Ion-pair and Ion-cluster Formation Induced by Water Structure

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THAT water is an extremely good ion-solvating medium for most ions is well established as also is the fact that water at ordinary temperatures has an extensive three-dimensional structure. It might, therefore, be expected that for certain electrolytes these two properties would oppose each other and the aim of the present work was to discover systems for which the latter property of water dominated.

It has already been suggested by Diamond[1] that ions might begin to pair as a result of water structure when the ions are greater than a certain size. In seeking suitable systems our attention was drawn to the extensive work on the absorption spectra of cationic and anionic dyes in solution.[2] It is clear from these results that water does, indeed, occupy a very special place amongst solvents. In general two bands are detected, *M*-bands at low concentration and *H*-bands at high concentration. The results show a steady trend in solvent order such that good solvents favour the *M*-band and poor solvents the *H*-band for a given concentration of dye. Water, however, is anomalous and if fitted in to the scale would have an apparent dielectric constant[2a] of about 2·5.

Most theories assign the *M*-band to a monomer species (for cationic dyes we will call this D^+) and the *H*-band to either dimers (D_2^{2+}) or clusters. In order that dimerisation should cause the spectral modification, interaction must be strong and the model taken for theoretical discussion is of two dye ions lying parallel with each other having no intervening solvent or gegen ion.[3] Then the special role of water is that it can solvate doubly charged ions (D_2^{2+}) more readily than can poorer solvents.[2b]

In our view, these spectral changes are better understood in terms of water-structure. We suggest that these dye ions are so large that surrounding water molecules prefer to bond to water than to the dye ions which therefore stabilise themselves by ion-pair or ion-cluster formation. In accord with this is the marked increase in the intensity of the *M*-band of Methylene Blue on heating, and the very rapid increase in the intensity of the *M*-band on addition of solvents such as t-butanol (where complete conversion into the *M*-band has occurred in the 0·1 mole fraction alcohol region).

These and similar experiments are, however, not definitive. We have accordingly studied the electron spin resonance spectra of the *NN*-dimethyl-4,4′-dipyridyl monocation as prepared from Methylviologen (chloride) by either photolysis[4] or chemical reduction[5] of the solution. The absorption spectra show the expected *M*- and *H*-bands in water as a function of concentration. The electron spin resonance spectrum was identical to that reported by others[4] and no marked changes were observed in the concentration range

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[1] R. M. Diamond, *J. Phys. Chem.*, 1963, **67**, 2513.

[2] Key references will be found in (a) R. B. McKay and P. J. Hillson, *Trans. Faraday Soc.*, 1965, **61**, 1800; (b) W. West and S. Pearce, *J. Phys. Chem.*, 1965, **69**, 1894.

[3] H. Devoe, *J. Chem. Phys.*, 1965, **41**, 393.

[4] C. S. Johnson and H. S. Gutowsky, *J. Chem. Phys.*, 1963, **39**, 58.

[5] E. M. Kosower and J. L. Cotter, *J. Amer. Chem. Soc.*, 1964, **86**, 5524.

corresponding to the colour change. The lines were narrow (ΔH_{ms} = approx. 0·1 gauss) and frozen solutions at 77°K showed only a single structureless line having ΔH_{ms} equal to approx. 6 gauss and a g-value close to 2. The intensity of the absorption increased steadily with increase in concentration and there was no evidence for the formation of a diamagnetic species.

We can therefore say that if dimers are present, they are neither singlet species nor a strongly interacting triplet species. Dimerisation is not eliminated, but if it does occur the paramagnetic cations must be separated by at least 10 Å and clearly there will be intervening solvent molecules or gegen ions. It seems highly improbable that such dimerisation could be the driving force which causes the optical spectral changes in water although the spectral change itself could be caused in some instances by such dimerisation. We conclude that the modifications in absorption spectra are the result of ion-pair formation[2a] and that the driving force is the desire for neighbouring water molecules to be part of the bulk structure.

An experiment was designed to test the difference between individual water molecules and bulk water. We selected a solvent system of low dielectric constant such that both H- and M-bands appeared in the spectrum of the dye Methylene Blue. Water in low concentration was then added. The effect was a drastic increase in the intensity of the M-band despite the fact that in pure water under these conditions the spectrum of the dye shows hardly any M-band at all. Thus in the absence of bulk water, water molecules are solvating the ions very effectively.

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