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A Study of Ion-Solvent Interaction of Tetraalkylammonium and Common Alkali Metal Ions in Ethylene Carbonate from Electrolytic Conductance Data

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Synopsis. Ion-solvent interaction in solutions of some tetraalkylammonium and common alkali metal iodides in ethylene carbonate, from the point of view, of electrical conductance and the derived Walden product, has been examined in this communication. The Debye-Hückel-Onsager equation appears to hold good for all the salts in the temperature and concentration range studied here. Dependence of the Walden product on temperature and radius of cation reveals that the R_4N^+ ions do not interact appreciably with the solvent but Li^+, Na^+, K^+, and Rb^+ ions appear to be solvated.

Ion-solvent interaction studies in some highly polar and non-hydrogen bonded solvents, having medium dielectric constant, namely, dimethylsulfoxide (DMSO)[1,2] and propylene carbonate (PC),[3,4] have been reported in earlier communications from this laboratory. It appears interesting to study the behavior of these salts in an aprotic, dipolar solvent of high dielectric constant like ethylene carbonate (EC) in order to have a wider picture of solute-solvent interaction. This solvent is, like DMSO and PC, highly polar and non-hydrogen bonded; its dielectric constant[5] is 85.81 at 40 °C. A few studies on conductance of electrolytes have been reported in this solvent,[6] but these are confined to 40 °C only and hence of little use in studying ion-solvent interaction. This situation and the interesting solvent properties of ethylene carbonate prompted the investigation reported in this communication.

Experimental

Ethylene carbonate (Fluka, purum) was fractionally crystallized three times. The sample thus obtained was distilled under reduced pressure. The middle fraction of the distillate was collected in a dark colored bottle and kept in a dry box. The sample was found to melt sharply at 36.5 °C and its electrical conductance was of the order of 10^{-6} Ω^{-1} cm^{-1}.

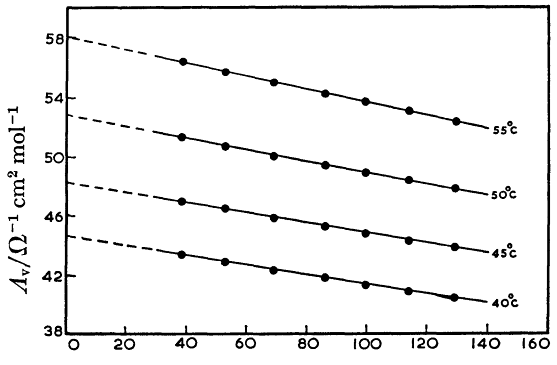

Fig. 1. Λ_v *vs.* $\sqrt{C}$ curves for Me_4NI at different temperatures in ethylene carbonate.

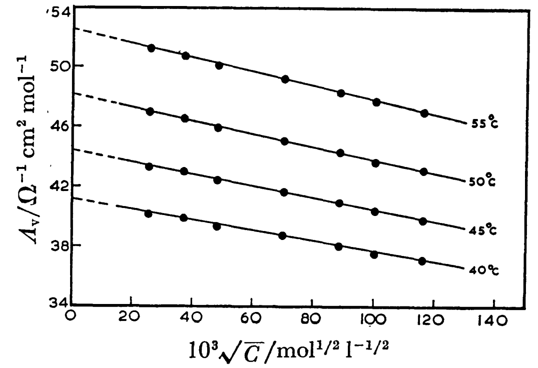

Fig. 2. Λ_v *vs.* $\sqrt{C}$ curves for KI at different temperatures in ethylene carbonate.

Tetraalkylammonium iodides (DPI, USA) and the common salts (BDH, AR) were purified in the usual manner.[7] The experimental procedure for measuring the electrical conductance was the same as described earlier. The precision of measurement was about ±0.03%.

Table 1. Limiting equivalent conductivities Λ_0/Ω^{-1} cm^2 mol^{-1} of some salts in EC

Salt	Limiting equivalent conductivity at			
	40 °C	45 °C	50 °C	55 °C
LiI	32.18	34.76	38.06	42.15
NaI	37.89	40.94	44.53	48.85
KI	41.20	44.42	48.10	52.50
RbI	42.35	45.52	49.20	53.80
Me_4NI	44.75 (44.81)	48.19	52.88	58.20
Et_4NI	42.70 (42.83)	45.87	49.49	53.84
Pr_4NI	39.75	42.60	46.16	50.30
Bu_4NI	37.45 (37.40)	40.70	44.08	47.86
Pen_4NI	35.68	38.25	41.50	45.52
Hex_4NI	33.40	35.70	38.94	47.81
Hep_4NI	31.96	34.25	37.05	40.50

Values in parenthesis are from Ref. 6.

Table 2. Slopes S_T and S_E in ethylene carbonate at 40 °C

Salt	S_T/Ω^{-1} cm^2 mol$^{-3/2}$ l$^{2/1}$ (Theoretical slope)	S_E/Ω^{-1} cm^2 mol$^{-3/2}$ l$^{1/2}$ (Experimental slope)	Deviation $\frac{(S_T-S_E)}{S_E}\times 100$
LiI	32.15	30.58	−4.6
NaI	33.30	31.45	−5.8
KI	33.72	33.50	+0.65
RbI	33.92	34.65	+1.8
Me_4NI	34.34	33.60	−2.2
Et_4NI	33.98	34.58	+1.7
Pr_4NI	33.47	35.40	+5.4
Bu_4NI	33.07	36.50	+9.5
Pen_4NI	32.76	40.45	+19.2
Hex_4NI	32.37	38.45	+15.8
Hep_4NI	32.11	34.34	+6.5

Table 3. Walden product of some salts in ethylene carbonate

Salt	Walden product ($\Lambda_0\eta_0/\Omega^{-1}$ g cm^{-1} mol^{-1}) at			
	40 °C	45 °C	50 °C	55 °C
LiI	0.555	0.599	0.606	0.615
NaI	0.702	0.705	0.709	0.713
KI	0.762	0.765	0.766	0.766
RbI	0.783	0.784	0.784	0.785
Me_4NI	0.828	0.836	0.832	0.835
Et_4NI	0.789	0.790	0.788	0.785
Pr_4NI	0.735	0.734	0.738	0.734
Bu_4NI	0.693	0.701	0.702	0.698
Pen_4NI	0.660	0.658	0.662	0.664
Hex_4NI	0.618	0.615	0.620	0.610
Hep_4NI	0.590	0.591	0.590	0.592

Results and Discussion

From the electrolytic conductance data thus obtained, Λ_V *vs.* $\sqrt{C}$ curves were drawn for different salts at various temperatures. The plots for Me_4NI and KI are given in Figs. 1 and 2, as typicals of tetraalkylammonium and common salts respectively. It may be noted that the plots are almost straight lines suggesting that the simple Debye-Hückel-Onsager theory of electrolytic conductance is applicable to these solutions and the salts are completely ionized in ethylene carbonate. The limiting equivalent conductivities of different salts at various temperatures, obtained from the usual extrapolation procedure, are given in Table 1.

The theoretical slope S_T of the Λ_V *vs.* $\sqrt{C}$ curves, according to Debye-Hückel theory is given by

$$S_T = A + B\Lambda_0,$$

where $A = \frac{82.42}{\eta_0(\varepsilon T)^{1/2}}$ and $B = \frac{8.203\times 10^6}{(\varepsilon T)^{3/2}}$.

From the Λ_0 values given in Table 1, S_T values for different cases at 40 °C have been calculated and compared with the corresponding experimental slopes S_E in Table 2. The value of the dielectric constant used for calculating the experimental slope is $\varepsilon_{40\,^\circ C}=85.81$ and viscosity $\eta/\mathrm{g\ m^{-1}\ s^{-1}}=1.850$, as determined experimentally in this laboratory. Table 2 clearly shows that there is a good agreement between the experimental and theoretical slopes indicating that the simple Debye-Hückel-Onsager theory of strong electrolytic conductivity is applicable to these solutions.

The nature of ion-solvent interaction in EC may be examined from the temperature and ionic radius dependence of the Walden product. Unfortunately, due to lack of the ionic conductance data, at different temperature, only the electrolytic Walden product can be used for the present study. It is assumed that the variations in the Walden product are mainly due to cations since large anions do not interact appreciably in aprotic solvents. Viscosities of the solvent at different temperatures, required to calculate the Walden product, were obtained experimentally and are $\eta/\mathrm{g\ m^{-1}\ s^{-1}}=$ 1.850 (40 °C), 1.722 (45 °C), 1.590 (50 °C) and 1.459 (55 °C). The values of the Walden product, $\Lambda_0\eta_0$, for different salts at various temperatures, are given in Table 3.

Although the temperature dependence of the Walden product, can be examined from the data given in Table 3, the plots of $\Lambda_0\eta_0$ against temperature, given in Fig. 3, make it more explicit. It may be noted that $\Lambda_0\eta_0$ for the smaller alkali metal iodides appears to increase slightly with the rise in temperature, indicating a net structure promoting effect of these salts in EC. As pointed out in the earlier paragraph, anions, more particularly the larger ones, are not expected to interact strongly with the aprotic solvents, it is reasonable to presume that the structure enhancement is due to the cation-solvent interaction. Besides, since the Walden product of the larger alkali metal and R_4N-iodides in which the cation may be expected to interact very weakly, if at all, with the solvent, is almost independent of temperature, I^- ion would also be more or less unsolvated. Thus increase in the Walden product with the rise of temperature for smaller alkali metal iodides must be ascribed to the cations which interact appreciably with the solvent molecules and are solvated. The large R_4N^+ ions do not appear to interact significantly, with EC.

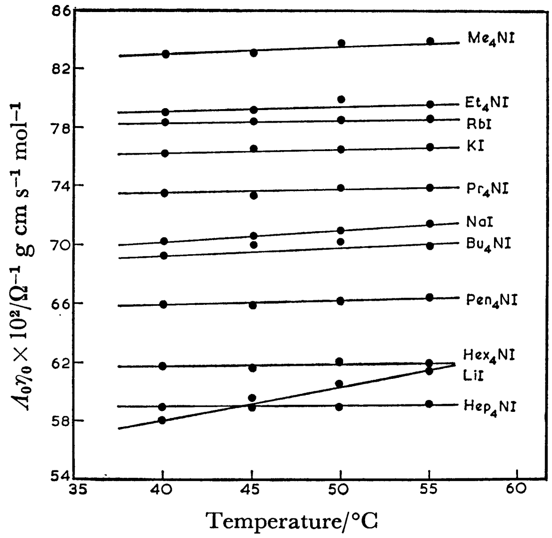

Fig. 3. Walden product $\Lambda_0\eta_0$ *vs.* temperature plots in ethylene carbonate for some electrolytes.

The same conclusions can be arrived at if the variation of the Walden product with the radius of the cation is examined. Since iodide ion is common to all the salts studied here, it may be assumed, as before, that the variation in the Walden product is due to cation only. It may be noted that for the alkali metal salts, the Walden product varies directly with the radius of the cation; this indicates that the size of the cation in solution is larger, the smaller its radius or in other words, the smaller the cation, the more highly solvated it is. Opposite appears to be the case with the R_4N^+ ions. for which the Walden product varies inversely as the radius showing that these ions are not solvated to any appreciable extent. Their size remains almost unchanged in solution and there is no appreciable electrostatic ion-solvent interaction with EC.

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