Anion Solvation in Protic Solvents

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Summary Spectroscopic evidence is advanced in favour of the concept of continuous hydrogen-bonding from anions into bulk solvent with no intervention of an intermediate structureless region.

FOR many years the most popular pictorial model for ionic solvation[1] has been one comprising concentric regions of solvent molecules, the first, primary shell (A) strongly 'bonded' to the ion, the next, secondary shell weakly interacting with the ion (B), a third region of disorder (C) and finally, bulk solvent (D). For some ions, and in some models, the secondary shell (B) is dispensed with, but the broken structure region (C) is always thought to be significant. One of us has expressed the view that this region (C) is improbable in protic media.[2] Instead, a continuous hydrogen-bonded system is envisaged such that the primary solvent molecules are directly bonded into the 'bulk' solvent system. Evidence for or against this concept is sparse. For Mg^{2+} and Al^{3+} there is some ^1H n.m.r. evidence in favour of strong secondary (B) solvation,[3] but this is not compelling. We have recently acquired some i.r. spectroscopic data which seem to disprove the normal model, and to provide strong evidence in favour of the concept[2] of continuous structure.

Although room-temperature i.r. spectra in the O–H stretching region of water and alcohols are so broad as to be relatively uninformative, we have found that on freezing suitable solutions to the glassy state the component bands often narrow sufficiently to give reasonable resolution.[4] In general, we find that the O–H groups directly bonded to anions give rise to narrow components usually on the high-frequency side of the band for pure solvent, and frequencies of the band maxima can be measured quite accurately. An example is given in the Figure. The cation effects are generally smaller and result in an apparent shift of the main solvent band. The results for the anions can be compared with those obtained for solvates in inert solvents, $R_4N^+X^- \cdots HOR$, in which only one solvent is hydrogen-bonded to the anion. For example, for chloride there is a shift of $+60\,cm^{-1}$ on going from the mono-solvate to that in bulk methanol. For bromide the shift is $+35\,cm^{-1}$ and for iodide, $-25\,cm^{-1}$.

These shifts are interpreted in terms of two factors; (a) an increase in primary solvation causing a fall in the anion hydrogen-bond strength; this effect falls as the primary solvation number falls and (b) secondary solvation, which results in an increase in the strength of the anion hydrogen-bonds. For chloride, (a) dominates, but for iodide, (b) is slightly more important.

These conclusions are supported by the observation of multiple bands for glassy solutions of tetra-alkylammonium halides containing an inert solvent. Some are shifted to low frequencies relative to the mono-solvates, indicative of secondary solvent: $R_4N^+X^- \cdots HO(Me) \cdots HOMe$, and some to higher frequencies, indicative of two or more primary solvent molecules.

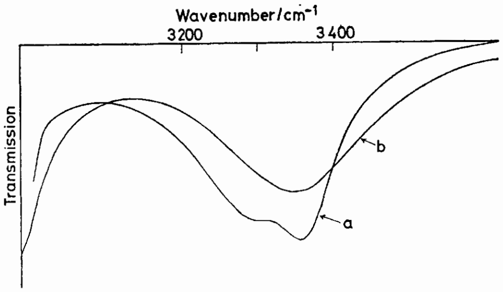

FIGURE. I.r. spectrum for a 3·7 molal solution of lithium bromide in methanol at *ca.* 150 K (a) and room temperature (b).

The fact that in bulk solvents the anion bands are all on the high-frequency side of the solvent band arises not because solvation is weak but because the solvation number is high compared with that for the solvent itself (*cf.* the fact that water accepts two hydrogen bonds, and alcohols only one per molecule.) We stress that there is no evidence for any free or weakly bonded OH groups even though the technique is very sensitive to their presence. This suggests the absence of any outer layer (C) in which solvent molecules are in a non-structural condition.

Strong support for this conclusion comes from studies of the overtone region for aqueous (HOD) solutions. These spectra show a narrow feature at $7120\,cm^{-1}$ assigned to $(OH)_{free}$ groups. Tetra-alkylammonium halides, generally, cause a marked fall in the intensity of this feature, even at elevated temperatures when clathrate cage effects are of little importance. This demonstrates that the halide ions scavenge $(OH)_{free}$ groups, as expected, and there is no support for the concept of a region of non-bonded water molecules.

We conclude that the best model for anions in protic media is one in which there is a layer of solvent molecules (probably 4—6) that act as hydrogen-bond donors to the anions and acceptors to solvent molecules in the next shell. These, in turn, are bonded to neighbouring solvent molecules in much the same manner as any other bulk solvent molecules. Secondary solvation (B) can thus be viewed *not* purely as a phenomenon induced by the anions, but as a natural manifestation of the solvent molecules' desire to act as hydrogen-bond donors and acceptors. Region (C) on this model is redundant.

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[3] M. C. R. Symons, *Spectrochim. Acta*, 1975, **71A**, 1105.
[4] I. M. Strauss and M. C. R. Symons, *Chem. Phys. Letters*, 1976, **39**, 471.