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Ion-Solvent Interaction of Tetraalkylammonium and Some Common Ions in *N*-Methylformamide from Viscosity Data

Pushti Prakash Rastogi

Chemistry Department, Lucknow University, Lucknow, India

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Solute-solvent interaction of tetraalkylammonium iodides (R_4NI) and some common electrolytes has been studied in *N*-methylformamide (NMF) from the viscosity point of view. From the obtained results it has been concluded that common electrolytes like LiCl, KI, CsI are net structure promoters while R_4NI salts are net structure breakers in this solvent.

The interaction of the tetraalkylammonium (R_4N^+) ions with *N*-methylacetamide (NMA) molecules has already been reported from the point of view of conductance in a previous[1] communication. Another method commonly employed, for investigating ion-solvent interaction in solution, is to study the temperature dependence of the coefficient *B* of the viscosity equation of Jones and Dole,[2] namely,

$$\eta = \eta_0(1+A\sqrt{C}+BC)$$

$$\text{or} \quad (\eta/\eta_0-1)/\sqrt{C} = A + B\sqrt{C} \qquad \text{(i)}$$

This approach provides valuable information about the mode of solute-solvent interaction[3] on account of the fact that the coefficient *B* represents the interaction between the solvent molecules and the ions of the dissolved electrolyte. Ion-solvent interaction in aqueous solutions, from this point of view, has been studied by several workers.[4-6] According to Kaminsky[4] the coefficient *B* has a negative temperature coefficient for the highly hydrated ions like Li^+, Be^{2+}, Mg^{2+}, Ce^{3+}, *etc.*; on the other hand, *B* has a positive temperature coefficient for the less hydrated ions like Cs^+, Rb^+, I^-, NO_3^-, *etc.* These results led him to suggest that the former are net structure makers while the latter are net structure breakers in aqueous solutions. Nightingale[5] and Kay and coworkers[6] concluded that Pr_4N^+ and Bu_4N^+ ions are excellent structure promoters but Me_4N^+ ion is a net structure breaker, while the structure breaking and making effects almost balance one another for Et_4N^+ ion in aqueous solutions. In view of the current interest in the behaviour of R_4N^+ ions, on account of their "abnormal" properties in aqueous solutions and of their special structual features, one is tempted to investigate their behaviour in solvents other than water but similar to water in having high dielectric constant so that the complications arising out of ion-association may be avoided. Some interesting solvents of this type are monoalkyl-substituted amides, *e.g.*, NMF, NMA and *N*-methylpropionamide (NMP).

The present communication reports a study of the ion-solvent interaction of R_4NI salts in NMF from the viscosity data. Some common salts like LiCl, KI and CsI have also been included in the study for the sake of comparison.

Experimental

R_4NI salts were purified in the usual manner as described.[1] Merk's A. G. reagents LiCl, KI and CsI were twice recrystallized from conductivity dried in an electric oven and were kept in a vacuum desiccator until used.

NMF, obtained from M/s Distillation Products Industries, U.S.A., was left overnight on some freshly ignited quicklime and was then distilled under reduced pressure. The middle fraction of the distillate was collected and redistilled. The process of purification was continued until the specific electrical conductance of the middle fraction of the distillate was reduced to less than 10^{-6} ohm^{-1} cm^{-1}. The purified samples were collected in dark amber-coloured bottles which were kept in a dry box. A rapid variation in electrical conductance and viscosity of NMF with time was observed immediately after distillation. However, after several hours the changes were slow. Hence NMF was used after keeping it for about 24 hr.

Measurements of density and viscosity were carried out in a thermostat with maximum temperature fluctuation ±0.01°C. Solutions were prepared on molar basis at 25°C and were corrected for the changes in volume at other temperatures.

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[1] R. D. Singh, P. P. Rastogi and R. Gopal, *Can. J. Chem.*, **46**, 3525 (1968).

[2] G. Jones and M. Dole, *J. Amer. Chem. Soc.*, **51**, 2950 (1929).

[3] R. W. Gurney, "Ionic Processes in Solution," McGraw Hill Book Co. Inc., New York (1953), pp. 159—171.

[4] M. Kaminsky, *Discuss. Faraday Soc.*, **24**, 150 (1957).

[5] E. R. Nightingale, Jr., *J. Phys. Chem.*, **66**, 894 (1962).

[6] R. L. Kay, T. Vituccio and D. F. Evans, *ibid.*, **70**, 2336 (1966).

Table 1. Values of $\eta_{sp}/\sqrt{C}$ from viscosity data in NMF

$C \times 10^2$	25°C	30°C	35°C
	Me_4NI		
0.25	0.019	0.025	0.030
0.50	0.026	0.035	0.042
1.00	0.038	0.046	0.051
1.43	0.042	0.050	0.061
2.00	0.053	0.060	0.068
	Et_4NI		
0.25	0.026	0.030	0.039
0.50	0.041	0.043	0.046
1.00	0.052	0.059	0.067
1.43	0.061	0.067	0.074
2.00	0.073	0.081	0.090
	Pr_4NI		
0.25	0.035	0.042	0.047
0.50	0.050	0.055	0.059
1.00	0.066	0.073	0.078
1.43	0.079	0.086	0.094
2.00	0.095	0.102	0.106
	Bu_4NI		
0.25	0.041	0.046	0.051
0.50	0.060	0.063	0.068
1.00	0.080	0.087	0.095
1.43	0.100	0.106	0.112
2.00	0.111	0.121	0.128
	Pen_4NI		
0.25	0.052	0.057	0.061
0.50	0.068	0.075	0.081
1.00	0.094	0.102	0.108
1.43	0.113	0.119	0.127
2.00	0.133	0.140	0.148
	Hex_4NI		
0.25	0.057	0.062	0.069
0.50	0.082	0.086	0.091
1.00	0.110	0.118	0.121
1.43	0.131	0.140	0.148
2.00	0.158	0.162	0.168
	Hep_4NI		
0.25	0.063	0.067	0.074
0.50	0.090	0.094	0.106
1.00	0.103	0.136	0.141
1.43	0.151	0.160	0.164
2.00	0.180	0.189	0.197
	LiCl		
0.25	0.035	0.030	0.025
0.50	0.046	0.042	0.037
1.00	0.065	0.060	0.054
1.43	0.072	0.067	0.060
2.00	0.083	0.078	0.074
	KI		
0.25	0.040	0.036	0.031
0.50	0.049	0.044	0.037
1.00	0.061	0.057	0.050
1.43	0.072	0.067	0.060
2.00	0.088	0.082	0.075
	CsI		
0.25	0.036	0.032	0.026
0.50	0.045	0.040	0.036
1.00	0.065	0.058	0.054
1.43	0.072	0.067	0.060
2.00	0.089	0.080	0.074

Density was determined with a dilatometer which was provided with a graduated stem on which volume could be read upto 0.005 m*l* within an error of ±0.002 m*l*. A modified Ubbelohde viscometer with a flow time of about 500 sec, for NMF at 25°C, was employed for measuring the viscosity. The readings within the maximum deviation of ±0.1 sec were recorded and taken into account while the widely varying ones were discarded. A 40% sugar solution of known viscosity was used to determine the viscosity of NMF. The density and viscosity of NMF determined at different temperatures, were found to agree very closely to those reported in literature as is clear from the following table:

Temp. °C	Density and Viscosity of NMF			
	Density in g/ml		Viscosity in poise	
	Exptl.	Literature*	Exptl.	Literature*
25	0.9990	0.9988	0.0168	0.0165
30	0.9947	—	0.0155	—
35	0.9905	—	0.0144	—

* C.M. French and K.H. Glover, *Trans. Faraday Soc.*, **51**, 1418 (1955).

The viscosity of solution was calculated with help of the usual relation, namely,

$$\eta = \frac{d}{d_0} \times \frac{t}{t_0} \times \eta_0 \qquad \text{(ii)}$$

The viscosity data were subjected to the kinetic energy corrections which were usually negligible. From the corrected data, the factors $\eta_{sp}/\sqrt{C}$ ($\eta_{sp}=\eta/\eta_0-1$) were obtained for different solutions at various temperatures. The values of $\eta_{sp}/\sqrt{C}$ are given in Table 1. The factor $\eta_{sp}/\sqrt{C}$ was plotted against $\sqrt{C}$ for different salts at different temperatures. The plots are almost linear, the slopes of which give the values of B and are summarized in Table 2, whereas the ordinate intercepts give the coefficients A (which represent the contribution from interionic forces[7]).

Table 2. Viscosity B coefficients in N-methylformamide

Salt	25°C	30°C	35°C
Me_4NI	0.38	0.42	0.48
Et_4NI	0.49	0.52	0.57
Pr_4NI	0.68	0.71	0.75
Bu_4NI	0.81	0.85	0.88
Pen_4NI	0.97	1.00	1.03
Hex_4NI	1.11	1.15	1.17
Hep_4NI	1.28	1.30	1.33
LiCl	0.59	0.55	0.53
KI	0.56	0.54	0.51
CsI	0.60	0.58	0.57

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7) H. Falkenhagen and E. L. Vernon, *Phys. Z.*, **33**, 140 (1932).

Results and Discussion

It may be noted from Table 2 that B values increase with the increase in the radius of the ion, *i.e.*, dB/dr (r being the radius of the ion) is positive, which leads to the conclusion that R_4N^+ ions behave, more or less, like large spheres moving in a dielectric continuum as was postulated by Einstein. The value of B according to the Einstein theory[8] is given by:

$$B = 2.5(v/C) \qquad \text{(iii)}$$

where v is the total volume of the ions per ml of solution and C the molar concentration. So, for a particular solvent the value of B for different ions should be proportional to v. If the crystal radii of these ions as estimated by Robinson and Stokes[9] are used, it is found that $B \propto r^3$ as is clear from Fig. 1, in which the experimental values of B are plotted against r^3. Thus the ion-solvent interaction as shown by the dependence of B on radius of the R_4N^+ ions, shows that the larger the ion, the greater the resistance for its movement in the solvent medium and there is no other ion-solvent interaction. However, the variation of B with temperature does indicate some interaction.

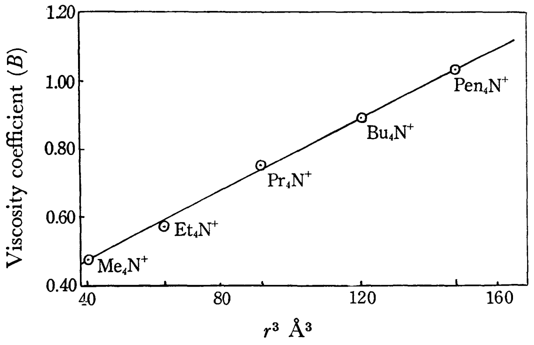

Fig. 1 *N*-Methylformamide temperature 35°C.

B values given in Table 2 indicate that dB/dt is positive for the R_4NI salts and negative for common electrolytes like LiCl, KI, CsI studied here in NMF. A positive dB/dt implies a net structure-breaking of the solvent at lower temperature in the presence of R_4NI salts so that the local viscosity around the ions does not decrease with temperature rise as rapidly as the viscosity η_0 of the pure solvent. The temperature coefficient (*i.e.*, dB/dt) is negative for common electrolytes containing cations like Li^+, K^+, Cs^+ *etc.*, because of the possible long range ordering (or secondary solvation) of the solvent molecules around them. As the temperature rises, long range ordering is disturbed by the thermal agitation and the local viscosity around the ions decreases faster than η_0 and this leads to a negative dB/dt. Although R_4NI salts appear to be structure breakers in these solvents, they do not give rise to long range ordering because of the low surface charge density, and hence dB/dt is positive. This is in contrast with their behaviour in aqueous solutions in which the temperature coefficient of B, *i.e.*, dB/dt, is negative[5,6] for the R_4N^+ (except Me_4N^+); this has been explained on the ground of the strong "hydrophobic solvation" of the R_4N^+ ions; strong hydrophobic solvation is equivalent to long range ordering of the water structure, similar to the electrostatic hydration of Li^+, Be^{2+}, Mg^{2+} and Ce^{3+} ions for which dB/dt is negative.[4-6,10] For larger common cations and for the halide ions, dB/dt is positive in aqueous solutions. In NMF, such hydrophobic ordering of the solvent by R_4NI salts does not occur, presumably because the solvents and R_4N^+ ions have methyl or similar organic groups, in both of them making the solvent and the solute similar in nature.

It appears that structure breaking effect goes on decreasing with the increase in the radius of the ion. This can be expected because the larger R_4N^+ ions have low surface change density; so the electrostatic ion-solvent interaction is not strong enough to break the hydrogen-bonded structure of the solvent.

It appears that R_4N^+ ions are net structure breakers (in the sense of breaking of hydrogen bonds) whereas the alkali metal ions are structure promoters (*i.e.*, the long range order makers) in NMF solutions.

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[8] A. Einstein, *Ann. Phys.*, **19**, 289 (1906); **34**, 591 (1911).

[9] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Publications, Ltd., London (1959), pp. 124—126.

[10] D. Feakins and K. G. Lawrence, *J. Chem. Soc.*, *A*, **1966** 217.