- \qquad (5)$$

We can therefore set the experimental salt shift equal to $x^+.\Delta\nu_M' + x^-.\Delta\nu_A' + (x^- - x^+).\Delta\nu_{LP}'$ [or $+(x^+ - x^-).\Delta\nu_{OH}'$]. We know $x^-.\Delta\nu_A'$, $\Delta\nu_M'$, and $\Delta\nu_{LP}'$. Hence, in the former case we can calculate x^+. This regime is followed for many salts, and hence x^+ can be found for several ions (Table 2). For example, $x = 5$—6 for Na^+ and ≈ 4 for Li^+.

By procedures such as this,[37] we have been able to estimate solvation numbers for many simple cations and anions, as indicated in Table 2. One point gives us confidence in the method, namely that for Mg^{2+}. The −70 °C value is direct, since both $\Delta\nu$ (i.r.) and $\Delta\nu'$ (n.m.r.) are known. The point for 25 °C is derived from the rapid average shift using $x = 6$. Since it is clearly established that $x = 6$ at low temperatures this is almost certainly correct. Hopefully, the other values are not greatly in error.

One important result emerging from our present data is that the solvation number for an ion may well vary, especially for weakly solvated ions. In particular, the solvation of one type of ion may vary with the nature of the other ion, and both may be temperature dependent. This is more likely to be true for solutions in methanol than solutions in water. The reason is clear: cations solvate *via* lone-pairs whilst anions use OH protons. In the extreme of equal solvation numbers both ions are fully satisfied. In the other extreme that only one ion type is solvated (*e.g.* $\mathrm{R_4N^+A^-}$ salts) these ions must compete with solvent structure for their solvation. This is an important problem which is ignored in most computer simulation 'experiments'.

3 Water

This section is relatively brief, not because there is less information than for methanolic systems, quite the reverse, but because the stage has been set in Section 2, and because, for the sake of brevity, I omit reference to many studies of peripheral importance to the present theme.

A. Water + Bases in Inert Solvents.—In contrast with methanol, water is very sparingly soluble in inert solvents. This can be understood as follows: like the methanol dimer, the water dimer is far more reactive than the monomer. However, the growing, reactive dimer and oligomer cannot become inert *via* cyclization

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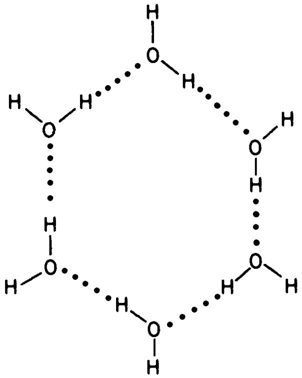
[37] M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, submitted.



(5)

since even a cyclic structure such as (5) has two points of attachment per water molecule. Hence collision with monomer molecules will result in further growth, and collision with other oligomers will lead to extensive aggregation. This, in turn, leads to phase separation. However, water is soluble enough in tetrachloromethane for infra-red and n.m.r. studies of systems containing added bases or $R_4N^+A^-$ salts to give useful information. Attempts to obtain infra-red–n.m.r. correlation diagrams such as that in Figure 3 have not so far been successful,[38] because infra-red spectroscopy can only give accurate information about HOH ··· B units, whilst n.m.r. limiting shifts inevitably relate to B ··· HOH ··· B units. However, a good correlation can be obtained using dilute solutions of water in basic aprotic solvents, and we will be using this in future studies.

B. Water + Aprotic Solvent Systems.—A major difference between bulk water and methanol is the presence of strong infra-red absorption in the $(OH)_f$ region in the 2ν (OH) spectrum for water and the almost complete absence thereof in the comparable spectrum for methanol. This contrast is even more striking when one recalls that, at room temperature, water is far closer to being a solid than is methanol. Nevertheless, the difference is, I think, only to be expected, since methanol, with its 'linear' chains and cyclic structures offers little resistance to motion whilst water, with its attempted infinite, three-dimensional structure, must suffer the breaking of many bonds as motion occurs.

(i) *Vibrational Spectroscopy.* In all that follows, I refer to studies on the O—H stretching mode of HOD in D_2O. This is a greatly simplified system spectroscopically since intra- and inter-molecular vibrations are decoupled, and problems over Fermi resonance with $2\nu_2$ are avoided. Work on the ν_2 band of H_2O is not yet extensive, and will not be discussed herein, although spectral effects in this region are of interest.

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[38] V. K. Thomas, Ph.D. Thesis, Leicester University, 1980.

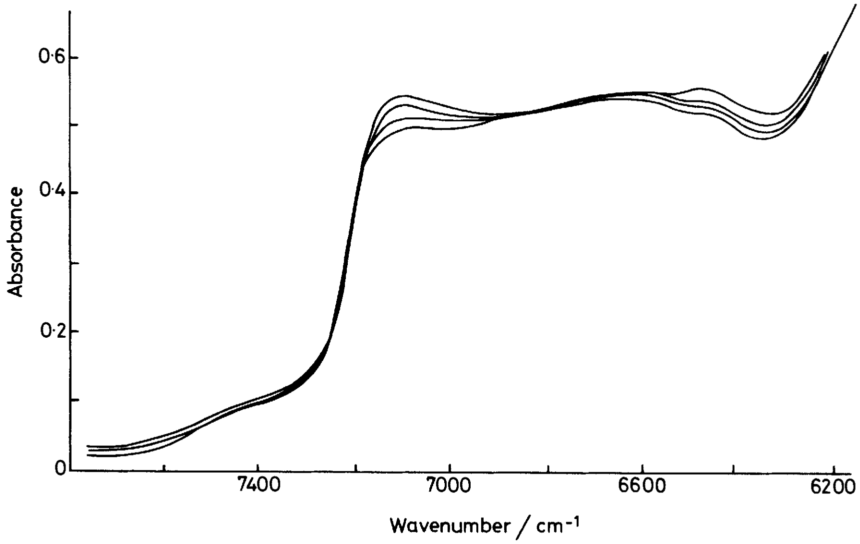

Figure 15 *Infra-red spectrum for water* (HOD *in* D_2O) *in the first overtone region showing the decrease in* $(OH)_f$ *oscillators* (7050 cm^{-1}) *on the addition of a basic co-solvent* (*DMSO*): a, HOD; b, +0.02 MF *DMSO*; c, +0.04 MF *DMSO*; d, +0.06 MF *DMSO*

Even using HOD in D_2O, the fundamental O—H stretching mode is not very informative except for certain salt solutions and glasses at low temperatures.[39] However, in contrast with methanol, the first and second overtone regions are of unusual interest because there is a switch in relative oscillator strengths, so that features due to weakly or non-bonded OH groups dominate the spectra (Figure 15), whereas in the fundamental region the strongly hydrogen-bonded oscillators dominate. (The true distribution is somewhere between those of the intensities in the fundamental and first overtone regions.) For some years these features have been used to monitor concentration changes, but there are differences of opinion regarding the nature of the species responsible for the absorption and the nature of the effects responsible for changes therein.

Since the high-frequency peak at *ca.* 7060 cm^{-1} is close to that for HOD in the gas-phase, the liquid-phase peak was first assigned to water monomers. Later it was concluded that the concentration of monomers must be spectroscopically insignificant and that the absorption was largely due to $(OH)_f$ groups.[40] This idea has been promulgated particularly by Luck and his co-workers[41] and by ourselves[1,2] amongst several others.[42] However, the protagonists of the con-

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[39] I. M. Strauss and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2518.

[40] L. M. Kleiss, H. A. Strobel, and M. C. R. Symons, *Spectrochim. Acta, Part A*, 1973, **29**, 829.

[41] W. A. P. Luck and W. Ditter, *Ber. Bunsenges. Phys. Chem.*, 1966, **70**, 1113; *Z. Naturforsch., Teil B*, 1969, **24**, 482.

[42] J. D. Worley and I. M. Klotz, *J. Chem. Phys.*, 1969, **45**, 2868.

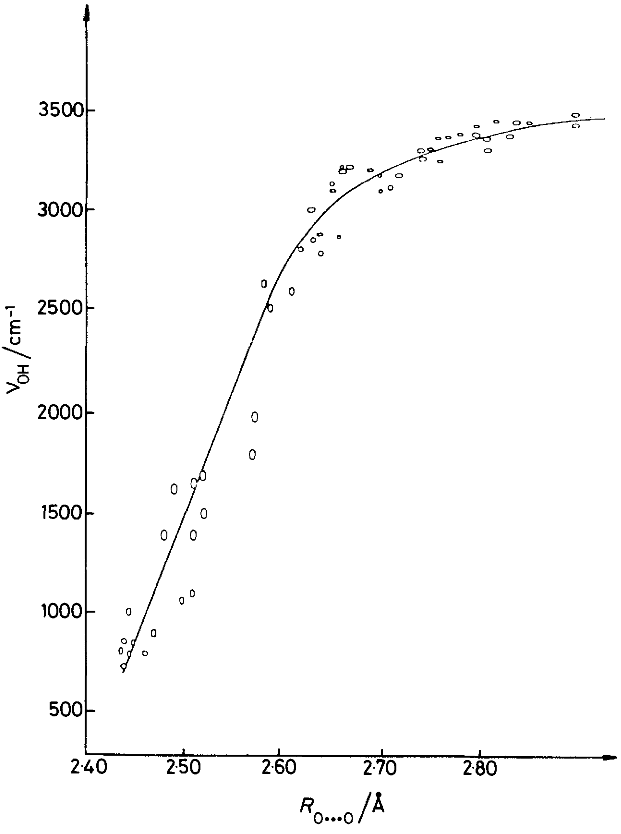

Figure 16 *Typical correlation between ν_{OH} and the oxygen ··· oxygen separation for a range of hydrogen-bonded systems*

tinuum theory of water structure seem to abhore the idea that there might be significant concentrations of $(OH)_f$ groups in liquid water (I don't understand why), and point out that it is possible to build up curves of the type shown in Figure 15 by assuming a suitable distribution of O ··· O separations, with no discrete $(OH)_f$ oscillators.[43] I'm sure this is possible since it is clear that very weakly bound O—H groups will have an absorption virtually identical with that for non-bonded groups since the shift from the $(OH)_f$ value is initially asymptotic, changing slowly for weak bonds, but rapidly for strong bonds (Figure 16).

Does this mean that we cannot obtain meaningful information from these

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[43] A. P. Zhukovskii, *Translated from Zh. Struckt. Khim.*, 1981, **22**, 56—63.

spectral regions? I don't think so, but clearly a great deal of caution needs to be used.

I have long maintained that if there are very weak hydrogen-bonds in liquid water there *must* also be broken bonds.[1,2] The literature is full of discussions about when a hydrogen bond ceases to be a genuine 'bond'. Such discussions seem to presuppose a continuing correlation between the OH groups and 'lone-pairs'. Surely, given that the majority of water molecules retain four hydrogen bonds of variable strength, then $(OH)_f$ and $(LP)_f$ groups can be envisaged as being uniformly distributed in a sea of 4-bonded molecules, there being no correlation between them? It might be supposed that the issue could be readily resolved by consulting the results of computer simulation experiments (Monte Carlo or molecular dynamics). Unfortunately, this is not the case, because the question to be asked is quite subtle. It is not enough to analyse for $H\cdots O$ distances or $O-\hat{H}\cdots O$ angles since the proton of any $(OH)_f$ group, for example, must always be quite close to oxygen atoms of surrounding, fully hydrogen-bonded, water molecules. The question must be extended to ask if the near neighbours are themselves fully hydrogen-bonded, or if one of them forms only three good bonds. It seems that in the present literature, this problem has not been specifically investigated. It will be very interesting to see what answers are eventually forthcoming.

In all that follows, I assume that equation (6) is of great importance for water, the concentrations of $(OH)_f$ and $(LP)_f$ units being several percent at ambient temperatures. My prejudice is that this simple equation is just as significant in determining the chemistry of water as is the auto-ionization equation.[1,2]

$$(H_2O)_b \rightleftharpoons (OH)_f + (LP)_f \tag{6}$$

For both the first and second overtone regions of the O—H stretching mode for HOD in D_2O, we have used a variety of methods for dividing the absorption at the $(OH)_f$ value into contributions from genuine $(OH)_f$ units and from very weakly bound (OH) groups. Probably the best method is based on a titration procedure, in the sense that it is a functional method. That is, it seems to assess the number of $(OH)_f$ groups directly available to added substrates. We find that when strongly basic aprotic solvents are added to water, there is a fall in the absorption in the $(OH)_f$ region, but this levels off in the region of *ca.* 60% absorption, leaving a broad feature with a less well-defined maximum shifted to low frequencies from the $(OH)_f$ band (Figure 15). In a more refined procedure, allowance is made for changes in the concentration of weakly bound (OH) groups which must modify the absorption in this region.[44] The contribution from $(OH)_f$ still comes out to be *ca.* 40% of the total.

This method breaks down for weakly basic co-solvents such as cyanomethane (MeCN). This is because units such as $MeCN\cdots HOH$ (or possibly the di-solvate) make such large contributions in the $(OH)_f$ spectral region that there is actually a gain in absorption rather than a loss. (The same applies, for example, to

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[44] G. Smith, Ph.D. Thesis, Leicester University, 1982.

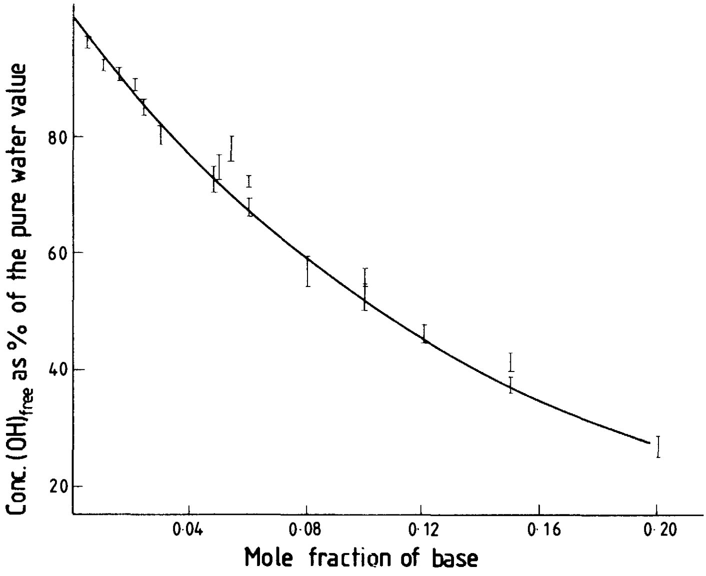

Figure 17 *Estimated fall in the $[(OH)_f]$ groups (%) on the addition of a range of strongly basic aprotic solvents to water. The line is based on the assumption of dihydrates and on initial 8% of $(OH)_f$ groups in pure water*

solutions of ClO_4^- ions.) It has been argued that this is evidence that MeCN acts as a 'structure-breaker'.[45] I'm not sure what this means. However, we can at least show that our reasoning—that there is a loss of $(OH)_f$ groups but a gain in weakly bound O—H groups which is greater because of the effect of equilibrium (6) gives a satisfactory explanation of the spectral changes. This, taken together with our evidence from studies of the C—N stretching mode, that MeCN is fully hydrogen-bonded in water, gives us confidence that the 'structure-breaking' process, which presumably *generates* both $(OH)_f$ and $(LP)_f$ groups, is less satisfactory.

The results, some of which have been published,[46] show that strongly basic co-solvents seem to behave consistently, as can be judged from Figure 17. Our more recent results,[44] using the second overtone region with a more refined analysis still support these general concepts.

It is curious that almost all co-solvents that are mixable with water are basic-aprotic or difunctional. We know of none that are primarily 'acidic', *i.e.* which interact with $(LP)_f$ units rather than $(OH)_f$. We predict that such solvents should cause an increase in $(OH)_f$ absorption. Good examples are $H—CCl_3$ or $RC{\equiv}C—H$ which are known to form good hydrogen-bonds. We

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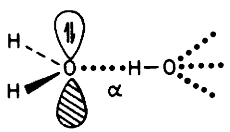
[45] J. Paquette and C. Jolicoeur, *J. Solution Chem.*, 1977, **6**, 403.

[46] M. C. R. Symons, J. M. Harvey, and S. E. Jackson, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 256.

think that this solubility difference occurs because $(OH)_f$ groups are more 'reactive' than $(LP)_f$ groups, and hence tend to pull molecules into solution more effectively. This can, perhaps, be understood in part, in that lone-pairs are not strongly directional. Indeed, planar units such as (6) will be important, as in the solvation of cations (see below). These structures will have a relatively low basicity prior to pyramidalization whilst the hydrogen-bond α will be strong.



(6)

As with methanol, it is possible to estimate positions of the O—H stretch absorption bands for $\left[\mathrm{B}\cdots\mathrm{HO}\vdots\right]$ units, especially when low temperatures can be reached, but the results are less clear-cut than those for MeOH, partly because of the far greater range of structures, and partly because cooling so often results in phase separation. Fortunately, the infra-red technique is very sensitive to phase separation, since ice (HOD in D_2O) gives a relatively sharp feature which is easily recognized against the background of broad lines, and also the increase in scattering results in an overall increase in absorption for phase-separated systems.[39]

(ii) *N.m.r. Spectroscopy.* Changes in $[(OH)_f]$ groups are also of major importance in determining proton resonance shifts for water protons when solutes are added.[46] I recall that $(OH)_f$ groups are not important in liquid methanol, and this contrast, in our view, accounts for the marked difference in trends in the shifts for methanol (Figure 7) and water (Figure 18) as basic aprotic co-solvents are added. Thus, for methanol, there are almost no $(OH)_f$ groups to assimilate, so reaction (2) occurs with generation of $(LP)_f$ groups which contribute an up-field shift to the averaged resonance (see above). In contrast, water suffers loss of $(OH)_f$ groups and hence loss of a strong up-field contributor. For many basic co-solvents this causes a net slight down-field drift in the 0—0.1 mole-fraction region (Figure 18). These proton resonance results strongly support the concept that $(OH)_f$ and $(LP)_f$ groups are important in liquid water.

The task of reproducing the proton resonance shifts for water–aprotic solvent systems is dominated by two factors, the solvation number of the co-solvent and its variation with concentration, and the effective concentration of $(OH)_f$ groups in liquid water at various temperatures. The former can often be determined by studying the spectra of the co-solvents: the latter has yet to be firmly established. Certainly, the n.m.r. shifts can be reproduced using self-consistent parameters:[46] what is required is a careful study of a range of co-solvents of known solvation number using a range of spectroscopic techniques. This task, which is underway,[44] should lead to good values for $[(OH)_f]$ and hence to the equilibrium constants

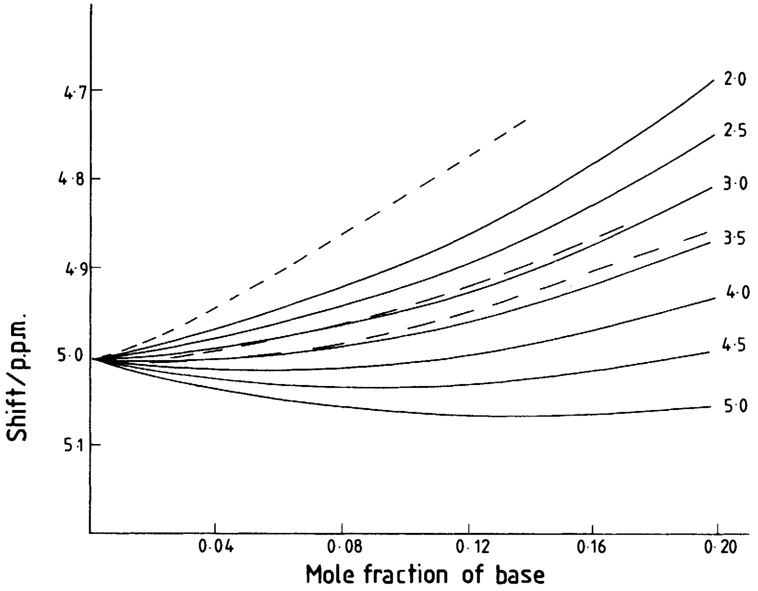


Figure 18 *Proton resonance shifts for water as a function of the mole fraction of added base: dashed curves* (a) *DMSO*, (b) *DMF*, (c) *THF*, (d) Me_2CO, (e) MeCN. *The full curves are reconstructions based on the loss of* $(OH)_f$ *groups and guessed shifts for the base solvates given in parenthesis*/p.p.m.

governing its concentration at various temperatures. Present results suggest that *ca.* 8% bond-breakage is about correct at 25 °C. As I have stressed elsewhere,[2] I am convinced that the presence of such a high concentration of free, reactive groups is of major importance in the chemistry of liquid water.

C. Use of Probes.—It is remarkable that the ‘acceptor number’ for water,[16] is far larger than those for alcohols. Our results for the P—O stretching frequency of Et_3PO shows that there is good agreement between the infra-red trends and those for ^{31}P resonance on which acceptor numbers are based.[15] We have obtained similar results for many other probes, including ^{14}N hyperfine coupling for R_2NO radicals,[13] the C=O stretch for acetone,[8] the S—O stretch for Me_2SO, and the C=O stretch for various amides.[47] In all cases, solutions in water exhibit far greater low-frequency shifts than solutions in alcohols.

Our results show that this occurs *not* because water forms stronger hydrogen bonds, but because it forms more. Thus, studies of mixed solvent systems, typified by that shown in Figure 20, show that Et_3PO in water forms three hydrogen bonds, whereas in methanol it forms mainly two. Similarly, acetone has two hydrogen bonds in water, but mainly one in methanol. Indeed, when one water

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[47] G. Eaton, Ph.D. Thesis, Leicester University, 1983.

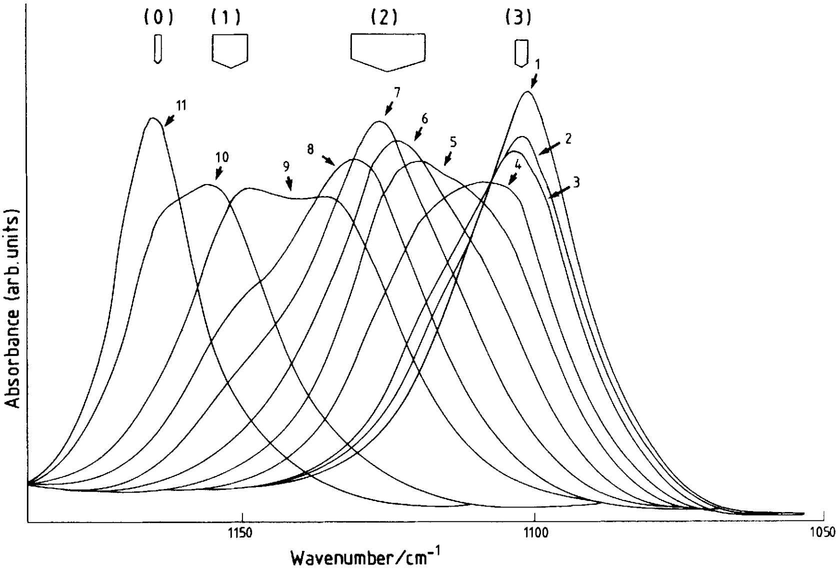


Figure 19 *Infra-red spectra for dilute solutions of* $\mathrm{Et_3PO}$ *in water* + MeCN *systems. Key (in mole fractions):* 1 = 0.00, 2 = 0.03, 3 = 0.07, 4 = 0.16, 5 = 0.36, 6 = 0.65, 7 = 0.79, 8 = 0.95, 9 = 0.97, 10 = 0.99, 11 = 1.00. *Band maxima are indicated by broad arrows which span their shifts, the numbers indicating the postulated number of water molecules*

molecule is removed from these molecules the new absorption maxima are close to those for methanolic solutions.

The trends seen in Figure 19 have been analysed in terms of gain and loss of four bands, assigned consecutively to $\left[\mathrm{Et_3PO}\begin{array}{l}\cdot\cdot\,\mathrm{HO-}\\ \cdot\cdot\,\mathrm{HO-}\\ \cdot\cdot\,\mathrm{HO-}\end{array}\right]$, $\left[\mathrm{Et_3PO}\begin{array}{l}\cdot\cdot\,\mathrm{HO-}\\ \cdot\cdot\,\mathrm{HO-}\end{array}\right]$, $[\mathrm{Et_3PO}\cdots\mathrm{HO-}]$, and $\mathrm{Et_3PO}$ with no hydrogen bonds. These trends are indicated in Figure 20.

These trends can be understood in terms of competition reactions such as:

$$\mathrm{B + Et_3PO(HO-)_3 \rightleftharpoons B\cdot(\cdot\, HO-) + Et_3PO(HO-)_2}, \tag{7}$$

but in the water-rich region this is mediated by water molecules and $(\mathrm{LP})_{\mathrm{f}}$ groups. It is important to note that the band maxima, especially those for the di- and mono-hydrates, are solvent dependent. The bands shift to high frequencies as the $[\mathrm{H_2O}]$ falls. This is to be expected, since tertiary and secondary water molecules are being progressively replaced by aprotic solvent. This weakens the hydrogen bonds to $\mathrm{Et_3PO}$ because of the loss of co-operativity.

Thus we have a good picture of the way $\mathrm{Et_3PO}$ is solvated in a range of mixed aqueous solvents, and hence we can attempt to interpret the $^{31}\mathrm{P}$ n.m.r. shifts exhibited by $\mathrm{Et_3PO}$ in such solvent systems. These shifts and our reconstructions

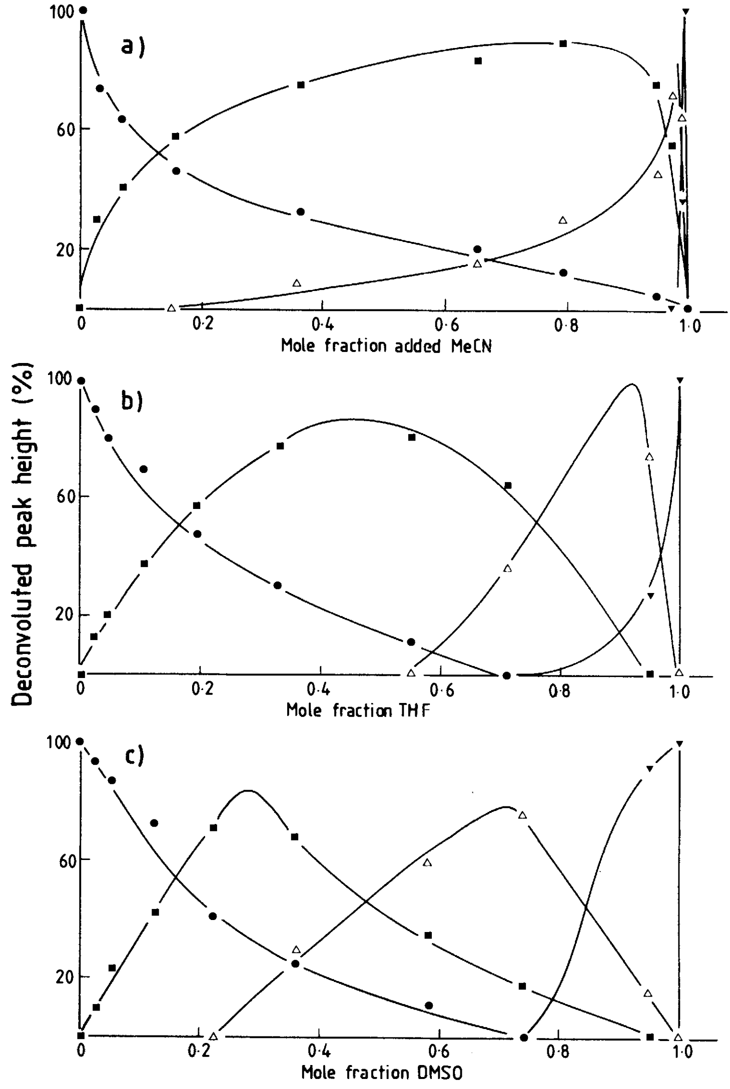


Figure 20 *Trends in the intensities of the deconvoluted* ν(P—O) *bands for individual solvates in mixed aqueous systems.* ●, $3H_2O$; ■, $2H_2O$; △, $1H_2O$; ×, $0H_2O$. (a) H_2O + MeCN, (b) H_2O + *THF*, (c) H_2O + *DMSO*

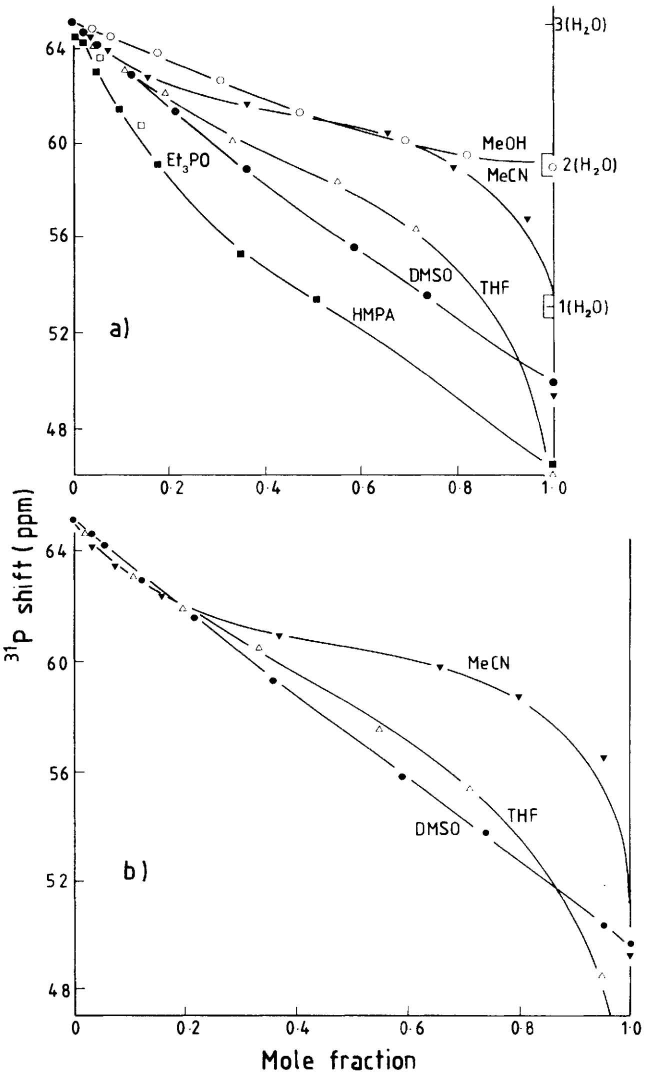
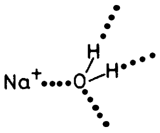


Figure 21 *^{31}P resonance shifts for Et_3PO in water + base systems as a function of the mole fraction of base. The points marked $3H_2O$, $2H_2O$, and $1H_2O$ were deduced from the infra-red spectra*

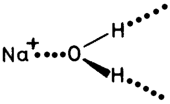
based on Figures 9, 19, and 20 are shown in Figure 21. Trends of this sort have often been displayed previously, together with a range of interpretations. We suggest that in the absence of infra-red results it would be impossible to obtain proper interpretations, since the number of solvates and their shifts cannot be determined from the ^{31}P data alone.

D. Water + Salts.—(i) $2\nu(\mathrm{OH})$ *Studies.* When $R_4N^+A^-$ salts are added to water (HOD; D_2O) there is a rapid fall in absorption in the $(OH)_f$ region. Our latest results[48] suggest that this fall, for the halide ions, is *ca.* three times as rapid as that for typical bases with solvation numbers equal to 2. This is in nice accord with the fact[35] that Cl^- forms bonds to six O—H groups.

In marked contrast, addition of $Na^+BPh_4^-$ ions gives a large increase in absorption in this region. The most obvious explanation is that Na^+ scavenges $(LP)_f$ groups whilst BPh_4^- ions remain unsolvated. As these results predict, salts such as NaCl induce relatively small changes in the $(OH)_f$ absorption, the change indicating that Na^+ solvation involves somewhat more $(LP)_f$ groups than the number of $(OH)_f$ groups taken up by Cl^- [*i.e.* 6]. If we argue that Na^+ solvates are as in structure (7), this implies a number of *ca.* 7 for Na^+. If, however, we accept the results of diffraction studies[35] and computer simulations,[49] that the solvation number is 6, then we need to argue that some water molecules use both (LP) groups, as in structure (8). The latter conclusion seems to me to be most reasonable, in which case there must be a rather fine balance between these two structures. This is in accord with the results of neutron diffraction studies.[35]



(7)



(8)

(ii) *N.m.r. Shifts.* As with methanol, we must conclude that the methods we originally proposed for obtaining individual ion shifts [50] for water protons are suspect, since they must contain contributions from changes in the concentrations of $(OH)_f$ and $(LP)_f$ groups. Making proper allowance for these changes is not an easy task, but once this has been accomplished, the method should give an alternative and independent estimate of effective solvation numbers. Preliminary results suggest that good values will be forthcoming,[48] but more work is required.

This method is based upon our proposal that we can use shifts in the O—H stretch of water (HOD) to estimate band positions for the proton resonance of water molecules attached to ions. We can say that these shifts are very similar

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[48] H. L. Robinson, unpublished results.

[49] M. Mezei and D. Beveridge, *J. Chem. Phys.*, 1981, **74**, 6902; R. O. Watts, *Mol. Phys.*, 1976, **32**, 659; G. Palinkas, W. O. Riede, and K. Heinzinger, *Z. Naturforsch., Teil A*, 1977, **32**, 1137.

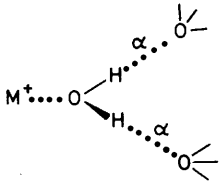
[50] J. Davis, S. Ormondroyd, and M. C. R. Symons, *Trans. Faraday Soc.*, 1971, **67**, 3465.

to those for methanolic O—H groups. Thus poorly solvated ions such as ClO_4^-, BF_4^-, or $CF_3CO_2^-$ induce only small shifts from the $(OH)_f$ values. F^- ions cause low-frequency shifts, as expected, but Cl^- ions at room temperature cause shifts comparable with that for bulk water, but the shifts are less temperature dependent than that for water. Shifts for Br^-, I^-, and NO_3^- are intermediate between those for ClO_4^- and Cl^- ions.

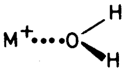
Monovalent cations in general cause proton resonance shifts which are very similar to those for bulk water and hence are difficult to monitor accurately. Divalent ions such as Mg^{2+} cause low-frequency shifts but the bands are broad and shift to low frequency on cooling in a manner comparable with water.

For many anions the high-frequency shifts from bulk water indicate weaker hydrogen-bonding. This may seem surprising, in view of the negative charges, but is really quite reasonable. Thus ClO_4^- ions are extremely weak bases, and also they are solvated by several (~4) OH groups. Also, ions like I^- form weak bonds because their filled orbitals are very diffuse: good hydrogen-bonds are usually associated with rather localized 'lone-pair' orbitals. However, in my view, the origin of the apparent weakness lies mainly in the high solvation number of these ions. The greater the solvation number, the weaker the individual bonds must be although the total interaction energy increases.

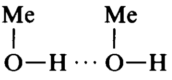
For the cations, the shifts are, in my view, largely a reflection of the strength of the hydrogen-bonds (α) formed by bound water, as in (9). We argue that the effect of replacing water by monovalent cations is small since the cations reinforce the strength of the hydrogen-bonds in (9) to about the same extent as does water. This view is in marked contrast with those of most other workers in



(9)

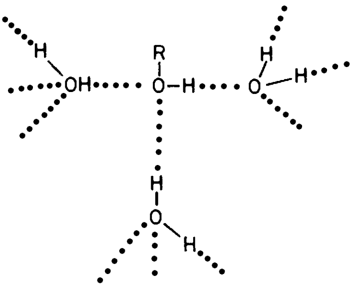


(10)

this field, who argue that the shifts are caused by the cation, no notice being taken of the hydrogen bonding in (9). In this context it is worth recalling that the shift induced in the $(O—H)_f$ oscillator of, say, MeOH, in the unit  $\overset{\text{Me}}{\overset{|}{\text{O}}}\text{—H}\cdots\overset{\text{Me}}{\overset{|}{\text{O}}}\text{—H}$ is very small indeed compared with shifts induced by direct hydrogen-bonding. Unfortunately, no shifts are known for non hydrogen-bonded units such as (10).

E. Water–Alcohol Systems.—In a full account of the applications of spectroscopy to the study of solvation phenomena, we should now move on to consider binary systems of different protic solvents, including water, alcohols, amines, and amides. These systems are much more complicated because of the large variety of types of hydrogen-bonds that can be formed. Because of space limitations, I confine myself to a few comments on water–alcohol mixtures.

One striking feature is the rapid loss of water $(OH)_f$ groups when alcohols are added to water. The results suggest that alcohols are effectively monobasic in low concentrations. We suggest[44] that this can be understood in terms of the tri-functional nature of alcohols and the general principle, elaborated herein, that water brings out the maximum solvation number for solutes. Hence when alcohols dissolve in water they form three hydrogen-bonds as in (11). This causes an effective uptake of one $(OH)_f$ group per molecule since the effects of the other two nearly cancel out. This conclusion accords with the OH proton shift for dilute solutions of alcohols in water, which is strongly down-field from the values for pure alcohols.[51] As the concentration of alcohol (methanol or ethanol) increases, this resonance shifts up-field towards the normal alcohol value, indicating loss of the third water molecule.



(11)

One nice aspect of our discovery that at low temperatures at optimum pH conditions both water and alcohol resonances can be detected, is that any specific interactions of a given solute can now be probed. We have recently shown that this procedure is very useful for aqueous sugars interacting with electrolytes,[52] but preferential interactions in simple water–alcohol systems do not seem to be very marked.

Acknowledgements. In conclusion, I should like to thank various research students for their help, and especially Dr. V. K. Thomas and Mr. G. Eaton for extensive help throughout the course of these studies. I also thank Miss V. Orson-Wright and Mrs. C. A. Crane for help in preparing the typescript.

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[51] J. M. Harvey, S. E. Jackson, and M. C. R. Symons, *Chem. Phys. Lett.*, 1977, **47**, 440.

[52] M. C. R. Symons, J. A. Benbow, and H. Pelmore, *J. Chem. Soc. Faraday Trans. 1*, 1982, **78**, 3671.