TABLE 2 — ACTIVATION PARAMETERS (AT 48·2°) FOR THE SOLVOLYSIS OF SODIUM MONOCHLOROACETATE IN WATER-ETHANOL SOLUTIONS

Ethanol (% by wt)	Mole fr. of water	E_a kcal mole^{-1}	ΔH^* kcal mole^{-1}	ΔS^* cal deg^{-1} mole^{-1}	ΔG^* kcal mole^{-1}
0	1·000	22·52	21·88	12·53	17·85
20·8	0·907	22·00	21·36	14·28	16·77
38·6	0·803	21·05	20·41	16·68	15·05
52·0	0·703	21·40	20·76	15·27	15·85
69·5	0·530	22·55	21·91	10·75	18·46
83·9	0·330	24·10	23·46	4·70	21·95
95·5	0·105	24·70	24·06	2·42	23·28

of activation, are listed in Table 2. It can be seen that the activation parameters pass through a minimum at about 0·8 water mole fraction. The positions of the ΔH^* and ΔS^* minima appear to coincide, which is characteristic of binary solvent mixtures in which both components are hydroxylic[1,2]. The results for methanol-water[1] and ethanol-water are quite similar. The decrease in ΔH^* at higher mole fraction of water simulates the behaviour observed in the case of methanol as the co-solvent. The solvolysis of monochloroacetate ion in water-ethanol solutions produces a decrease of 4 cal/deg mole in ΔS^* between water mole fractions of 1 and 0·8 water corresponding to a change in ΔH^* of about 1·5 kcal/mole for the same composition range. Here, the principal contribution toward increasing rate over the range 0 to 40% by weight ethanol (1·0 to 0·8 water mole fraction) is from the decrease in ΔH^*. In contrast, at water mole fraction of < 0·8 ΔS^* decreases by more than 12 cal/deg mole and its effect becomes increasingly important, sufficiently so as to outweigh by far the actual reversal of the trend in ΔH^*. For solvolysis in water-methanol solutions, the ΔH^*-ΔS^* minimum is located at about 0·7 water mole fraction. Moreover, the depth of the minimum relative to pure water amounts to 12 cal/deg mole for ΔS^* and 4 kcal/mole for ΔH^*. These results are in agreement with observations[5-7] that the extrema in ΔH^* and ΔS^* shift to lower concentration in the case of alcohol of ethanol with bulky group. The results are in conformity with the conclusion that the relative amount of alcohol compatible with a three-dimensional quasi-aqueous structure is directly dependent on the bulk of the group[5,6]. Furthermore, the extremum behaviour in ΔH^* and ΔS^* in aquo-organic solvent mixtures was observed for many solvolysis reactions[1,2,5-9]. This behaviour has been interpreted on the basis that the breakdown of solvent structure as a consequence of charge separation in the activation process parallels the sensitivity to changes in the solvent composition[6,10].

The experimentally calculated values of the free energies of activation (Table 2) do not change much with solvent composition, due mainly to the linear compensation between ΔH^* and ΔS^*. This behaviour is similar to that reported for many solvolysis reactions[1,6] and is to be expected if the solvents in a series perform closely similar roles in the reaction.

References

1. AZZAM, AHMED M. & DIEFALLAH, EL-HUSSIENY M., Z. physik. Chem. (Neue Folge), 91 (1974), 44.
2. WINSTEIN, S. & FAINBERG, A. H., J. Am. chem. Soc., 79 (1957), 5937.
3. INGOLD, C. K., Structure and mechanism in organic chemistry (Cornell University Press, Ithaca), 1953, Chapter 7.
4. FROST, A. A. & PEARSON, R. G., Kinetics and mechanism (John Wiley, New York), 1961, Chapter 7.
5. ROBERTSON, R. E. & SUGAMORI, S. E., Can. J. Chem., 50 (1972), 1353.
6. ROBERTSON, R. E. & SUGAMORI, S. E., J. Am. chem. Soc., 91 (1969), 7254.
7. GOLINKIN, H. S. & HYNE, J. B., Can. J. Chem., 46 (1968), 125.
8. MARTIN, J. G. & ROBERTSON, R. E., J. Am. chem. Soc., 88 (1966), 5353.
9. HYNE, J. B. & WILLS, R., J. Am. chem. Soc., 85 (1963), 3650.
10. ARNETT, E. M., BENTRUDE, W. G., BURKE, J. J. & DUGGLEBY, P. M., J. Am. chem. Soc., 87 (1965), 1541.

A Study of Ion-Solvent Interaction in Propylene Carbonate from Viscosity Data

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Interaction of the common and tetraalkylammonium (R_4N^+) ions in propylene carbonate has been examined from the viscosity point of view, using the dependence of coefficient B of the Jones and Dole viscosity equation, on temperature and radius of the cation. While the temperature coefficient dB/dt fails to indicate any interaction in this solvent, the variation of B with radius reveals that smaller common cations are solvated but not the larger R_4N^+ ions.

A STUDY of solute-solvent interaction in propylene carbonate (PC) from electrical conductance measurements[1] indicates that the ionic Walden product is almost temperature independent and hence fails to give any indication about the nature of ion-solvent interaction. A closer look on the values of ionic conductivities and the derived Walden products shows that while the conductivity of the R_4N^+ ions decreases with the increase in the radius of the ion, opposite is the case with the small alkali metal ions for which conductivity increases, although slowly, with the increase in the ionic radius. These observations suggest that the R_4N^+ ions remain almost bare (unsolvated) in solution but the small alkali metal ions are associated with the solvent molecules (i.e. solvated), their number varying inversely as the radius of the ion in question. It appears, therefore, worth while to examine this problem from the viscosity point of view since this property of salt solutions has been used as an effective tool for studying solute-solvent interaction[2-10]. Although viscosity of some salt solutions in PC has been reported recently[12,13], the studies have been confined to one temperature and hence the data inadequate. This prompted us to measure the viscosity of the solutions of some alkali metal and tetraalkylammonium iodides in PC at 30°, 35°, 40°, 45° and 50° and the results obtained are reported in this note.

Propylene carbonate (Fluka, purum) was kept on freshly ignited quicklime overnight and then distilled under reduced pressure, the middle fraction being retained; this was redistilled. The process was repeated till the conductivity of the middle fraction was reduced to 10^{-6} ohm^{-1} cm^2 or less. The tetraalkylammonium and common salts were purified and dried in the usual manner. Solutions were prepared on weight basis and their volume concentrations were obtained from the density data determined side by side; contact of solutions with atmospheric moisture was avoided as far as possible.

Measurements of density and viscosity were carried out in a thermostat with a temperature control of $\pm 0.01°$. Density was measured with a dilatometer of about 20 ml capacity and provided with a graduated stem on which volume could be read up to 0·005 ml within an error of ± 0.002 ml. A modified Ubbelohde viscometer was used for measuring viscosity. The viscometer was flushed with dry nitrogen before use.

Viscosity was calculated from the data thus obtained. Kinetic energy correction was neglected. From the viscosity data, specific viscosity $\Psi[=(\eta_s-\eta_0), \eta_0]$ was calculated and $\Psi/\sqrt{C}$ vs $\sqrt{C}$ curves for different electrolytes at various temperatures were drawn. Such curves for tetramethylammonium iodide are given in Fig. 1, as a representative of the electrolytes studied presently.

The linear nature of the curves in Fig. 1 suggests that the Jones and Dole viscosity equation[2], namely $\Psi/\sqrt{C}=A+B\sqrt{C}$ is applicable to these solutions. The values of the coefficient B which gives an idea about solute-solvent interaction, obtained from the slopes of $\Psi/\sqrt{C}$ v rsus $\sqrt{C}$ curves at different temperatures, are given in Table 1. It may be noted that B is almost independent of temperature and $dB/dt \approx 0$ in all the cases. So the coefficient B fails to give any indication of the nature of solute-solvent interaction. It may be recalled that the Walden product[1] is also independent of temperature. Thus the temperature dependence of both the coefficient B and the Walden product
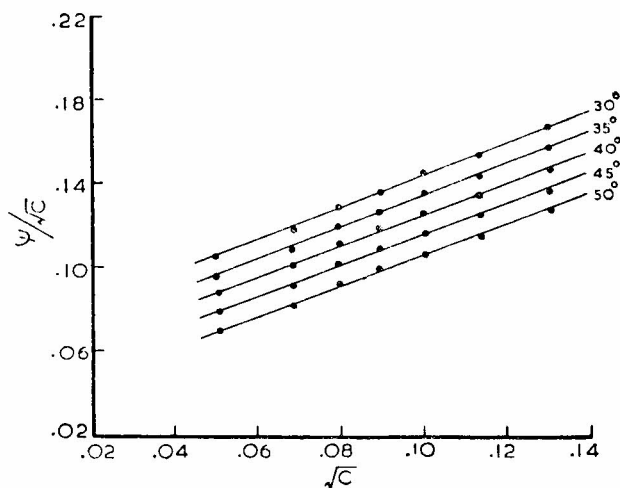

Fig. 1 — Plot of $\Psi/\sqrt{C}$ versus $\sqrt{C}$ for tetramethylammonium iodide

TABLE 1 — B VALUES OF SOME SALTS AT DIFFERENT TEMPERATURES

Salt	B value at				
	30°	35°	40°	45°	50°
Me$_4$NI	0·729	0·730	0·730	0·730	0·729
Et$_4$NI	0·912	0·912	0·913	0·912	0·913
Pr$_4$NI	0·929	0·928	0·928	0·929	0·929
Bu$_4$NI	0·939	0·941	0·939	0·940	0·940
Pen$_4$NI	0·959	0·958	0·959	0·959	0·949
Hex$_4$NI	1·380	1·381	1·379	1·380	1·380
Hep$_4$NI	1·425	1·424	1·425	1·425	1·425
LiI	1·288	1·284	1·279	1·286	1·289
NaI	0·901	0·898	1·900	0·901	0·900
KI	0·886	0·885	0·887	0·887	0·886
RbI	0·734	0·735	0·734	0·735	0·732

fails to indicate whether a salt is net structure breaker or maker in propylene carbonate.

Since the anion is common for all the electrolytes used in this study, any variation in B coefficient will thus then be due to the cation. It may be observed from Table 1 that for the salts containing the larger R$_4$N$^+$ ions, the coefficient B increases with the increase in radius of the cation, which indicates that the electrostatic ion-solvent interaction, if at all, is very weak in these cases and resistance to the movement of ions in solution depends on the size of the bare ion only. Reverse appears to be the case with the salts containing small common cations which are very small as compared to the R$_4$N$^+$ ions. In these cases, B decreases with the increase in the radius of the cation, which suggests that the size of the solvated alkali metal ions varies inversely as the radius, and the smaller the ion, the stronger the electrostatic ion-solvent dipole interaction. The size of the solvated ions or of the salvodynamic unit in solution follows the order: Li$^+$ > Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$. It thus appears that the common cations are associated with some PC molecules due to electrostatic ion-solvent dipole interaction.

It may be recalled that in a hydrogen-bonded solvent, B coefficient values and the Walden products are temperature dependent and the electrostatic ion-solvent interactions are projected by the changes in these two parameters. The reverse is true for the solvent like PC which has neither a hydrogen-bonded structure nor any appreciable molecular association. It appears that in such cases, only the correlation of B values and the Walden product (or ionic conductivity) with the radius of the ion could be helpful in getting a qualitative picture of the ion-solvent interaction and solvation.

References

1. SINGH, S., JHA, J. S. & GOPAL, R., Indian J. Chem., 14A (1976), 127.
2. JONES, G. & DOLE, M., J. Am. chem. Soc., 51 (1929), 950.
3. GURNEY, R. W., Ionic processes in solution (McGraw-Hill Book Co. Inc., New York), 1953, 159.

4. HARNED, H. S. & OWENS, B. B., *Physical chemistry of electrolyte solutions* (Reinhold Publishing Corporation, New York), 1959, 241.
5. KAMINSKY, M., *Discuss. Faraday Soc.*, 24 (1957), 150.
6. NIGHTINGALE (Jr), E. R., *J. phys. Chem.*, 66 (1962), 894.
7. KAY, R. L. & EVANS, D. F., *J. phys. Chem.*, 70 (1966), 2336.
8. GOPAL, R. & RASTOGI, P. P., *Z. phys. Chem.* (*Frankfurt*), 69 (1970), 1.
9. KRICKARD, K. & SKINNER, J. F., *J. phys. Chem.*, 73 (1969), 1079.
10. GOPAL, R., HUSAIN, M. M. & SINGH, P., *Z. phys. Chem.* (*Frankfurt*), 76 (1971), 216.
11. MUKERJEE, L. M. & BODEN, D. P., *J. phys. Chem.*, 73 (1969), 3965.
12. MUKERJEE, L. M., BODEN, D. P. & LINDAUER, R., *J. phys. Chem.*, 74 (1970), 1942.
13. HARRIS, W. S., *U.S. Atomic Energy Commun.*, UCRL, 77 (1958), 8381.

Conductance of Tetraalkylammonium Bromides in Formamide-Water Mixtures at 25°*

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Conductance data of tetraethylammonium bromide (TEAB) and tetrabutylammonium bromide (TBAB) in formamide-water mixtures at 25°±0·005° in concentration range 0·01 to 0·10N are being reported. The experimental data have been analysed on the basis of Fuoss equation [*J. phys. Chem.*, 79 (1975), 525]. The parameters Λ_0, K_A and R have been calculated for each system. Walden product ($\Lambda_0 \cdot \eta$) passes through an ill-defined minimum as formamide content increases in the solvent mixture. Association constant, K_A, is almost negligible for TEAB and is slightly more than unity in the case of TBAB. For a given solvent mixture Λ_0 is less for TBAB as compared to that for TEAB.

STUDIES on different physico-chemical properties like density, viscosity and dielectric constant of amide-water mixtures have been undertaken[1-3] with a view to throwing light on ion-solvent interactions and molecular association. Singh *et al.*[4] have determined the viscosities of solutions of sodium and magnesium sulphates in acetamide-water mixtures and the data were analysed in terms of intermolecular association in aqueous acetamide. However, a survey of literature reveals that the study of conductance of electrolytes in amide-water mixtures, which is basic to the elucidation of structure of electrolyte solutions, is lacking. We report here conductance data on tetraethylammonium bromide (TEAB) and tetrabutylammonium bromide (TBAB) in formamide-water mixtures. The data have been analysed in terms of conductance-concentration equation due to Fuoss based on a new model for ionic association[5].

Tetraethylammonium bromide (AR, BDH) and tetrabutylammonium bromide (Purum, Fluka) were further purified by Harkness's method[6]. Triply

*Dedicated to (late) Dr D. Singh.

distilled water (sp. cond. $0·4-0·9 \times 10^{-6}$ mho cm⁻¹) was used for preparing different solvent mixtures. KCl (AR, BDH) was recrystallized as suggested by Hawes and Kay[7]. Formamide (LR, BDH) was purified by the method of Dawson *et al.*[8] and the purified sample had a conductivity of $0·3-1·1 \times 10^{-5}$ mho cm⁻¹.

A conductivity bridge (Cambridge, model No. L-370873) was used for conductance measurements. All the measurements were carried out at $25° \pm 0·005°$ under N_2 atmosphere. Variation of the temperature was checked using a Beckmann thermometer with an accuracy of $\pm 0·002°$. Two conductivity cells of the type suggested by Daggett *et al.*[9] were used. Electrodes were slightly platinized. Cells were calibrated by determining the conductance of KCl solutions in water at 25° in concentration range 0·01-0·10N and using Fuoss equation[10]. Cell constants were found to be $0·3044 \pm 0·0002$ and $0·6132 \pm 0·0003$/cm. All the solvent mixtures were prepared by weight. Viscosity and density of the solvents were determined at $25° \pm 0·1°$ using a Cannon Ubbelohde viscometer (50/A703) and a calibrated pyknometer of 20 ml capacity respectively. Time of flow was reproducible within 0·1 sec. Dielectric constants of the solvent-mixtures were taken from literature[3].

The equivalent conductance of tetraethyl- and tetrabutyl-ammonium bromides at different concentrations and in various formamide-water mixtures are given in Table 1.

The three adjustable parameters, Λ_0, K_A and R, were obtained by solving Eqs. (1-3).

$$\Lambda = \gamma[\Lambda_0(1-\Delta X/X)-\Delta\Lambda_e] \qquad \ldots(1)$$

$$\gamma = 1-K_A c\gamma^2 f^2 \qquad \ldots(2)$$

$$\ln f = -\beta K/2(1+KR) \qquad \ldots(3)$$

where R is cosphere diameter[5] and other terms have their usual meanings. Expressions for $\Delta X/X$ and $\Delta\Lambda_e$ and the method of analysis adopted here were the same as given by Fuoss[5]. All computations were performed on IBM 7044 computer. Computer programmes were kindly supplied by Prof. R. M. Fuoss and these were used after making minor corrections to suit the computer. In most of the cases SCAN or PKV-SCAN programme was used. Calculated values of Λ_0, K_A and R are given in Table 2.

Viscosity of the solvent-mixtures increases progressively with an increase in the formamide content of the solvent. No minimum or maximum was observed indicating the absence of strong structure-breaking or structure-forming effects as well as possible loose association[3] of formamide with water molecules which will lead to increased viscosity. Decrease in Λ_0 with increase in formamide content of the solvent (Table 2) is attributable mainly to change in viscosity of solvent; influence of simultaneous increase in dielectric constant can be neglected as dissociation is almost complete in all the compositions. Walden product ($\Lambda_0\eta$) passes through an ill-defined minimum and then increases with increase in formamide content of the solvent. For a given solvent mixture, Λ_0 for TBAB is less