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SPECTROSCOPIC STUDIES OF IONIC SOLVATION (1)

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Abstract - Recent infrared and n.m.r. data for ionic solutions in methanol and water are compared. For methanolic solutions the results indicate that both cations and anions are solvated in such a manner that the primary solvent molecules are strongly hydrogen bonded to those in the bulk solvent. Monovalent cations slightly weaken such hydrogen bonds, but divalent cations increase their strength relative to the average hydrogen bonds in the bulk solvent.

The hydrogen bonds formed to anions are generally weaker than those formed by bulk solvent molecules, but they are nevertheless more precise and less temperature sensitive.

Aqueous solutions have been less informative, but qualitatively resemble those in methanol.

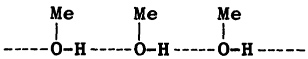
INTRODUCTION

Although aqueous solutions of electrolytes are of far greater importance and interest than those in methanol or higher alcohols, they are more complicated and hence spectroscopic studies are less directly informative. The simplification for methanol arises essentially because methanol generally behaves as if it were difunctional (though it may sometimes be trifunctional) whereas water is tetrafunctional. Some of the increased complexity that results is indicated below. Nevertheless, individual methanol molecules interact with solutes in a manner that more closely resembles water than does any other solvent. We have therefore studied methanolic systems in parallel with aqueous systems in the hope of being able to use the information gleaned from the former to enlighten results from the latter.

I - INFRARED AND RAMAN SPECTROSCOPY

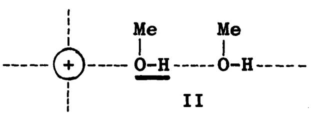
(i) Methanol

Generally, the effect of added electrolytes on the O-H stretching frequency of methanol is minor, resulting only in small shifts and line-width changes. This is true even when dilute solutions of CH_3OH are studied in CH_3OD (or CD_3OD) to minimise line-width effects from intermolecular coupling. Only for salts containing ClO_4^-, BF_4^-, PF_6^- or related anions are two distinct bands obtained (2-4). Unfortunately in these cases the new, high frequency, band (ca. 3550 cm^{-1} for methanol at room temperature) is close to the region in which "free" -OH groups (5) are expected to have a band, and hence assignment is not clear. We favour the concept that most of the intensity is due to OH groups solvating the anions (3), and this assignment is used in the following discussion. One approach to learning more about the effect of cations on the spectra of methanol has been to use metal perchlorates, making the assumption that the anions only affect the high frequency band, and hence that shifts in the main band are due to the cations (6). These results showed that cation effects are relatively small, monovalent cations causing shifts to high frequency and small divalent cations causing small low frequency shifts. Using the solvation model previously proposed (7,8), this means that the effects of the cations on methanol are comparable with that of methanol itself. That is to say that going from I to II hardly modifies the $\underline{\mathrm{OH}}$ hydrogen bond for such ions as Li^+ or Ca^{2+}, but the bond is clearly weakened for K^+ and



$$\text{-----}\overset{\mathrm{Me}}{\mathrm{O}}\text{-H-----}\underline{\overset{\mathrm{Me}}{\mathrm{O}}\text{-H}}\text{-----}\overset{\mathrm{Me}}{\mathrm{O}}\text{-H-----}$$

I



$$\text{-----}\oplus\text{-----}\underline{\overset{\mathrm{Me}}{\mathrm{O}}\text{-H}}\text{-----}\overset{\mathrm{Me}}{\mathrm{O}}\text{-H-----}$$

II

strengthened for Mg^{2+}.

These conclusions are strongly supported by recent low-temperature infrared results (9). We found that on cooling methanolic solutions of many electrolytes, a high frequency component became resolved (Fig. 1). This is clearly assignable to solvent molecules bound to the anions because of their marked anion sensitivity. In general these bands are narrower than the bulk methanol component, and markedly less temperature sensitive. Thus on warming, the bulk band shifts rapidly to high frequencies and also broadens, and overlap between the two bands becomes so severe that resolution is completely lost.

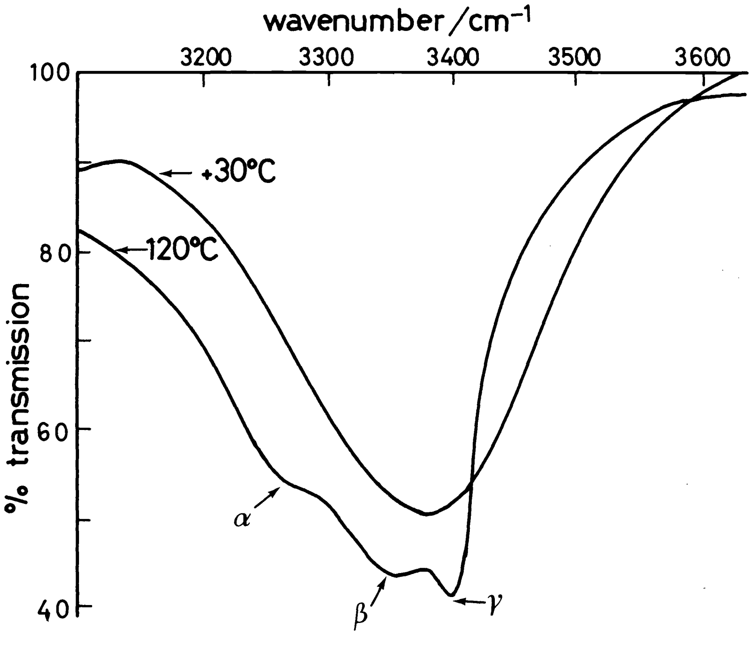
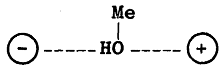


Fig. 1. The fundamental O-H stretching absorption for CH_3OH in CH_3OD containing LiI (3.7 mol kg^{-1}), (i) at 30°C, and (ii) at -125°C, showing the bulk methanol band shifted by Li^+ (α), the solvated iodide band (β), and the band assigned to solvent shared ion-pairs (γ).

The cations generally only induced shifts in the broad bulk methanol band. These shifts were similar to those obtained at room temperature for the perchlorate solutions (6) and hence we conclude that solvent molecules bound to the cations remain very similar to bulk solvent molecules. This is not surprising provided their OH groups are still bound to methanol chains and hence are subject to forces similar to those for bulk molecules. This is in contrast with expectation for methanol molecules directly bound to anions.

One important result is that, as the concentration of salt was increased, a third narrow band often grew in, as shown in Fig. 1. This band was always close to the "anion" band, the shift therefrom being similar to the shift of the bulk solvent band induced by the cations. Hence we assign this band to solvent molecules bound to both cation and anion as in III. This provides one of the most convincing methods for detecting solvent-shared ion-pairs,



$$\ominus\text{-----}\overset{\text{Me}}{\text{HO}}\text{-----}\oplus$$

III

whose significance was postulated some years ago (10).

Results for different anions are summarised in Fig. 2a. The order is that expected, but there are some interesting facets of the results that deserve attention. The most outstanding is that, apart from F^- (11), the bands are all on the high frequency side of the bulk band, implying weaker hydrogen-bonding than that in liquid methanol. This is less anomalous when one considers that, for example, Cl^- probably forms 5-6 hydrogen bonds to $\overset{\text{Me}}{\text{HO}}$-------- units whereas in the solvent, a given methanol molecule only forms one. Since progressive addition of methanol to an anion results in a steady fall in the solvation energy per methanol, this result is acceptable. The shifts can be compared with the O-H

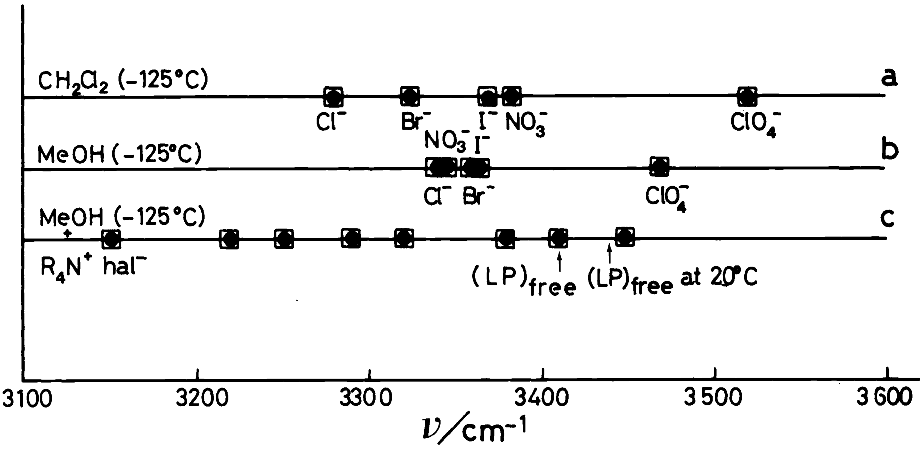


Fig. 2. Absorption maxima for O-H oscillators of methanol molecules bound to anions (A^-): a for A^-----HOMe units in CH_2Cl_2, b for A^- in bulk methanol, c for Cl^- in concentrated $Bu_4N^+Cl^-$ solutions in methanol. [The two high frequency bands are probably due to $(LP)_{free}$ units.]

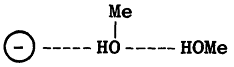
stretching frequencies for monomeric methanol bound to halide ions present as ion-pairs or clusters with tetraalkylammonium ions in inert media (11,12,13) (Fig. 2). These show clearly that when Cl^- binds only one methanol molecule, as in III, the interaction is indeed stronger than that in bulk methanol. This is despite the fact that this methanol molecule lacks the powerful reinforcing effect of a chain of molecules. Thus we have to consider two competing effects on the solvent molecules directly bound to the anion, as indicated in inserts IV–VI. Addition of a second molecule as in V will give two equivalent methanol

$\ominus$-----HOMe

IV

MeOH---$\ominus$---HOMe

V


$\ominus\text{-----}\overset{\text{Me}}{\overset{|}{\text{HO}}}\text{-----HOMe}$

VI

molecules each of which forms weaker bonds to the anion thus causing a high frequency shift. [The anion will, of course, experience an increase in bonding, as is shown, for example, by CTTS studies of iodide ions (14).] However, if the second molecule is added as in VI, bonding to the anion will be greatly enhanced and the primary solvent O-H stretch will appear at lower frequencies.

The comparison in a and b of Fig. 2 shows that for iodide ions there is almost no net shift on going from I^-----HOMe to the fully solvated ions. In this case the reinforcing effect of secondary solvent molecules just cancels the weakening effect of the primary molecules. For NO_3^- and ClO_4^- there is actually a reversal in the trend. For NO_3^- this may be linked to the fact that the ion remains asymmetrically solvated in the bulk solvent. For ClO_4^- ions it probably reflects the low polarisability of the ion. Thus increasing the primary solvation makes relatively little difference, and hence secondary solvation has an overriding effect.

Our results for concentrated solutions of tetraalkylammonium halides in methanol at low temperatures strongly support these contentions (15). A typical result is shown in Fig. 3. The most remarkable result is the appearance of a band to lower frequencies than that for the Cl^-----HOMe unit (12,13). This can only be caused by secondary solvation as in VI. Our tentative assignments are indicated in Fig. 2.

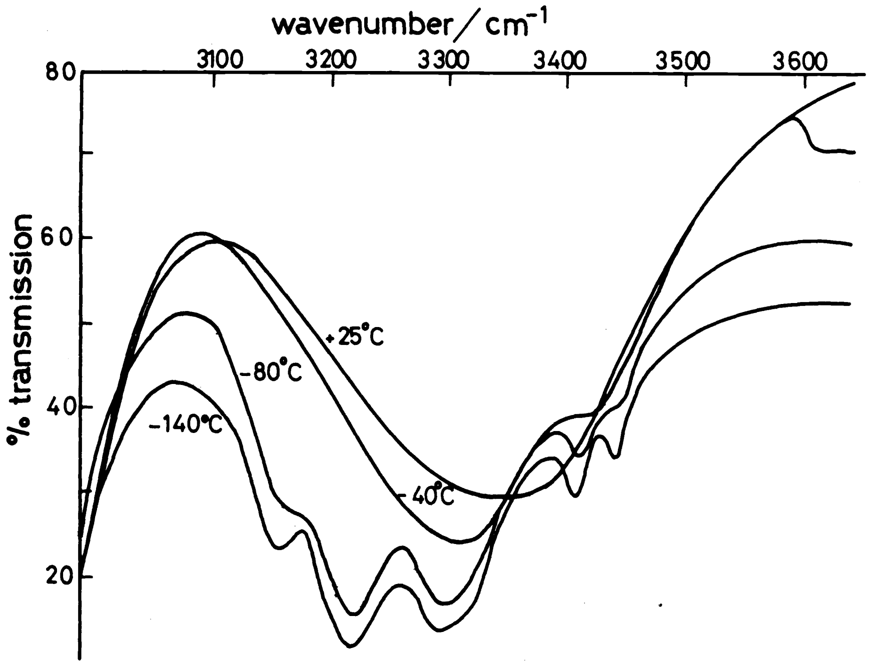
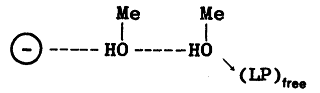


Fig. 3. Infrared spectra obtained from $Bu_4N^+Cl^-$ in methanol (CH_3OH in CH_3OD) at various temperatures.

One consequence of adding tetraalkylammonium salts to methanol must be the build-up of free "lone-pairs" on certain methanol molecules (16). Such terminal molecules are expected to form much weaker hydrogen bonds because of the loss of the reinforcing effect, and hence we have endeavoured to find a resolved O-H stretching band somewhere between those for bulk methanol and $(OH)_{free}$ oscillators. Because of the complexity of the halide spectra (cf. Fig. 3) we have studied the effect of added basic aprotic solvents on the spectrum of methanol. By choosing solvents such as dimethylsulphoxide or triethylamine which form very strong hydrogen-bonds to methanol we have obtained clear evidence for the growth of the expected intermediate band (at 3440 cm^{-1} at room temperature) which we confidently assign to $(LP)_{free}$ methanol molecules (Fig. 4) (17). Clearly, either of the two high frequency bands obtained from $R_4N^+Cl^-$ solutions (3410 and 3450 cm^{-1}) could be due to $(LP)_{free}$ molecules. Possibly one (3410 cm^{-1}) is the normal unit and the other (3450 cm^{-1}) is associated with an anion as in VII. So far as I am aware such terminal molecules have not previously



VII

been detected or even thought to be of significance.

(ii) Water

Because of our success with low-temperature methanol systems, we have also undertaken infra-red studies of aqueous salt solutions (18). [Again, we used dilute HOD in D_2O to avoid inter- and intra-molecular coupling.] One of the major problems is that on solidification phase separation often occurs. As a consequence we often obtained very good spectra for salt hydrates, some of them novel (18). Fortunately, in several instances broad features assignable to solvent molecules bound to the anions were obtained, and in general, the trends seem to be similar to those shown in Fig. 2 for anions in methanol. No clear evidence for $(LP)_{free}$ groups was obtained for solutions of tetraalkylammonium salts.

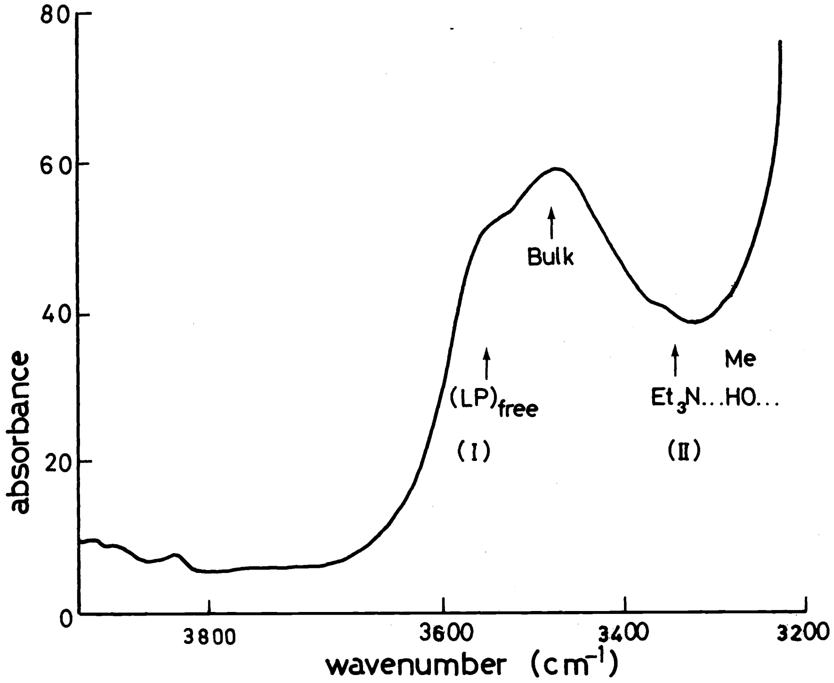
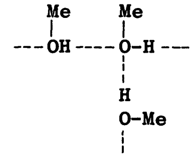


Fig. 4. Infrared spectrum in the O-H stretch region for MeOH and Et_3N systems: 0.7 MF MeOH showing features assigned to I, $(LP)_{free}$ groups, II Et_3N---HOMe--- units and bulk MeOH (central band).

II - OVERTONE INFRARED SPECTROSCOPY

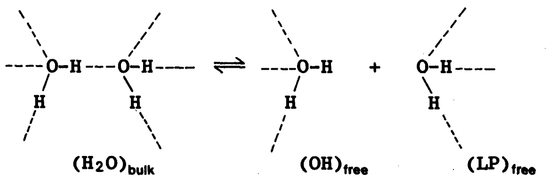
A major factor in the overtone regions of the O-H stretching frequency is that the fall in oscillator strength for $(OH)_{free}$ groups relative to the fundamental band is much less than that for strongly hydrogen-bonded OH groups. The consequence for water is that there is a well defined peak at ca. 7120 cm^{-1} in the first overtone (for HOD in D_2O) which is generally assigned to $(OH)_{free}$ groups (19-21). [No well defined band is obtained for methanol in this region, probably because $(OH)_{free}$ groups are rapidly scavenged by the large excess of lone-pairs not normally used for hydrogen bonding (8). Such units (VIII) ought themselves to have



VIII

a characteristic band, again between the $(OH)_{free}$ band and the bulk methanol band. Some evidence for this at ca. 7000 cm^{-1} has been obtained from solutions of $NaBPh_4$ in methanol (22).]

The $(OH)_{free}$ band for water provides a useful method for studying the way in which solutes scavenge (OH) groups or (LP) groups. We argue that the changes induced by added solutes can largely be understood in terms of the simple equilibrium:



(1)

Addition of basic aprotic molecules should result in a scavenging of (OH) groups and a consequent gain in the concentration of $(LP)_{free}$ groups. [As was found spectroscopically from methanol.] What we observe is a fall in the 7120 cm^{-1} band, and with some approximations, this can be converted into an estimate of the loss of $(OH)_{free}$ groups (23). To a first approximation, all strongly basic aprotic solvents induce the same loss. If we postulate that they only form one hydrogen bond per molecule (24), we can compare the results with those for tetraalkylammonium halides, and on the further assumption that the cations have little effect, we can obtain an estimate of the number of OH groups taken up by each anion. The result for Cl^-, for example, is *ca.* 5, in good agreement with the recent results from neutron scattering studies by Enderby and co-workers (25). This result strongly supports our contention (26) that, for $R_4N^+A^-$ salts, it is the anions that cause the fall in the concentration of $(OH)_{free}$ groups, not the R_4N^+ ions, as has previously been supposed (27,28). I am not saying that "clathrate cage" formation, frequently postulated for aqueous solutions of large alkylammonium ions, is not occurring, but only that the extent to which this causes a loss of $(OH)_{free}$ groups is small compared with the effect of the halide ions. This claim is supported by our results for $NaBPh_4$ in water (26). In this case a large growth in the concentration of $(OH)_{free}$ groups was observed. If we postulate that the BPh_4^- ions are largely unsolvated, then this growth is predicted from equation (1) since Na^+ ions will scavenge (LP) groups. The fit is good if the solvation number for Na^+ is in the region of 6-7 (23). Most salts give rise to relatively small changes that can be predicted fairly accurately from the values obtained for the halide and sodium ions as outlined above. Thus a reasonably self consistent picture has been obtained. The errors involved in these measurements are quite large. It is hoped that with more refined instrumentation some of the more subtle differences in the behaviour of individual ions can be deduced.

III - N.M.R. SPECTROSCOPY

I will confine my attention to shifts in the OH proton resonances for water and methanol, since these results link most directly with those from vibrational spectroscopy. The shifts induced by cations in methanol and water (29) reported some time ago (7,29), agree reasonably well with the infrared shifts discussed above (7). Thus cations that shift the proton resonance to high-fields shift the OH stretching band to high frequencies (weaker hydrogen bonding in both cases). Similarly, cations such as Mg^{2+} that give a low-field n.m.r. shift give a shift to low frequencies in the infrared. For the anions the correlation is less well defined, but in general the trends are similar. Thus F^- causes a large down-field shift in the n.m.r. spectrum but a relatively small low-frequency shift in the infrared. The other halide ions give rise to relatively small high-field shifts, in the n.m.r. spectra, and somewhat larger high frequency vibrational shifts. Correlation between n.m.r. shifts and O-H vibrational frequencies is quite good for mono-solvated anions in inert media. This correlation has been extended to include the effect of basic cosolvents on monomeric methanol (Fig. 5). This plot is interesting in that it underlines

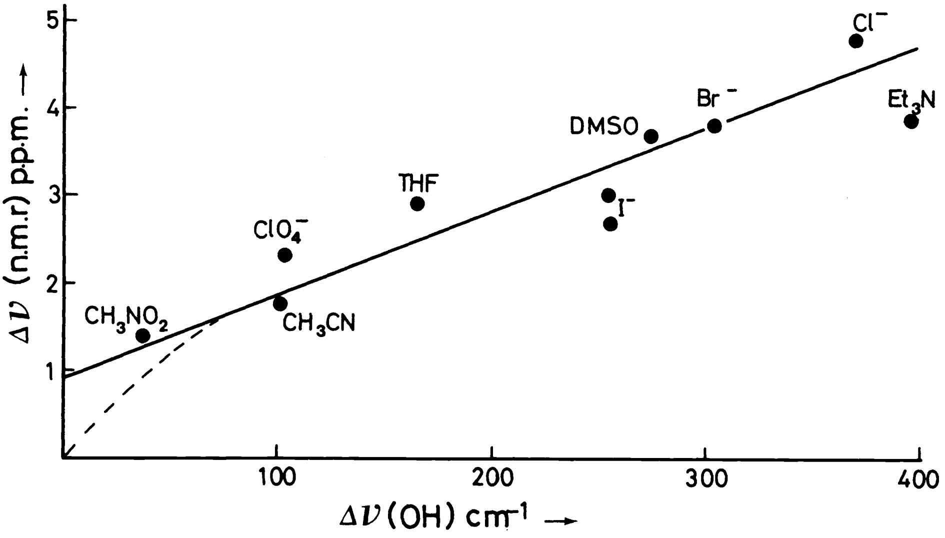


Fig. 5. Correlation between the base or anion induced shifts in the OH proton resonance of methanol in CH_2Cl_2/MeOH---B or CH_2Cl_2/MeOH---A^- systems and the corresponding shifts in the O-H stretching frequencies. In both cases the shifts are measured from the values for monomeric methanol.

the similarity between anions and basic aprotic cosolvents that is an underlying theme of this review. In particular there is clearly no special extra shift in the n.m.r. spectra for the ions associated with their charge. This supports my contention that ion-induced shifts in the OH resonance of protic solvents can properly be treated as a hydrogen-bonding phenomenon, and there is no need to invoke an extra shift purely due to the large electric field.

At low temperatures methanol molecules bound to Mg^{2+} ions give rise to a resolved OH proton resonance to low-field of the "bulk" OH resonance. Hence it is possible to study the effects of additives on both types of protons (30). Some results are shown in Fig. 6.
Basic aprotic solvents cause relatively rapid up-field shifts for pure methanol. Some

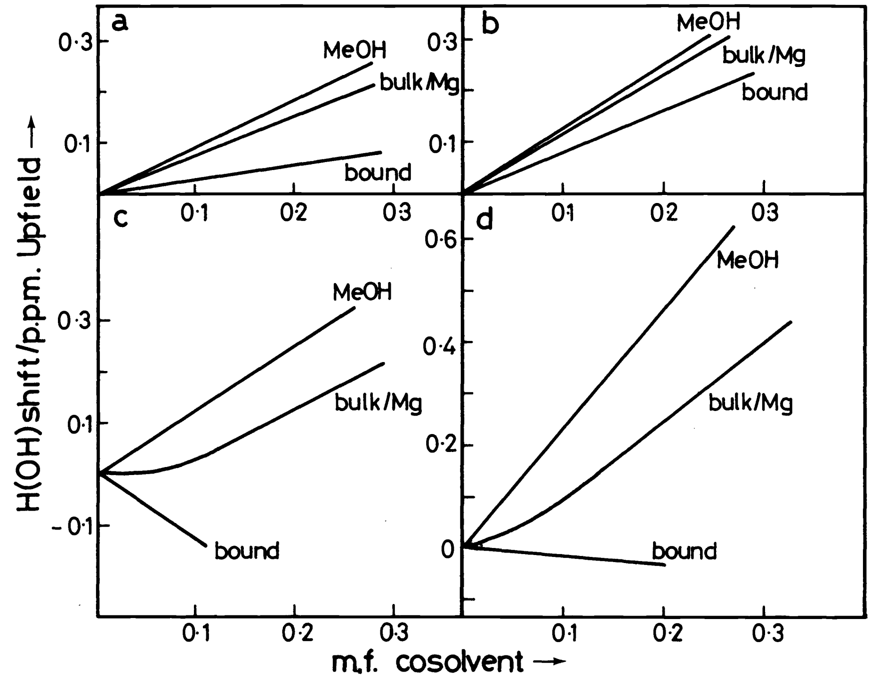


Fig. 6. Shift (ppm) of the $^{1}H(OH)$ resonance of methanol containing 0.5 M $Mg(ClO_4)_2$ at -70°C as a function of the MF of cosolvent.
(a) Acetone, (b) MeCN, (c) DMF, (d) DMSO.

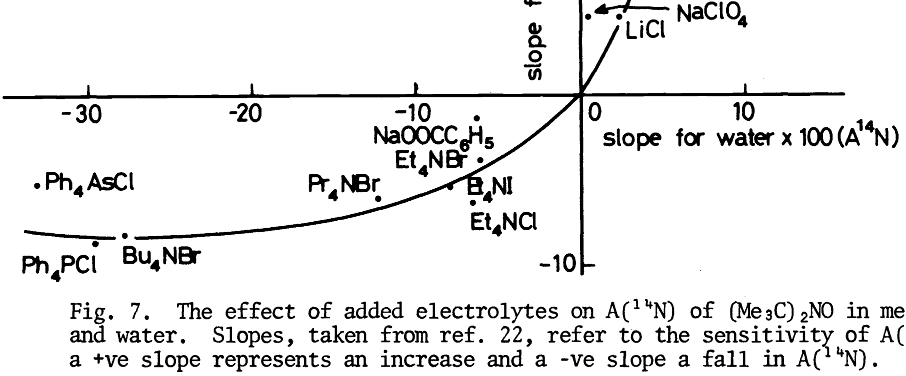
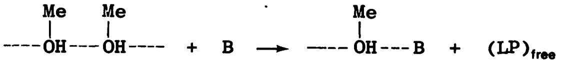


Fig. 7. The effect of added electrolytes on $A(^{14}N)$ of $(Me_3C)_2NO$ in methanol and water. Slopes, taken from ref. 22, refer to the sensitivity of $A(^{14}N)$: a +ve slope represents an increase and a -ve slope a fall in $A(^{14}N)$.

of these solvents added to water induce small down-field shifts prior to giving rapid high-field shifts: this anomalous trend is assigned to the scavenging effect on $(\mathrm{OH})_{\mathbf{free}}$ groups detected in the overtone infrared region. Since free (OH) groups resonate at very high fields, their loss gives a strong down-field increment. Liquid methanol contains few such groups and hence the resonance moves up-field directly.

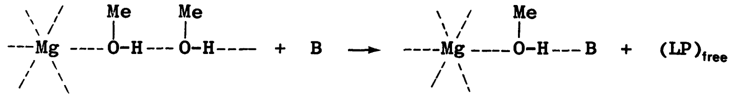
Our results show that in the presence of magnesium perchlorate these solvents cause a reduced initial shift in the bulk OH resonance. This has been discussed in terms of partial desolvation of the anions (30). However the OH resonance shift for MeOH bound to Mg^{2+} ions is greatly reduced and may even become negative for strongly basic cosolvents. We contend that this difference arises because for pure methanol the reaction is:



$$\text{----}\overset{\text{Me}}{\overset{|}{\text{OH}}}\text{---}\overset{\text{Me}}{\overset{|}{\text{OH}}}\text{----} + \text{B} \longrightarrow \text{----}\overset{\text{Me}}{\overset{|}{\text{OH}}}\text{---B} + (\mathbf{LP})_{\text{free}}$$

(2)

whilst for $Mg(MeOH)_6{}^{2+}$ it is



$$\text{---Mg----}\overset{\text{Me}}{\overset{|}{\text{O}}}\text{-H---}\overset{\text{Me}}{\overset{|}{\text{O}}}\text{-H---} + \text{B} \longrightarrow \text{----Mg----}\overset{\text{Me}}{\overset{|}{\text{O}}}\text{-H---B} + (\mathbf{LP})_{\text{free}}$$

(3)

The $(\mathrm{LP})_{\mathbf{free}}$ resonance, which, judging from the infrared results, shift well up-field of the bulk resonance, averages with bulk solvent and contributes a strong up-field shift to the bulk solvent resonance in both cases. The resonance from bound MeOH is only influenced by the formation of $\text{---Mg---}\overset{\text{Me}}{\text{OH}}\text{-----B}$ units, and this is therefore a new method of measuring the relative basic strengths of aprotic solvents. The results so far obtained agree well with other scales of hydrogen-bond basicity. Thus we now have a reasonable explanation of the apparent anomaly that strongly basic cosolvents induce strong up-field shifts in the methanol OH resonance.

Strongly basic cosolvents not only shift the resonance for $Mg(MeOH)_6{}^{2+}$ but they also cause the intensity of this resonance to fall with the concomitant growth of new resonances. These are due to $(MeOH)_5Mg\text{-}B^{2+}$, $(MeOH)_4MgB_2{}^{2+}$, etc., and we find that the ease of such displacements follows roughly the basicity of the cosolvent B, relative to that of methanol. [It is worth noting that water displaces methanol remarkably efficiently, indicating that it is much more basic than methanol when in dilute methanolic solution.]

The effect of added electrolytes on the two resonances has also been examined. The results show that, as expected, the magnesium solvent molecules interact only with the anions, via the formation of solvent shared ion pairs. For non-basic anions the interactions appear to be statistical, and the shifts induced are close to those previously assigned to the effect of anions on bulk methanol (7). This affords satisfactory support for these previous assignments. The bulk resonance is, of course, shifted by both cations and anions. The shifts differ from those in the absence of magnesium perchlorate in the initial regions in a manner comparable with that for added bases (Fig. 6). We tentatively suggest that this region of insensitivity is related to partial desolvation of the weakly solvated $ClO_4{}^-$ ions.

Finally, I want to refer briefly to our use of di-t-butyl nitroxide as a probe to study mixed water + solvent systems (31), and aqueous and methanolic electrolyte solutions (22). The most informative aspect of these studies has been the change in the ^{14}N hyperfine coupling constant. This is particularly sensitive to hydrogen bonding at oxygen and essentially monitors the strength and extent of this bonding. The results suggest that water forms stronger hydrogen bonds than methanol, but for mixed solvents, there is no indication of preferential solvation by water. When electrolytes were added, the methanolic solutions showed a greater response to cationic interactions and the aqueous solutions showed a greater response to anionic interactions (Fig. 7) (31). [Note, high values of $A_{iso}(^{14}N)$ correspond to strong hydrogen bonding: in the absence of hydrogen bonding values in the 15.5 - 15.6 G region are obtained.] The salt $Na^+BPh_4{}^-$ produces the expected increase in A_{iso} for methanolic solutions, but an unexpected fall for aqueous solutions. Given that the R_2NO molecules all form hydrogen bonds in water, we had expected to observe little change. The fall may well be due to clathrate-cage formation by the $BPh_4{}^-$ anions causing an induced encagement of the R_2NO molecules and a consequent loss of hydrogen-bonding. This would also explain the enhanced fall induced by large R_4N^+ ions relative to Me_4N^+ ions (22).

CONCLUSIONS

Some important general conclusions emerge. Protic solvent molecules, because of their amphoteric character, act as bridges linking cations or anions to bulk solvent molecules, or linking cations to anions. There is no spectroscopic evidence for the popular concept of a "disordered" region of solvent molecules around solvated ions. Anions are in general at least as precisely solvated as are cations, and tend to form large but precisely oriented primary solvent shells. Water is probably more acidic and more basic than methanol.

The simple concepts of $(OH)_{free}$ and $(LP)_{free}$ groups receive strong support from vibrational and n.m.r. spectroscopy. In my view the concentrations of these groups is of considerable chemical significance, especially for aqueous solutions. I think that this is an important factor when considering the reactivity of water since it is these groups that have the greatest opportunity for reacting with substrates (32,33).

Acknowledgement - I thank Mrs. V. K. Thompson for her unstinted help in this work, and Miss S. E. Jackson, Mr. I. M. Strauss, Dr. J. M. Harvey and Dr. T. A. Harvey for their contribution to various aspects of the work discussed herein.

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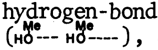
5. By "free" OH groups or $(OH)_{free}$, I mean OH groups in which the proton is not hydrogen-bonded. For methanol there will generally be one other hydrogen bond ( $\overset{\text{Me}}{\text{HO}}\text{---}\overset{\text{Me}}{\text{HO}}\text{----}$), and for water, three.
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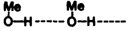
15. I. M. Strauss and M. C. R. Symons, *J.C.S. Faraday I* 74, 2146 (1978).
16. By free lone-pair groups or $(LP)_{free}$, I mean methanol molecules having no hydrogen-bonds to oxygen ( $\overset{\text{Me}}{\text{O}}\text{—H-----}\overset{\text{Me}}{\text{O}}\text{—H-----}$). For water there will again be three remaining hydrogen bonds.
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