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Ion-Solvent Interaction of Tetraalkylammonium Ions in Solvents of High Dielectric Constant. III. Conductance and Walden Product of Some Partially Substituted Alkylammonium Ions in *N*-Methylacetamide and *N*-Methylpropionamide at Different Temperatures

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Ion-solvent interaction of some partially substituted alkylammonium ions in *N*-methylacetamide (NMA) and *N*-methylpropionamide (NMP) has been investigated from the point of view of electrical conductance and the derived Walden product. From the results, it seems that like tetraalkylammonium (R_4N^+) ions, Me_3NH^+ and $CeMe_3N^+$ ions are structure breakers in these solvents while Me_3PhN^+ ion is neither structure breaker nor structure maker.

In previous communications,[1,2] ion-solvent interaction of some symmetrically substituted tetraalkylammonium (R_4N^+) ions in NMF, NMA, and NMP has been investigated from the conductance data. It would be interesting to investigate how the partial and unsymmetrical substitution in the NH_4^+ ion will affect the nature of the ion-solvent interaction in these solvents. With this aim in view, the conductances of some available such salts namely, Me_3NHI, Me_3PhNI, and $CeMe_3NBr$ in NMA and NMP at different temperatures have been reported in the present communication and the data have been used to throw light on the mode of ion-solvent interaction.

Experimental

Trimethylammonium iodide (Me_3NHI), trimethylphenylammonium iodide (Me_3PhNI) and cetyltrimethylammonium bromide ($CeMe_3NBr$), obtained from B.D.H., were purified as follows:

Me_3NHI and Me_3PhNI were recrystallized twice from a mixture of methanol and ether (3:1). The salts were dried in a vacuum desiccator.

$CeMe_3NBr$ was dissolved in methanol and precipitated

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

[2] R. D. Singh and R. Gopal, This Bulletin, **45**, 2088 (1972).

with ether. The precipitated salt was dried in a vacuum desiccator.

NMA and NMP were purified in the manner given elsewhere.[1,2] The purified samples were stored in dark amber-coloured bottles in a dry nitrogen box and were used, as far as possible, the day after distillation. Although the solvents appeared to be quite stable, solvent correction was applied in determining the conductances of solutions. The rest of the experimental procedure and the degree of reliability of the apparatus were the same as those given in the previous communications on NMF, NMA, and NMP.

Results and discussion

Within the concentration (0.0005M to 0.02M) and temperature (30° to 55°) ranges studied here, the plots of equivalent conductance Λ and $\sqrt{c}$ were found to be almost straight lines for all the salts in NMA and NMP. It appears, therefore, that these salts are completely dissociated in NMA and NMP as has been reported by earlier workers.[3-7] Extrapolation of Λ *vs.* $\sqrt{c}$ curves to zero concentration leads to Λ_0-values given in Table 1. From these Λ_0-values, the ionic conductances λ_0^+ of the cations at different temperatures were obtained, using the appropriate transport number data already reported in literature;[8] these λ_0^+-values are given in Table 1.

Table 1. Limiting equivalent conductance in NMA and NMP at different temperatures

Salt and cation	Limiting equivalent conductance at 30°C	35°C	40°C	45°C	50°C	55°C
			NMA			
Me_3NHI	···	25.15	27.68	31.11	34.26	37.00
Me_3NH^+	···	11.73	13.01	14.92	16.52	17.80
Me_3PhNI	···	22.40	24.89	27.95	30.50	33.05
Me_3PhN^+	···	8.98	10.22	11.36	12.76	13.85
$CeMe_3NBr$	···	19.89	21.88	24.41	26.64	28.96
$CeMe_3N^+$	···	8.17	9.01	9.54	10.90	11.90
			NMP			
Me_3NHI	15.15	17.03	19.09	21.17	23.65	···
Me_3NH^+	6.81	7.68	8.64	9.62	10.71	···
Me_3PhNI	14.50	16.50	18.47	20.60	22.90	···
Me_3PhN^+	6.16	7.15	8.02	9.05	9.90	···
$CeMe_3NBr$	12.73	14.43	16.16	18.09	19.83	···
$CeMe_3N^+$	5.69	6.38	7.21	8.04	8.79	···

The applicability of limiting Debye-Hückel-Onsager conductance equation to solutions under study was examined. The conductance equation for 1:1 electrolyte can be written in the form

$$\Lambda=\Lambda_0-\left[\frac{82.42}{(\epsilon T)^{1/2}\eta_0}+\frac{8.203\times10^5}{(\epsilon T)^{3/2}}\Lambda_0\right]\sqrt{c}$$

which simplifies to

$$\Lambda=\Lambda_0-(A+B\Lambda_0)\sqrt{c}=\Lambda_0-S_T\sqrt{c}$$

for a constant temperature. The values of A and B are

$$A=\frac{82.42}{(\epsilon T)^{1/2}\eta_0},\ B=\frac{8.203\times10^5}{(\epsilon T)^{3/2}}$$

and the theoretical slope $S_T=(A+B\Lambda_0)$.

From Λ_0-values and other appopriate data on dielectric constant[7,9] and on viscosity η_0 (determined in this laboratory,[1,2] the theoretical slopes S_T of the Λ *vs.* $\sqrt{c}$ curves have been obtained and are given in Table 2 at one temperature (40°C) only.

Table 2. Onsager slopes in NMA and NMP at 40°C

Salt	Theoretical slope (S_T)	Experimental slope (S_E)	% Deviation $\left(\frac{S_E-S_T}{S_T}\times100\right)$
		NMA	
Me_3NHI	−13.9	−15.6	12
Me_3PhNI	−13.7	−15.8	15
$CeMe_3NBr$	−13.5	−15.4	14
		NMP	
Me_3NHI	−12.1	−13.2	9
Me_3PhNI	−12.1	−13.4	11
$CeMe_3NBr$	−11.0	−13.3	12

It may be noted from Table 2 that the experimental slopes S_E of the Onsager plots for these salts in the two solvents, are numerically greater than the theoretical slopes S_T. In view of the high dielectric constant of these solvents, incomplete dissociation of the salts in the usual sense is unthinkable, although Dawson and coworkers[3,5,6] have tried to explain the conductance results in NMA and NMP on this ground. As discussed in previous communication,[2] these deviations may be ascribed to the penetration[10-13] of cations by anions causing a sort of association[14] or to the greater resistance offered to the movement of the cations by solvent molecules, than that caused by viscosity of the solvent medium, so that the movement of the cations is more sluggish than expected from the theory.

The Walden products of the partially substituted alkylammonium ions at different temperatures have been calculated from the appropriate λ_0^+-values (given in Table 1) and viscosity data. From the cationic Walden product data, thus obtained, $\lambda_0^+\eta_0$ *vs.* temperature curves have been drawn and are given in Figs. 1 and 2.

It is obvious from the curves that like those of symmetrical tetraalkylammonium (R_4N^+) ions, the Walden product of Me_3NH^+ and $CeMe_3N^+$ ions in these amides decreases with the rise of temperature while for Me_3PhN^+ ion, it is approximately constant. The decrease in

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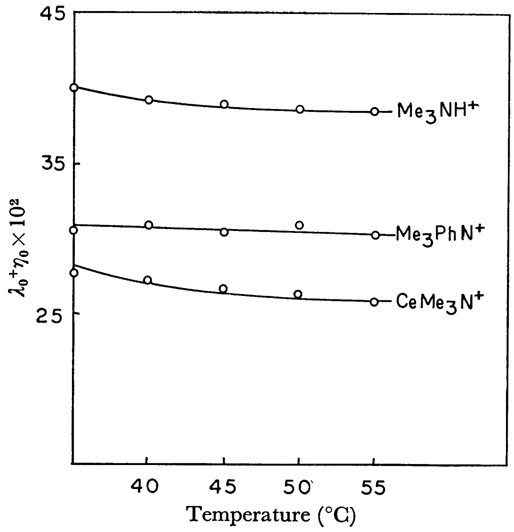

Fig. 1. Plot of $\lambda_0^+\eta_0$ *vs.* T in NMA

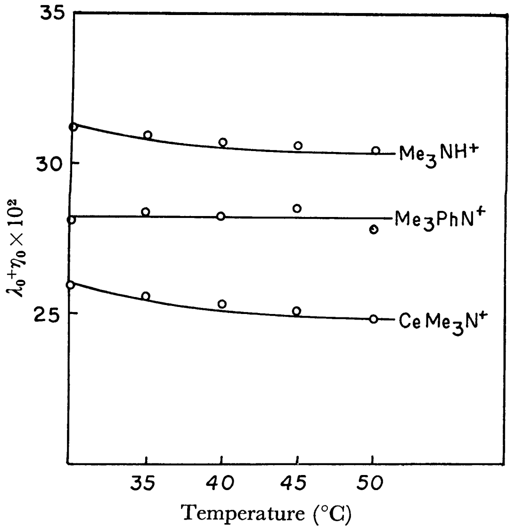

Fig. 2. Plot of $\lambda_0^+\eta_0$ *vs.* T in NMP

$\lambda_0^+\eta_0$ values of Me$_3$NH$^+$ and CeMe$_3$N$^+$ ions with the rise of temperature can be explained on the similar grounds as for R$_4$N$^+$ ions *i.e.*, electrostatic solvation and resultant breaking-up of the structure of the solvent medium occurs around the ions. The partially substituted alkylammonium ions, being similar to NMA and NMP in having the alkyl groups, do not promote the structure of the solvent[15] *i.e.*, "structure promotion" or "lyophobic solvation" is missing in these solvents in the presence of these ions. Further, although these ions are large which would reduce ion-solvent interaction, the large dipole moment[16] of the solvent molecule makes up for the large size of the ions so that an appreciable ion-solvent interaction would occur. Thus, there appears a net structure breaking[17] in the presence of the partially and mixed alkyl substituted ammonium ions because the electrostatic ion-solvent interaction would be stronger than the interaction between the solvent molecules themselves.

The approximate constancy of the Walden product of the Me$_3$PhN$^+$ ion indicates that this ion has, apparently no net effect on the structure of the solvents although it is rather unexpected since the CeMe$_3$N$^+$ ion which is quite large, appears to be a structure breaker. It may be that, due to the bulky phenyl group which may shield the positive charge on the nitrogen atom from the influence of the solvent dipole, the ion-solvent intraction is weak as is the case with the larger R$_4$N$^+$ ions in these solvents.[1,2]

Although it is rather unsafe to make any generalisation in view of the restricted number of salts studied, it appears that unsymmetrical and partially substituted ammonium ions, in general, behave similarly in NMA and NMP; also their behaviour is similar to that of R$_4$N$^+$ ions. The author feels the necessity of an extensive study, involving more ions of this type before a definite conclusion can be arrived at.

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