

## <sup>1</sup>H NMR STUDY OF CATION SOLVATION IN THE MIXED SOLVENT DIMETHYLFORMAMIDE-WATER

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Solvation effects of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  on the mixed solvent dimethylformamide-water were investigated by the <sup>1</sup>H NMR method. The dependence of the chemical shift of solvent protons on the mixed solvent composition was established for various concentrations of perchlorates. Isosolvation points were determined, and the dependences of charge transfer from solvent to cation on the chemical shift of solvent, as obtained by a quantum chemical calculation, were compared for the systems  $\text{DMF-M}^{n+}$  and  $\text{DMF-M}^{n+}\text{-H}_2\text{O}$ .

Solvation of metal cations by dipolar aprotic solvents or more complex systems has been the subject of numerous studies. A technique particularly useful for investigating ion-solvent interactions is the NMR spectroscopy because the NMR chemical shifts are solvent-dependent. The first measurements of ion-solvent interactions using the <sup>1</sup>H NMR method were carried out by Fratiello and coworkers<sup>1,2</sup>. In later studies<sup>3-5</sup> the NMR resonance of the interacting ion was investigated. Maximum information about the primary solvation shell can be obtained at low temperatures, where separate signals from coordinated and free solvent protons can be observed.

As part of a more comprehensive work on ion solvation, a <sup>1</sup>H NMR study has been made on solvation effects in the system dimethylformamide (DMF)-cation-water over the whole ranges of mixed solvent compositions and salt concentrations. Also, an attempt has been made to reproduce some of the observed solvation effects by theoretical calculation. The ions for the study (lithium, sodium and magnesium perchlorates) were selected with feasibility of quantum chemical calculations in mind.

### EXPERIMENTAL

<sup>1</sup>H NMR measurements were carried out on solutions with salt concentration ranging for each solvent mixture from  $0.1 \text{ mol dm}^{-3}$  to  $5 \text{ mol dm}^{-3}$ . The limitation on the concentration range was imposed by low solubilities of the salts in the mixed solvent. For magnesium perchlorate, the upper bound to the concentration range was even  $2 \text{ mol dm}^{-3}$  only. The measurements were made for mole fractions of DMF in the mixed solvent of 0, 0.1, 0.2, 0.3, 0.5, 0.9 and 1, and for the following salt concentrations ( $\text{mol dm}^{-3}$ ):  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ : 0.5, 1, 2, 3, 4 and 5;  $\text{Mg}(\text{ClO}_4)_2$ : 0.1, 0.3, 0.5, 1 and 2. Reference measurements with the mixed solvent alone were made at the same mole fractions of DMF as above.

Dimethylformamide (Merck) was dried by calcium chloride, freed from residual formic acid by calcium oxide, distilled, and stored over a 4A molecular sieve. The water content of DMF as determined by Karl Fischer method was 0.04%.  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  (Lachema) and  $\text{Mg}(\text{ClO}_4)_2$  (Merck) were dried before experiment by heating at 150°C for 48 h. Redistilled water was used in preparing the mixed solvent.

The experiments were performed on a Tesla BS 467 NMR spectrometer (60 MHz, CW mod 2 kHz, lock on external  $\text{H}_2\text{O}$ ). Tetramethylsilane was used as external standard.

All measurements were carried out at 20°C. Differences between chemical shifts of pure mixed solvents (with no ions present) and solutions were determined as a function of the mole fraction of the mixed solvent with an accuracy of 0.2 Hz. The proton resonances of both DMF and water were investigated.

## RESULTS AND DISCUSSION

Chemical shifts of the mixed solvent components were plotted as a function of mixed solvent composition at constant salt concentrations. Chemical shifts of solvent lines were counted negative for upfield displacement and positive for the opposite direction. Shifts of two singlets arising from internal rotation of methyl groups about the carbon–nitrogen bond were considered for dimethylformamide. Average values of the shifts were evaluated. The effects of solvation on the singlet of aldehydic hydrogen and on the relaxation time  $T_1$  and  $T_2$  were insignificant. The signal widths remained virtually constant. Where the chemical shift plots showed apparent linearity, straight lines were fitted by the polynomial regression method and isosolvation points (defining regions in which the two solvents are subject to equal forces) were determined. The points are shown in Fig. 1, and their numerical coordinates are given in Table I. The remaining cases were not treated mathematically because of a small number of experimental points. Results obtained for the system  $\text{DMF}-\text{MClO}_4-\text{H}_2\text{O}$  ( $\text{M} = \text{Li}, \text{Na}, \text{Mg}$ ) are represented graphically in Figs 1 and 2.

Considering that the strength of ion-solvent interaction is proportional to the chemical shift, we can see from absolute values of the chemical shift of water protons in solution (Figs 1 and 2) that, except in the region of isosolvation points, water is the stronger solvating species in the immediate environment of an ion, *i.e.* in the primary solvation shell, over the whole ranges of salt concentrations and mixed solvent compositions. The difference between the degrees of solvation and hydration increases as  $x_{\text{solvent}}$  and salt concentration are increased. An isosolvation point occurs at a ratio of mixed solvent components at which the ion-solvent interactions for the two solvents are of equal strength so that there is not preference for either solvent in the primary solvation shell. For lithium and magnesium ions, the isosolvation points lie within the ranges 0.15–0.4  $x_{\text{DMF}}$  and 0.05–0.3  $x_{\text{DMF}}$ , respectively. The isosolvation points for the sodium cation were not determined because of high rate of solvent exchange between the primary solvation shell and its environment ( $1/\tau = 10^{11}$ , *ref.*<sup>6</sup>).

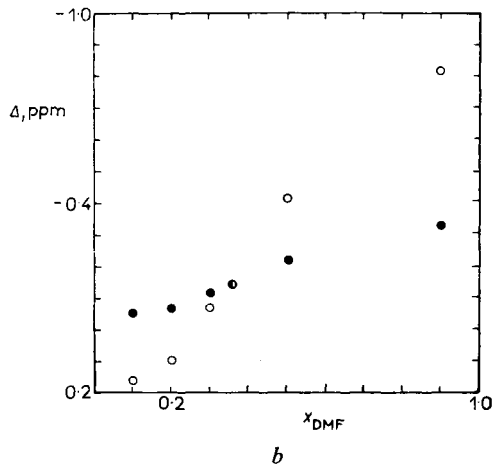
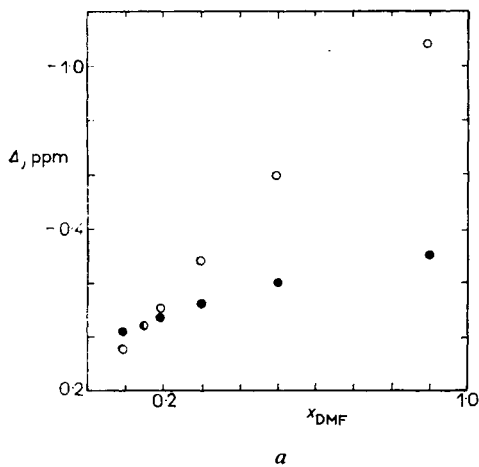


FIG. 1  
<sup>1</sup>H Chemical shift (ppm) of DMF + H<sub>2</sub>O mixed solvent components (○ H<sub>2</sub>O, ● DMF, ◐ isosolvation point) as a function of the mole fraction of dimethylformamide. *a*)  $c_{\text{LiClO}_4} = 2 \text{ mol dm}^{-3}$ ; *b*)  $c_{\text{NaClO}_4} = 2 \text{ mol dm}^{-3}$ ; *c*)  $c_{\text{Mg}(\text{ClO}_4)_2} = 2 \text{ mol dm}^{-3}$

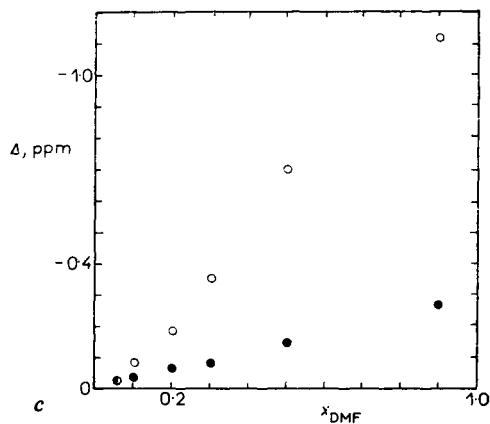
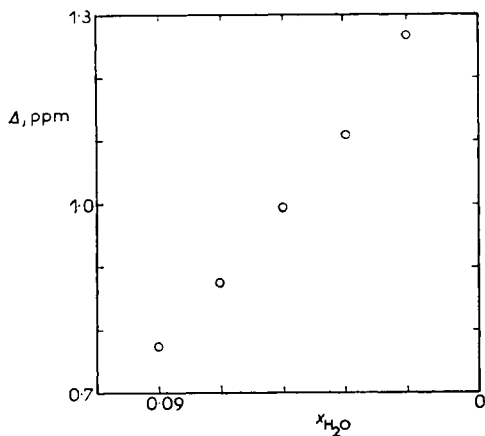


FIG. 2  
<sup>1</sup>H Chemical shift (ppm) of water in the mixed solvent DMF-H<sub>2</sub>O as a function of the mole fraction of water.  $c_{\text{Mg}(\text{ClO}_4)_2} = 0.5 \text{ mol dm}^{-3}$



Results of this work indicate that a non-aqueous dipolar aprotic solvent may compete with water for solvation in the region of small mole fractions ( $0.05 - 0.4 x_{\text{DMF}}$ ). Water, on the other hand, has a great hydrating power and preferentially solvates a cation even when present in small amounts ( $x_{\text{DMF}} \geq 0.9$ ). Therefore, a sudden increase in chemical shift is observed on going from  $x_{\text{DMF}} = 0.9$  to  $x_{\text{DMF}} = 1$ . In our opinion, these effects are due to hydrogen bonding in the structure of water. In a mixed solvent with a low content of non-aqueous component, the hydrating power is partially compensated for by interactions of free water molecules with the molecules of the primary solvation shell, which facilitates the entry of DMF molecules into the solvation shell of the ion. When, on the other hand, the water content of the mixture is small, the water molecules are not held back by mutual interactions and most of them easily penetrate through the weaker solvating medium ( $\epsilon_{\text{DMF}} = 36.7$ ;  $\epsilon_{\text{H}_2\text{O}} = 80$ ) to the ion. It should be pointed out that these conclusions have been drawn from average values of the shift of bound and free solvent in solution and are therefore to be regarded as hypothetical.

TABLE I

Isosolvation points for the systems DMF-cation-H<sub>2</sub>O

Cation	$c$ mol dm <sup>-3</sup>	Chem. shift ppm	$x_{\text{DMF}}$
Li <sup>+</sup>	0.5	-0.017	0.223
	1.0	0.076	0.378
	2.0	0.034	0.181
	3.0	0.054	0.336
	4.0	0.071	0.333
	5.0	0.032	0.376
Na <sup>+</sup>	0.5	--	--
	1.0	--	--
	2.0	0.146	0.360
	3.0	0.141	0.862
	4.0	--	--
	5.0	--	--
Mg <sup>2+</sup>	0.1	0.0	0.300
	0.3	-0.02	0.170
	0.5	0.02	0.150
	1.0	0.01	0.050
	2.0	0.02	0.040

The effect of magnesium cation hydration in water–DMF mixtures has been studied for very small values of  $x_{\text{H}_2\text{O}}$  (0.01–0.09). The measurements were carried out at  $\text{Mg}(\text{ClO}_4)_2$  concentrations of 0.01, 0.05, 0.1, 0.3 and 0.5 mol dm<sup>-3</sup>. The resulting shifts of water protons are represented in Fig. 2. It is seen from the figure that the chemical shift of water protons for all  $\text{Mg}(\text{ClO}_4)_2$  concentrations is maximum at the lowest content of water in the mixed solvent and that its value decreases as the mole fraction of water is increased. If we take the magnitude of the chemical shift of solvent protons as a measure of ion–solvent interaction, we see that this interaction is strongest for low values of  $x_{\text{H}_2\text{O}}$ . This lends some support to the above hypothesis that at low water content of the mixture water molecules are not restrained by mutual interactions and penetrate readily through the poorly solvating medium of dimethylformamide into the primary solvation shell of the ion.

Our hypothesis may further be reinforced by quantum chemical calculations using the *ab initio* method (GAUSSIAN 70 program<sup>7</sup>) and the Mulliken population analysis<sup>8</sup>. By these methods the distribution of the overall charge among the individual atoms was determined for the systems under study. The data obtained served as the basis for qualitative interpretation of NMR results. In our case, we treated a molecular complex, the supermolecule DMF...ion...H<sub>2</sub>O, using the minimum STO-3G base of wave functions. The results are able to account for the greater chemical shift of the methyl protons of neat dimethylformamide coordinated to a cation relative to that for the system DMF–cation–water. Since the electrical field of a cation is the principal factor influencing the magnitude of the chemical shift of a solvent proton, it is of interest to compare its magnitude for the systems DMF–M<sup>n+</sup> and DMF–M<sup>n+</sup>–H<sub>2</sub>O (Table II).

Inspection of Table II shows that the charge donation from the amide system to the cation is less in DMF than in the DMF + H<sub>2</sub>O mixture. Consequently, the diamagnetic electronic shielding for DMF is not so attenuated as in the case of the

TABLE II

Charge transfer from solvent to cation,  $q^{\text{M}^{n+}}$ , calculated by the *ab initio* method, at various chemical shifts of solvent,  $\delta$  (ppm)

Ion	Solvent			
	DMF		DMF + H <sub>2</sub> O	
	$q^{\text{M}^{n+}}$	$\delta$	$q^{\text{M}^{n+}}$	$\delta$
Li <sup>+</sup>	–0.428	0.45	–0.530	0.28
Na <sup>+</sup>	–0.119	0.42	–0.220	0.27
Mg <sup>2+</sup>	–0.379	0.48	–0.591	0.37

mixed solvent. This, in turn, is consistent with a higher value of chemical shift for the system DMF- $M^{n+}$ . The same argument applied to the electronic charge on an important solvation position of DMF, the oxygen atom.

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