Ion-Solvent Interaction of Tetraalkylammonium Ions in Solvents of High Dielectric Constant. II. Conductance and Walden Product of Tetraalkylammonium Ions in *N*-Methylformamide and *N*-Methylpropionamide at Different Temperatures

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Ion-solvent interaction of the tetraalkylammonium ions (R_4N^+) in *N*-methylformamide and *N*-methylpropionamide has been investigated from the electrical conductance point of view. It appears that the R_4N^+ ions act as net structure breakers in these solvents as in *N*-methylacetamide. The appreciable negative deviation of the experimental slope of the Λ *vs.* $\sqrt{c}$ curves from the theoretical slope suggests some kind of obstruction to the movement of the R_4N^+ ions, probably due to their unwieldy size or to some kind of cation-anion association, although the usual kind of association is ruled out in view of the high dielectric constant of these solvents. The cation-anion interaction may be the penetration of the cations by the anions which has been suggested as a possible reason for the negative slope in the apparent molal volume *vs.* $\sqrt{c}$ curves, obtained at higher concentrations, to which apparent molal volume measurements usually have to be confined on account of difficulties in accurate density measurements at low concentrations. The smaller alkali metal ions appear to be more solvated than the R_4N^+ ions, so much so that the λ_0^+-values of Na^+ and K^+ ions are lower than the corresponding values of the Me_4N^+ and Et_4N^+ ions.

Earlier studies[1,2] on the conductance of the tetraalkylammonium ions (R_4N^+) in *N*-methylacetamide (NMA) suggest that these ions are net structure breakers in this solvent. It seems desirable to extend the study to other similar solvents, such as *N*-methylformamide (NMF), *N*-methylpropionamide (NMP) which have high dielectric constant and strong hydrogen bonding. The study should give us a more general idea about the behaviour of these ions in highly polar nonaqueous solvents of high dielectric constant and strong hydrogen bonding. The study should give us a more general idea about the behaviour of these ions in highly polar nonaqueous solvents of high dielectric constant. The present communication deals with the results on the study of conductance of some R_4NI salts ($R=CH_3-$ to $R=C_7H_{15}-$) in NMF and NMP.

Experimental

R_4NI salts, obtained from M/S Distillation Products Industries, U.S.A., were purified by fractional crystallisation from suitable solvents or their mixtures.

Solvents (NMF and NMP) were purified by repeated drying over freshly ignited quicklime and vacuum distillation as for NMA. The conductivity of the samples of the solvents thus obtained was around 10^{-6} mho. Solvents were stored in dark amber-coloured bottles in a dry nitrogen box and were used, as far as possible, the day after distillation. While NMP appeared to be stable, NMF was found to be slightly unstable. 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 communication on NMA[1].

Results and Discussion

The equivalent conductance Λ was plotted against Λ *vs.* $\sqrt{c}$ curves were found to be almost straight lines for all the R_4NI salts in NMF and NMP, within the concentration and temperature ranges studied. The Λ *vs.* $\sqrt{c}$ curves for different salts are given in Figs. 1 and 2 at one temperature only (25°C in NMF and 40°C in NMP); the curves at other temperatures are similar and hence have been omitted. Extrapolation of Λ *vs.* $\sqrt{c}$ curves to infinite dilution leads to Λ_0-values given in Tables 1 and 2. From these Λ_0-values, the ionic conductances, λ_0^+, of the R_4N^+ ions at different temperatures, were obtained, using the appropriate transport number data given in literature;[3,4] these λ_0^+-values are given in Tables 1 and 2.

The applicability of the Debye-Hückel-Onsager conductance equation to solutions under study was examined.

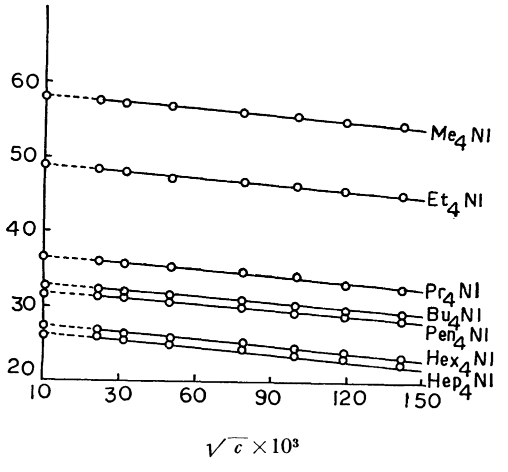

Fig. 1. Λ *vs.* $\sqrt{c}$ curves for R_4NI salts in NMF at 25°C.

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

[2] C. M. French and K. H. Glover, *Trans. Faraday Soc.*, **51**, 1428 (1955).

[3] R. Gopal and O. N. Bhatnagar, *J. Phys. Chem.* **70**, 3007 (1966).

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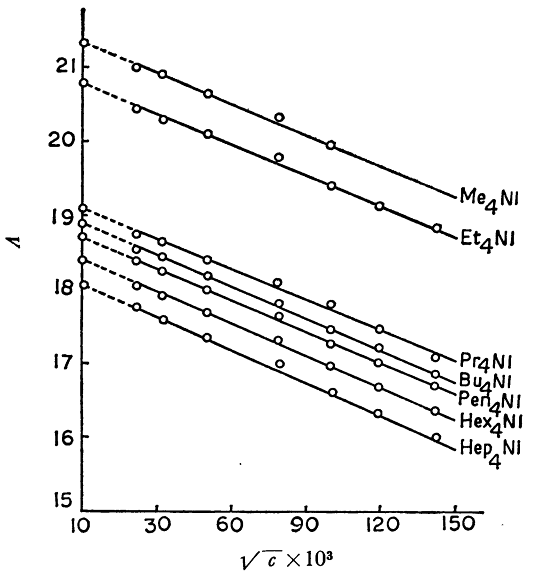

Fig. 2. Λ *vs.* $\sqrt{c}$ curves for R$_4$NI salts in NMP at 40°C.

Table 1. Limiting equivalent conductance of R$_4$NI salts and R$_4$N$^+$ ions at different temperatures in NMF

R$_4$NI salt and R$_4$N$^+$ ion	Limiting equivalent conductances at 15°C	20°C	25°C	30°C	35°C
Me$_4$NI	50.10	54.12	58.22	61.72	66.41
Me$_4$N$^+$	30.90	33.13	35.46	37.15	40.06
Et$_4$NI	42.32	45.10	48.95	51.55	55.14
Et$_4$N$^+$	23.12	24.11	26.19	26.98	28.79
Pr$_4$NI	31.81	34.25	36.70	39.18	42.10
Pr$_4$N$^+$	12.61	13.26	13.94	14.61	15.75
Bu$_4$NI	28.35	30.90	33.06	35.29	37.68
Bu$_4$N$^+$	9.15	9.91	10.30	10.72	11.33
Pen$_4$NI	27.74	29.75	32.29	34.55	36.70
Pen$_4$N$^+$	8.54	9.76	9.53	9.98	10.35
Hex$_4$NI	23.47	25.35	27.30	29.20	31.10
Hex$_4$N$^+$	4.27	4.36	4.54	4.63	4.75
Hep$_4$NI	22.97	24.84	26.71	28.60	30.61
Hep$_4$N$^+$	3.77	3.85	3.95	4.03	4.26

From Λ_0-values and other appropriate data on dielectric constant[5,6] and on viscosity η_0 (determined in this laboratary[7]), the theoretical slopes S of the Λ *vs.* $\sqrt{c}$ curves have been obtained and compared with the experimental slopes S_E in Table 3, in which the data for solutions in NMA have also been included for the sake of comparison.

Table 2. Limiting equivalent conductances of R$_4$NI salts and R$_4$N$^+$ ions at different temperatures in NMP

R$_4$NI salt and R$_4$N$^+$ ion	Limiting equivalent conductances at 30°C	35°C	40°C	45°C	50°C
Me$_4$NI	17.00	19.10	21.35	23.60	26.30
Me$_4$N$^+$	8.66	9.75	10.90	12.05	13.36
Et$_4$NI	16.55	18.60	20.80	23.00	25.71
Et$_4$N$^+$	8.21	9.25	10.35	11.45	12.77
Pr$_4$NI	15.19	17.07	19.10	21.15	23.70
Pr$_4$N$^+$	6.85	7.72	8.65	9.60	10.76
Bu$_4$NI	15.04	16.90	18.92	20.98	23.48
Bu$_4$N$^+$	6.70	7.55	8.47	9.43	10.54
Pen$_4$NI	14.89	16.75	18.72	20.75	23.24
Pen$_4$N$^+$	6.55	7.40	8.27	9.20	10.30
Hex$_4$NI	14.64	16.48	18.41	20.40	22.85
Hex$_4$N$^+$	6.30	7.13	7.96	8.85	9.91
Hep$_4$NI	14.38	16.14	18.08	20.03	22.43
Hep$_4$N$^+$	6.04	6.79	7.63	8.48	9.49

Table 3. Onsager slopes in NMF, NMP, and NMA

Salt		Theoretical slope (S_T)	Experimental slope (S_E)	% deviation $\frac{S_E-S_T}{S_T}\times 100$
	NMF (temp.=25°C)			
Me$_4$NI	58.22	−25.2	−26.9	7
Et$_4$NI	48.95	−24.6	−27.1	10
Pr$_4$NI	38.70	−23.8	−27.4	16
Bu$_4$NI	33.06	−23.6	−27.6	17
Pen$_4$NI	32.29	−23.5	−27.8	18
Hex$_4$NI	27.30	−23.2	−28.1	21
Hep$_4$NI	26.71	−23.2	−28.3	22
	NMP (temp.=40°C)			
Me$_4$NI	21.35	−12.3	−14.2	16
Et$_4$NI	20.30	−12.3	−13.8	12
Pr$_4$NI	19.10	−12.1	−13.8	14
Bu$_4$NI	18.92	−12.1	−14.2	17
Pen$_4$NI	18.72	−12.1	−14.4	19
Hex$_4$NI	18.41	−12.1	−14.4	19
Hep$_4$NI	18.08	−12.1	−14.6	21
	NMA (temp.=40°C)			
Me$_4$NI	26.75	−13.8	−16.6	20
Et$_4$NI	26.25	−13.8	−16.0	16
Pr$_4$NT	23.80	−13.6	−15.4	13
Bu$_4$Nl	22.50	−13.6	−15.5	14
Pen$_4$NI	22.00	−13.5	−15.7	16
Hex$_4$NI	21.80	−13.5	−16.1	19
Hep$_4$NI	21.47	−13.5	−16.5	20

It is to be noted from Table 3 that there is a significant negative deviation from the theoretical slope S_T for the R$_4$NI salts in all the three solvents. The percentage deviation, in general, increases with the increase in the radius of the R$_4$N$^+$ ion. In view of the high dielectric constant of these solvents, incomplete dissociation of the salts in the usual sense is un-

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[5] G. R. Leader and J. F. Gormley, *J. Amer. Chem. Soc.*, **73**, 5731 (1951).

[6] T. B. Hoover, *J. Phys. Chem.*, **68**, 876 (1964).

[7] Viscosity of NMF

15°C	20°C	25°C	30°C	35°C
0.0199	0.0182	0.0165	0.0154	0.0141 poise

Viscosity of NMP

30°C	35°C	40°C	45°C	50°C
0.04568	0.04004	0.03541	0.03173	0.02825 poise

thinkable, although Dawson and coworkers[8,9] have tried to explain their conductance results in NMA on this ground. Does this behaviour (appreciable negative deviation) indicate penetration of R_4N^+ ions by anions causing a sort of association,[10] or does it simply indicate that the solvent molecules offer a greater resistance to the movement of the R_4N^+ ions, than that caused by viscosity of the solvent medium, so that the movement of these ions is more sluggish than expected from theory? There is, apparently, no way to decide which factor is actually responsible. Since the larger the ion, the larger the deviation, one feels that the geometry and size of the ions have something to do with their sluggish movement; their tetrahedral, open structure and their large volume will favour their penetration by anions and will also cause obstruction in their movements. It should be mentioned that penetration has been ascribed as one of the factors responsible for the reported abnormal negative slope in the apparent molar volume *vs.* $\sqrt{c}$ curves of these salts in aqueous and nonaqueous solvents.[11,17] The conductance data of these salts at higher concentrations in a variety of solvents can be expected to throw further light on their behaviour.

The cationic Walden products of different R_4N^+ ions at different temperatures have been calculated from the appropriate λ_0^+-values (given in Tables 1 and 2) and viscosity data given earlier. From the Walden product data, thus obtained, $\lambda_0^+ \eta_0$ *vs.* temperature curves have been drawn and are given in Figs. 3 and 4.

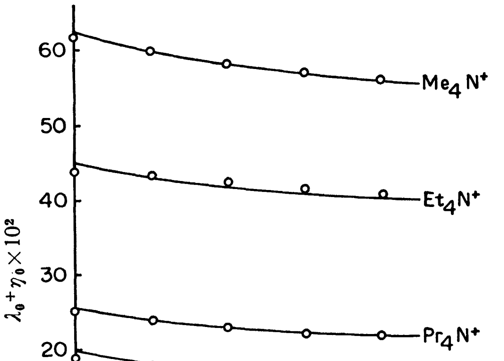

Fig. 3. Plot of $\lambda_0^+\eta_0$ *vs.* t°C in NMF.

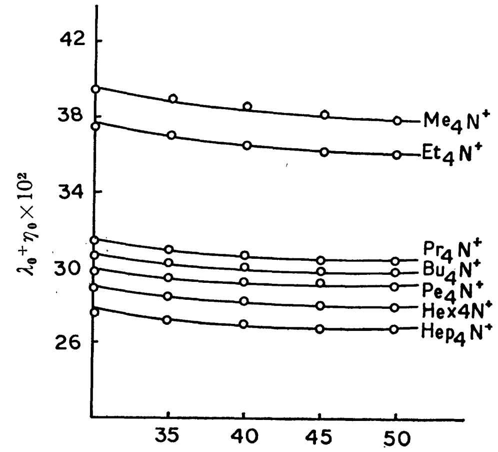

Fig. 4. Plot of $\lambda_0^+\eta_0$ *vs.* t°C in NMP.

It is obvious that the Walden product decreases with the rise in temperature in both solvents, as in NMA,[1] indicating a net structure breaking role of the R_4N^+ ions in these amides. It should be pointed out that in aqueous solutions, the dependence of Walden product on temperature indicates that Me_4N^+ ion (perhaps Et_4N^+ ion also) is a net structure breaker whereas the larger R_4N^+ ions are net structure promoters.[18]

A comparison of λ_0^+-values of R_4N^+ ions in the three solvents with those in water brings out some points of interest. Both Λ_0 and λ_0^+-values are comparatively lower in these solvents than the corresponding values in water, probably on account of the highly viscous nature of these solvents and, perhaps, due to a possible stronger ion-solvent interaction.[1,19,20] It may be noted that λ_0^+ of the smaller R_4N^+ ions are actually larger than those of the alkali metal ions, *e.g.*, in NMF at 25°, $\lambda_0(Me_4N^+)=35.45$ and $\lambda_0(Et_4N^+)=26.19$, whereas $\lambda_0(Na^+)=21.64$ and $\lambda_0(K^+)=22.20$ and in NMP at 30°, $\lambda_0(Me_4N^+)=8.66$ and $\lambda_0(Et_4N^+)=8.21$, whereas $\lambda_0(Na^+)=5.06$ and $\lambda_0(K^+)=5.36$, in spite of the much larger radii of the R_4N^+ ions. This obviously indicates a stronger solvation of alkali metal ions in NMF and NMP as compared to R_4N^+–NMF and R_4N^+–NMP interactions, as one would expect from the much higher electrical charge density on the smaller alkali metal ions. This also indicates a net structure breaking role of R_4N^+ ions and a possible structure promotion by the smaller alkali metal ions.

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