Ion-Solvent Interaction of Tetraalkylammonium Ions in Dimethyl Sulphoxide from Electrolytic Conductivity Data

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(Received July 26, 1974)

Ion-solvent interaction of some tetraalkylammonium ions in dimethyl sulphoxide has been studied in this communication from the point of view of electrolytic conductivity and the derived Walden product. The R_4N^+ ions do not appear to interact strongly with this solvent; further, the salts examined appear to be completely dissociated in the concentration range studied here.

During the past few years, considerable interest has been shown to study the properties of the tetraalkylammonium ions (R_4N^+) in water and non-aqueous media.[1] Studies on R_4N^+–solvent interaction, using electrolytic conductivity data, in some solvents of high dielectric constant like *N*-methylformamide, *N*-methylacetamide and *N*-methylpropionamide, have been recently reported from this laboratory.[2,3] Dimethyl sulphoxide (DMSO) is an interesting solvent as it is highly polar[4] which would promote strong ion–solvent dipole interaction; it has no hydrogen bonding which distinguishes it from NMF, NMA and NMP. So it appears a little surprising that only a few studies, specially on electrolytic conductivity,[5–10] have been reported in this solvent. Electrolytic conductivities of some tetraalkylammonium halides and other salts in DMSO have been reported by Arrington and Griswold[11] at 25 °C; these studies appear to be rather sketchy, and a more detailed investigation appears very desirable. As the temperature dependence of electrolytic conductivity and the derived Walden product can be used to throw light on ion–solvent interaction, it is proposed to investigate the same in DMSO in this communication.

Experimental

DMSO (Fluka, purum) was purified by the method described in an earlier communication;[12] the purified sample was found to have conductivity $\approx 10^{-6}\Omega^{-1}\,cm^2$. Tetraalkylammonium salts (DPI, USA) were purified in the usual manner.[2] Solutions were prepared at 30 °C in a thermostat, and the concentration was corrected for the changes in volume at other temperatures from the corresponding densities which were also determined experimentally. The conductance of the solvent was taken into account while calculating the molar conductivities of the electrolytes. The conductance measurements were made with a suitably grounded Wheatstone Bridge and the cell was placed in a thermostat regulated to within ± 0.01 °C in the lower temperature range and ± 0.02 °C in the higher temperature range. The accuracy of measurements was checked by determining the electrolytic conductivity of some electrolytes of known conductivity.[5,11]

Results and Discussion

The plots of the molar conductivity Λ against the square root of concentration C, at different temperatures, are found to be almost straight lines. Such curves for 40 °C are given in Fig. 1. Extrapolation of the Λ *vs.* $\sqrt{C}$ curves to infinite dilution gives Λ_0-

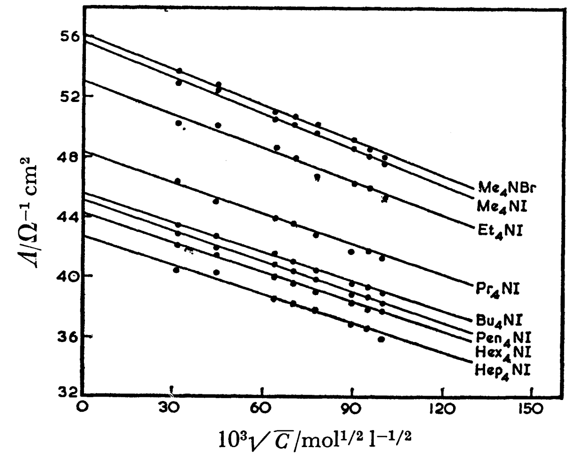

Fig. 1. Λ *vs.* $\sqrt{C}$ curves for R_4NX salt in DMSO at 40 °C.

values* which are given in Table 1; from these values, the molar ionic conductivities of the R_4N^+ ions, *i.e.*, Λ_0^+, have been obtained by using the Λ_0^--values of the bromide ion, obtained from the cationic transport number of KBr[13] and its electrolytic conductivities at 25, 30, 40, and 50 °C. These data are recorded in Table 1.

From the Λ_0-values, the theoretical slope, S_T, of the Λ *vs.* $\sqrt{C}$ curves for different salts at 40 °C, was estimated and compared with the corresponding experimental slope, S, in Table 2. Values of the dielectric constant and viscosity, used for estimating S, are 43.97 and 1.508 $g\cdot m^{-1}\cdot s^{-1}$. respectively and have been obtained graphically from the data of Yao and Bennison.[8]

The fact that the plots of Λ *vs.* $\sqrt{C}$ gave straight lines indicates that, in dilute solution, these salts are completely ionized in DMSO. It may be noted from Table 2 that there is a good agreement between the experimental and theoretical slopes. Hence the Debye-Hückel-Onsager theory of conductivity of electrolytes in solution appears to be very closely applicable. It

* It may be mentioned that Arrington and Griswold[11] analyzed their conductivity data with the help of Fuoss-Onsager relation for unassociated electrolytes, namely,

$$\Lambda = \Lambda_0 - S\sqrt{C} + EC\log C + (J - F\Lambda_0)C$$

This analysis appears unnecessary since the electrolytic conductivity data of these workers give a reasonable straight-line Λ *vs.* $\sqrt{C}$ plot as 25 °C in different cases and this plot gives Λ_0-values in reasonable agreement with that obtained from the Fuoss-Onsager relation in most cases.

TABLE 1. THE Λ_0/Ω^{-1} cm^2 VALUES OF R_4NX SALTS, R_4N^+, Br^- AND I^- IONS AT DIFFERENT TEMPERATURES

Salt or ion	Limiting conductivity at					
	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C
Br^-	25.97	—	30.76	—	35.57	—
Me_4NBr	47.07	51.51	56.04	61.06	65.66	71.36
Me_4N^+	21.10	—	25.28	—	30.09	—
Me_4NI	46.82	51.32	55.72	60.23	64.88	69.70
I^-	25.72	—	30.44	—	34.79	—
Et_4NI	44.65	48.80	53.02	57.31	61.62	66.83
Et_4N^+	18.93	—	22.58	—	26.83	—
Pr_4NI	40.96	44.42	48.34	52.56	56.86	61.90
Pr_4N^+	15.24	—	17.90	—	22.02	—
Bu_4NI	38.51	41.85	45.57	49.49	53.51	57.83
Bu_4N^+	12.79	—	15.13	—	18.72	—
Pen_4NI	38.03	41.50	45.15	48.96	52.94	57.12
Pen_4N^+	12.31	—	14.71	—	18.15	—
Hex_4NI	37.05	40.58	44.23	48.06	51.98	56.10
Hex_4N^+	11.93	—	13.79	—	17.19	—
Hep_4NI	36.18	39.36	42.68	46.12	49.90	53.87
Hep_4N^+	10.46	—	12.94	—	15.11	—

TABLE 2. ONSAGER SLOPE IN DMSO AT 40 °C

Salt	S_T/Ω^{-1} cm^2· mol$^{-1/2}$ l$^{1/2}$	S_E/Ω^{-1} cm^2· mol$^{-1/2}$ l$^{1/2}$	% Deviation $\frac{S_T-S_E}{S_T}\times 100$
Me_4NI	−74.59	−79.7	+6.85
Me_4NBr	−74.75	−77.9	+4.21
Et_4NI	−73.22	−74.2	+1.34
Pr_4NI	−70.84	−68.4	−3.44
Bu_4NI	−69.43	−65.7	−5.37
Pen_4NI	−69.22	−68.1	−1.62
Hex_4NI	−68.75	−65.8	−4.99
Hep_4NI	−67.96	−63.3	−6.85

may be mentioned that the studies on apparent molar volume of these salts in DMSO[12] appear to indicate appreciable ionic interaction at higher concentrations, but in dilute solutions, the salts appear to be completely dissociated.

The cationic Walden product, $\Lambda_0\eta^0$, of the R_4N^+ ions at different temperatures were obtained using the Λ_0-values** given in Table 1; viscosities used are: η^0/g·m^{-1} s^{-1}=1.908(25 °C), 1.814(30 °C), 1.508 (40 °C), 1.275(50 °C). The $\Lambda_0\eta^{0+}$ *vs.* t plots are given in Fig. 2 for different R_4N^+ ions. It may be noted that the plots are straight lines with approximately zero slope, *i.e.*, $\Lambda_0\eta^0$ is almost independent of temperature. This shows that these ions neither promote nor break the structure of DMSO for the simple reason that no hydrogen-bonded structure is present originally in the pure solvent nor it can be formed. Electrostatic ion–solvent dipole interaction, if any, is not likely to be affected by a few degrees changes in temperature. It may be mentioned that similar conclusions have been arrived at for $(isoamyl)_3BuN^+$, Na^+, $B(Ph)_4^-$, ClO_4^-, SCN^-, and $CF_3SO_3^-$ ions.[8]

** Values of electrolytic conductivity at 25 °C used are those of Arrington and Griswold.[11]

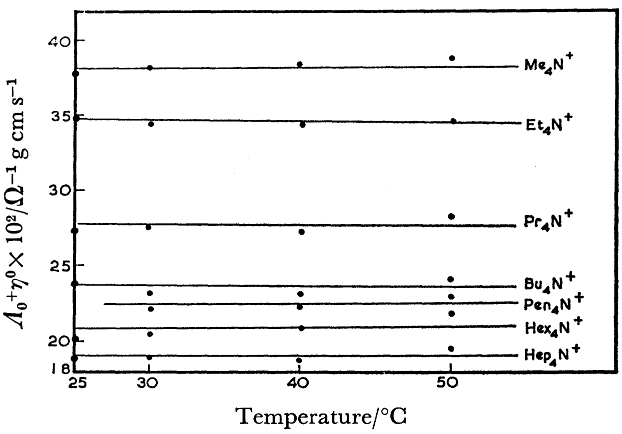

Fig. 2. Plot of $\Lambda_0\eta^0$ *vs.* temperature/°C in DMSO.

One of us (J.S.J.) is grateful to the Governments of Nepal and India for providing a research scholarship under Technical Co-operation Scheme of the Colombo Plan. Authors are thankful to the Society of the Sigma Xi of U.S.A. for the help in importing some of the chemicals from abroad.

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