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Ionic Solvation by Water in Dimethylsulfoxide

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Interactions between certain ions and water, at low concentrations, have been studied in dimethylsulfoxide mainly by near-infrared and proton magnetic resonance spectroscopies. The equilibrium constant for the hydration of the proton was found to be equal to 0.47 by IR spectroscopy. Hydration constants were determined by proton NMR for Li^+, Na^+ *and* Cl^- *whilst* ClO_4^-, $CF_3SO_3^-$, NEt_4^+ *and* NBu_4^+ *do not appear to bind water. The results are compared with those reported for two other dipolar aprotic solvents.*

Introduction

Drastic changes are often noted when one compares the reactivity of ions, and particularly that of small anions, in hydrogen-bonded solvents such as water, and in dipolar aprotic (DPA) solvents such as dimethylsulfoxide (DMSO). Such changes are related to differences in ionic solvation.[1] In the case of binary mixtures of water with a DPA solvent, (such as aqueous DMSO) selective solvation of ions[2] may take place and lead to widely different effects on equilibria and reaction rates, according to the ionic reaction and the DPA solvent considered. The understanding of such effects is important as it may help to compare the solvating properties of water and the DPA solvent. Such understanding may also shed some light on the role of water as a solvent, as water structure in these mixed media is, depending on the DPA solvent involved, either reduced or eliminated, although water is still an effective nucleophile. Furthermore, because the removal of water from DPA solventes is never complete, studies of the effect of residual water on the ion-solvent interactions are of practical interest.

This paper reports the results of an investigation of the interactions in DMSO, between water and a few anions and cations including H^+, in which conductivity, near-infrared and NMR spectroscopies were used.

Experimental Section

Baker reagent-grade DMSO was treated according to a method previously reported.[3] The water content of the purified solvent as determined by Karl Fischer titration was 1×10^{-2} *M*. Lithium and sodium perchlorates, tetraethylammonium chloride and tetrabutylammonium perchlorate were respectively from Smith, Eastman Kodak and Coleman Matheson and Bell. The preparation of sodium trifluoromethanesulfonate was given elsewhere[3] and the tetraethylammonium salt was obtained in a similar manner. Trifluoroacetic acid (Eastman Kodak) and trifluoromethanesulfonic acid (3M) were used as received, titrations of the acids giving assays of 99.2 and 99.8% respectively.

The conductivity bridge used was described before.[3] Near-infrared spectra were recorded with a Cary 14 spectrophotometer using 5mm Hellma (110/Q1) cells. NMR measuremente were carried out at 27°C with a JEOL spectrometer at 60MHz. Chemical shifts δ were measured with respect to solvent methyl protons which are a suitable reference, but are reported relative to internal tetramethylsilane.

Results and Discussion

Conductivity data. The equivalent conductivities λ of DMSO solutions of the two acids HCF_3SO_3- (0.044M) and HCF_3CO_2 (0.11*M*) varied but little upon addition of water. For HCF_3SO_3, a strong acid in DMSO,[3] λ increased from 29.06 to 29.21 ohm^{-1} cm^2 $mole^{-1}$ when the water concentration was varied from 1.94×10^{-2} to 8.43×10^{-2} *M*. For HCF_3CO_2 a weak acid in DMSO,[3] λ increased from 2.493 to 2.556 ohm^{-1} cm^2 $mole^{-1}$ for the same change in water concentration. If water acts as a base in DMSO (S), the following equilibria will account for the reaction taking place: $SH^+ + H_2O \leftrightarrows H_3O^+ + S$ [1] or $HA + H_2O \leftrightarrows H_3O^+ + A^-$, according to the strength of the acid HA considered. The present results indicate either that the equivalent conductivities $\lambda_{H_3O^+}$ and λ_{SH^+} are nearly identical or that the equilibrium constant of reaction [1] is low. At any rate the variations of λ were too small to be interpreted further.

Near-infrared data. Absorption measurements in the near-infrared region were used to calculated the free water concentration in aqueous DMSO solutions of HCF_3SO_3, and hence, to attain the equilibrium constant of reaction [1]. Determinations were made at 1.945μ which corresponds to the combination band $(\nu_3 + \nu_2)$ of water. At this wavelength, the absorbance varies linearly with the water concentration, the molar absorbance coefficient ε being 2.18 ± 0.04 cm^{-1} $mole^{-1}$ litre. Known amounts of water were

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(1) G. Choux and R.L. Benoit, *J. Amer. Chem. Soc., 91*, 6221 (1969).
(2) H. Schneider in «Solute-Solvent Interactions», edited by J.F. Coetzee and C.D. Ritchie, M. Dekker, New York, (1969), p. 301.
(3) R.L. Benoit and C. Buisson, *Electrochim. Acta, 18*, 105 (1973).

added to DMSO solutions of the strong acid HCF_3SO_3. From the measured absorbance and ε, the free water concentration was calculated and by difference the H_3O^+ concentration was obtained. The SH^+ concentration was then deduced from the total acid and H_3O^+ concentrations. The calculated equilibrium constant $K = \frac{[H_3O^+]}{[SH^+][H_2O]}$ corresponding to equation [1] is given in Table I together with the experimental data.

Table I. Near infrared determination of the equilibrium constant for $SH^+ + H_2O \rightleftharpoons H_3O^+$.

$C_{HCF_3SO_3}$ (M)	C_{H_2O} (M)	A (1.945μ)	K
0.587	0.056	0.048	0.53
	0.111	0.098	0.41
	0.167	0.145	0.46
	0.278	0.241	0.49
0.879	0.111	0.082	0.53
	0.222	0.169	0.54
	0.333	0.273	0.41
1.015	0.111	0.079	0.51
	0.222	0.168	0.47
	0.333	0.181	0.49
	0.444	0.331	0.52
	0.556	0.422	0.49

The mean value of the concentration constant K is 0.47 ± 0.06. This result is in good agreement with the value 0.45 obtained by Kolthoff and Reddy[4] using 2,6-dinitro-4-chlorophenol as indicator in $4.4 \times 10^{-4}M$ HCl. Although these authors took HCl to be a strong acid, the error thus made is small as $K_{HCl} = 10^{-2.0}$[3,5] and the acid concentration is low. It appears therefore that H_3O^+ is a fairly strong acid in DMSO ($K_{H_3O^+} = 10^{+0.3}$) and H_2O a weak base. However, it is difficult to come, from these results, to any conclusion regarding the relative basicity of DMSO and bulk water.

NMR data. When water is added to a DMSO solution of a strong acid, there is a single proton resonance line, which indicates a fast exchange between the protons of SH^+; H_2O and H_3O^+ and the signal moves to high field. For example, a 0.561*M* HCF_3SO_3 solution containing 0.024*M* H_2O has a δ value which decreases from 14.10 ppm to 8.34 ppm for 0.525M H_2O. Attempts were made to calculate the equilibrium constant K of reaction [1] as well as $\delta_{H_3O^+}$ from such experimental results and the fast exchange relation $\delta = \frac{\sum_i \delta_i C_i}{\sum_i C_i}$ where C_i is the proton concentration of the species SH^+, H_2O and H_3O^+ and δ_i the corresponding specific chemical shifts. δ_{SH^+} was obtained by extrapolation and found to be 14.50 ppm.[3] δ_{H_2O} is equal to 3.38 ppm at infinite dilution and varies but very little with the water concentration, this implies that hydrogen-bonding to DMSO dominates the interaction rather than hydrogen-bonded self-association. However, it was found impossible to calculate both K and $\delta_{H_3O^+}$. Taking then K = 0.5 from the near infrared results, the value obtained for $\delta_{H_3O^+}$ was not constant but varied somewhat around 13 ppm. It would therefore appear that the NMR method is not applicable, either because our experimental results are not accurate enough to account for the small contribution of the H_3O^+ protons or that the implicit assumptions that δ_{SH^+} and $\delta_{H_3O^+}$ are independent of the medium composition, are erroneous.

However, the proton NMR method could be used to study the hydration of salt electrolytes in DMSO. The salts studied were $LiClO_4$, $NaClO_4$, $NaCF_3SO_3$, NEt_4Cl, NBu_4ClO_4 and $NEt_4CF_3SO_3$ in the 0-1*M* concentration range. For different concentration of each salt, δ was determined as a function of water concentration between 0.02 and 0.5 *M*. In each case, the variations of δ were usually less than 0.03 ppm and δ could be extrapolated to zero water concentration. The extrapolated values δ were plotted in Figure 1 as a function of the salt concentration. To interprete the results in terms of single ion hydration constants K for reactions such as $I^{\pm} + H_2O \rightleftharpoons I^{\pm} . H_2O$, an assumption is needed. The curves of Figure 1 provides this assumption as they can be simply explained by supposing that hydration of any of the large ions NEt_4^+, NBu_4^+, ClO_4^- or $CF_3SO_3^-$ is negligible compared to hydration of the small ions Li^+, Na^+ and Cl^-. This assumption is borne out by the results reported for two other DPA solvents.[6,7] Then the hydration constants K for Na^+, Li^+ and Cl^- can be calculated respectively from the curves, for $NaCF_3SO_3$ and $NaClO_4$, which are nearly identical and for $LiClO_4$ and NEt_4Cl. The equation used, $\delta - \delta_{H_2O} = K . C(\delta_I - \delta_{H_2O}) \ / \ 1 + K C$, where C is the salt concentration and δ_I the specific chemical shift of water in $I^{\pm} . H_2O$, is valid for low water concentrations and weak association and is derived from mass balance and the fast exchange relations. The equation

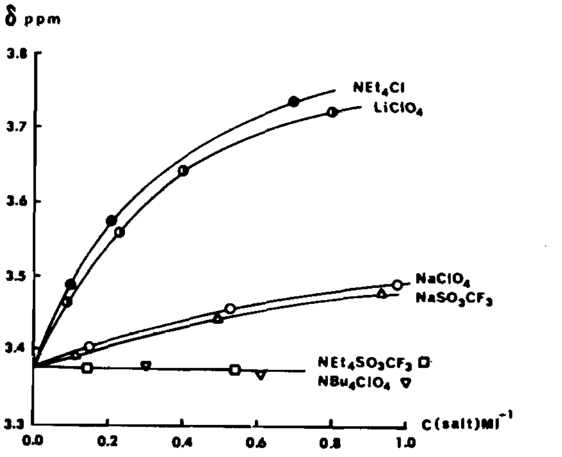

Figure 1. Variation of chemical shift of water protons with salt concentration.

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(5) J.A. Bolzan and A.J. Arvia, *Electrochim. Acta*, *15*, 39 (1970).
(6) D.R. Cogley, J.N. Butler, and E. Grunwald, *J. Phys. Chem.*, *75*, 1477 (1971).
(7) M.K. Chantooni, Jr., and I.M. Kolthoff, *J. Amer. Chem. Soc.*, *89*, 1582 (1967).

is solved[6,8] for K and δ_I by plotting δ-δ_{H_2O}/C as a function of δ-δ_{H_2O}. Straight lines are obtained, the slopes give-K and the intercepts K[δ_I-δ_{H_2O}]. Results are summarized in Table II. The projected study of the hydration of F^- ran into difficulties because it has not been possible as yet to prepare DMSO solutions containing less than 1 mole of H_2O per mole of F^-. Nevertheless, high values of δ_F-$\delta_{H_2O} \geqslant 1.2$ ppm are indicated. Some attack of NR_4^+, or DMSO, by F^- also takes place at low water concentration, suggesting that poorly hydrated F^- is a powerful nucleophile.

Table II. Ionic hydration constants from NMR data.

Ion	Salt	K	δ_I—δ_{H_2O} ppm
Li^+	$LiClO_4$	2.2±0.5	0.55
Na^+	$NaClO_4$	1.2±0.5	0.22
	$NaCF_3SO_3$	1.1±0.5	0.21
Cl^-	NEt_4Cl	2.7±0.4	0.55

Table III. Ionic hydration constants K(mole^{-1}. kg) and K_a in DPA solvents.

Ion	DMSO		Acetonitrile [a]		Propylene carbonate [b]	
	K	K_a	K	K_a	K	K_a
H^+	0.4	16.	very large		very large (?)	
Li^+	2.1	85.	4.	13.	6.5	7.8
Na^+	1.1	45.	2.6	8.4	1.4	1.7
K^+			1.3	4.2	0.4	0.5
Cl^-	2.4	98.	11.	35.	6.2	7.5

[a] ref. 6.7; [b] ref. 6.

The values of hydration constants K, on the molal scale, are compared in Table III with K values for Li^+, Na^+, K^+ and Cl^- in acetonitrile[6,7] and propylene carbonate.[6]

The hydration constant K, in its definition, includes (H_2O), the water concentration, which does not reflect the interactions of water with the DPA solvent. These interactions should be taken in account, as they vary with the DPA solvent and thus make comparisons of K values less meaningful. With this in mind, the water concentration was replaced by the water activity $a_w = p/p_o$ as deduced from water vapour pressure data (p(mm Hg)) at low water concentration (mole . kg^{-1}) at 30°C. The following values were used: DMSO,[9] p = 0.66, (H_2O) = 0.85, acetonitrile,[10] p = 12.4 (H_2O) = 1.25 and propylene carbonate[9] p = 5.61, (H_2O) = 0.212. The values of the hydration constants K_a = ($I^\pm$. H_2O) / ($I^\pm$)a_w are given in Table III.

Comparison of K_a values in the three DPA solvents brings to light several interesting points. First, the affinity of H^+ towards H_2O does not follow that of Li^+, Na^+ and K^+ which increases with the solvent basicity. Second, since the replacement of one DPA solvent molecule by one water molecule in the metal or Cl^- ions solvation shell varies but little (less than 2 kcal mol^{-1}) with the solvent, it would appear that the solvation energies of each ion, Li^+, Na^+ and Cl^-, in the three DPA solvents, are not very different. This is confirmed, at least in the case of Cl^-, by the correspondingly small enthalpies and free energies of transfer.[1,11] Third, as already noted in the case of propylene carbonate,[6] the small hydration constants for Cl^-, indicate that there is no strong preference of Cl^- for water at low concentration. This sharply contrasts with the fact that bulk water solvates Cl^- much more strongly than DPA solvents.[1,11] The strong solvation of Cl^- by bulk water is therefore due to interactions which involve more than the first water molecule and are related to structural factors. Recent results of Kebarle *et al.*[12] on gas phase solvation of halide ions by acetonitrile and water molecules, interestingly, show that solvation by water is only favored for large numbers of solvating molecules. Chlorine-35 NMR studies[13] also suggest that Cl^- does not preferentially solvate water in both acetonitrile and DMSO. It would seem that selective solvation of singly charged ions by water in DPA solvents may be, if at all, restricted to that of the small anions OH^- and F^- and cation H^+. This agrees with the results of Kebarle on the gas phase hydration of ions.

Note added in proof. Our recent 100 MHz pmr spectra lead to smaller and more linear variations of chemical shifts than reported here. Somewhat lower hydration constants are obtained without extrapolations. Water vapour pressure measurements are being carried out to provide an independent method of study.

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