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A Conductometric Study of Ion–Solvent Interaction of Some Tetraalkylammonium and Common Ions in Sulfolane at Different Temperatures

Pankaj*

Department of Chemistry, Faculty of Science, Dayalbagh Educational Institute, Dayalbagh, Agra 282 005, India

M. M. Hussain

Department of Chemistry, Lucknow University, Lucknow 226 007, India

The ion–solvent interaction of several tetraalkylammonium (R_4N^+) ions, alkali metal cations, and anions in sulfolane has been examined from the conductance data. The Λ_v vs. $C^{1/2}$ plots are almost linear for all the salts studied, indicating their complete dissociation in solution. The limiting ionic equivalent conductivities of these ions at different temperatures have been obtained assuming n-Bu_4N^+ and BPh_4^- ions to have equal mobilities. The variation of the Walden product with temperature reveals that R_4N^+ cations and the common inorganic anions do not appear to interact appreciably with the solvent whereas Na^+, K^+, Rb^+, and Cs^+ ions are significantly solvated.

Introduction

Ion–solvent interaction studies in some polar and non-hydrogen-bonded solvents having medium dielectric constants, namely, dimethyl sulfoxide (Me_2SO) (*1*, *2*) and propylene carbonate (PC) (*3*, *4*), have been reported. Similar studies on ion–solvent interaction in an aprotic and dipolar solvent of high dielectric constant, namely ethylene carbonate (EC) (*5*), have also been undertaken recently. Such studies are now extended in a non-hydrogen-bonded, highly polar solvent of medium dielectric constant, viz., sulfolane ($\epsilon_{30°}$ = 43.3; μ = 4.81 D) in which electrolytic conductance studies (*6*–*8*) appear to have been reported at 30 °C only and therefore of limited use in studying the general nature of ion–solvent interaction. This situation has prompted the present investigation.

Experimental Section

Sulfolane (Fluka, puriss) was purified as reported earlier (*9*). Tetraalkylammonium iodides (R_4NI) were purified by the usual methods (*10*, *11*). The sulfolane used melts at 27 °C and its density was $d_{40°}$ = 1251.5 kg m^{-3} and the specific conductance 6.738 × 10^{-6} ohm^{-1} m^{-1}. The salts Me_4NBF_4, Me_4NPF_6, and n-Bu_4NBPh_4 and other common salts used were recrystallized according to known methods (*12*–*14*) and dried under vacuum. The conductances of the solutions between the concentration range 0.05–0.3 M were measured as described elsewhere (*1*–*5*). The precision of measurement was found to be about ±0.03%, as obtained from known solutions.

Table I. Λ_v Values of n-Bu_4NBPh_4 at Various Concentrations and Temperatures

		$\Lambda_v \times 10^4$, ohm^{-1} m^2 mol^{-1} at				
C	$C^{1/2}$	30 °C	35 °C	40 °C	45 °C	50 °C
0.012	0.112	5.83	6.61	7.52	8.02	8.47
0.014	0.120	5.79	6.50	7.47	7.98	8.41
0.018	0.135	5.72	6.44	7.39	7.92	8.37
0.021	0.147	5.64	6.34	7.29	7.81	8.26
0.029	0.172	5.55	6.21	7.14	7.69	8.11
0.034	0.185	5.43	6.14	6.93	7.60	9.02
0.046	0.215	5.31	5.98	6.81	7.45	7.92
0.057	0.240	5.19	5.78	6.78	7.25	7.79
0.067	0.260	5.03	5.66	6.65	7.13	7.71
0.083	0.288	4.92	5.48	6.48	7.05	7.54

Table II. Λ_v Values of KI at Various Concentrations and Temperatures

		$\Lambda_v \times 10^4$, ohm^{-1} m^2 mol^{-1} at				
C	$C^{1/2}$	30 °C	35 °C	40 °C	45 °C	50 °C
0.010	0.100	10.18	11.52	13.03	14.36	16.29
0.016	0.126	9.76	11.01	12.46	13.79	15.63
0.020	0.141	9.62	10.89	12.28	13.67	15.46
0.032	0.178	9.32	10.60	11.98	13.39	15.14
0.044	0.210	9.00	10.32	11.76	13.12	14.86
0.050	0.224	8.93	10.25	11.62	13.01	14.75
0.059	0.243	8.70	10.12	11.52	12.86	14.61

Table III. Λ_v Values of Et_4NI at Various Concentrations and Temperatures

		$\Lambda_v \times 10^4$, ohm^{-1} m^2 mol^{-1} at				
C	$C^{1/2}$	30 °C	35 °C	40 °C	45 °C	50 °C
0.005	0.070	10.19	11.54	12.90	14.43	15.90
0.006	0.078	10.12	11.48	12.80	14.39	14.83
0.010	0.103	9.95	11.28	12.66	13.98	15.50
0.020	0.141	9.64	10.84	12.14	13.50	14.89
0.029	0.170	9.16	10.30	11.50	12.80	14.15
0.039	0.199	9.03	10.20	11.29	12.60	13.90
0.051	0.226	8.69	9.77	10.90	12.15	13.43
0.060	0.246	8.76	9.86	11.01	12.25	13.51

Results and Discussion

Λ_v vs. $C^{1/2}$ plots at different temperatures were, in general, almost linear for all cases. Such plots for n-Bu_4NBPh_4, KI, and Et_4NI are given in Figures 1, 2, , and 3 as typical of the reference, tetraalkylammonium, and common salts, respectively. The numerical data of these figures are given in Tables I–III. The straight-line behavior suggests the applicability of Debye–Hückel–Onsager theory of electrolytic conductance in these cases and the salts are completely ionized in sulfolane in the temperature and concentration range studied here. The limiting equivalent conductance of ions as obtained from the usual extrapolation of Λ_v vs. $C^{1/2}$ curves are given in Table IV, assuming

$$\Lambda_0(n\text{-}Bu_4NBPh_4) = \tfrac{1}{2}\Lambda_0(n\text{-}Bu_4N^+) + \tfrac{1}{2}\Lambda_0(BPh_4^-)$$

The Λ_0 of some ions at 30 °C reported by Della Monica et al. (*8*) are also given for ready comparison.

The mode of ion–solvent interaction in sulfolane may now be examined. The viscosity coefficients of sulfolane at different temperatures required to calculate the Walden product were experimentally determined as η_0 = 0.010 307 (30 °C); 0.008 730 (35 °C); 0.007 709 (40 °C); 0.006 809 (45 °C); and 0.005 965 (50 °C) kg m^{-1} s^{-1}. Values of the Walden product,

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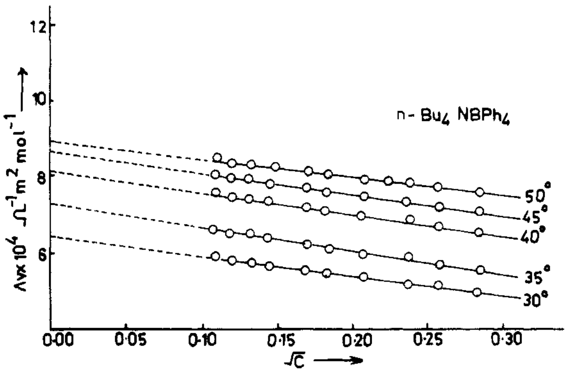

Figure 1. Λ_v vs. $C^{1/2}$ plots for n-Bu_4NBPh_4.

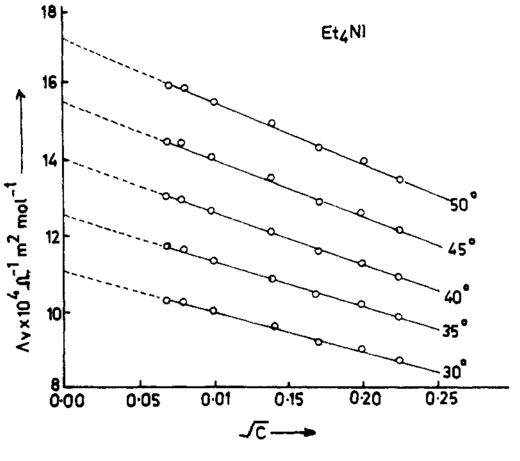

Figure 2. Λ_v vs. $C^{1/2}$ plots for Et_4NI.

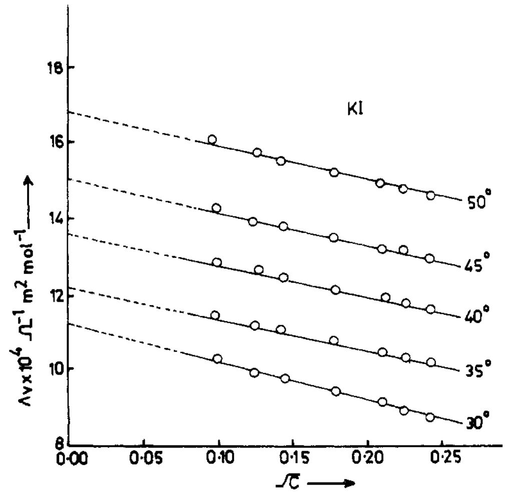

Figure 3. Λ_v vs. $C^{1/2}$ plots for KI.

$\Lambda_0\eta_0$, for different ions at different temperatures are given in Table V.

Table IV. Ionic Conductivities at Different Temperatures

ions	$\Lambda_v^{\pm} \times 10^4$, ohm^{-1} m^2 mol^{-1} at 30 °C	35 °C	40 °C	45 °C	50 °C
Na^+	3.73 (3.61)	4.27	4.58	5.02	5.30
K^+	4.38 (4.05)	4.69	5.23	5.82	6.35
Rb^+	4.48 (4.16)	5.02	5.59	6.06	6.54
Cs^+	4.68 (4.27)	5.21	5.72	6.17	6.72
Me_4N^+	5.48 (4.31)	6.21	6.79	7.62	8.35
Et_4N^+	4.33 (3.95)	5.09	5.73	6.42	6.83
n-Pr_4N^+	3.58 (3.23)	4.09	4.53	4.72	5.13
n-Bu_4N^+	3.23 (2.80)	3.64	4.08	4.32	4.46
n-Pen_4N^+	2.92	3.19	3.28	3.32	3.51
n-Hex_4N^+	2.38	2.79	2.92	3.17	3.23
n-Hep_4N^+	1.93	2.69	2.68	2.67	2.68
Cl^-	9.17 (9.30)	10.18	10.96	12.03	13.32
Br^-	8.58 (8.92)	9.44	10.38	11.34	12.45
I^-	6.62 (7.22)	7.41	8.32	9.08	10.32
NO_3^-	6.54	7.22	7.84	8.83	9.77
BF_4^-	5.48	6.21	6.79	7.62	8.35
PF_6^-	5.92 (5.95)	6.67	7.46	8.32	9.32
BPh_4^-	3.23	3.64	4.08	4.32	4.46

Table V. Walden Product of Various Ions at Different Temperatures

ions	$\Lambda_0^{\pm}\eta_0 \times 10^5$,[a] ohm^{-1} m kg mol^{-1} s^{-1} at 30 °C	35 °C	40 °C	50 °C	55 °C
Na^+	0.3845	0.3728	0.3531	0.3418	0.3161
K^+	0.4514	0.4094	0.4032	0.3963	0.3788
Rb^+	0.4617	0.4382	0.4309	0.4126	0.3901
Cs^+	0.4824	0.4548	0.4405	0.4201	0.4008
Me_4N^+	0.5648	0.5421	0.5234	0.5188	0.4981
Et_4N^+	0.4463	0.4443	0.4417	0.4271	0.4074
n-Pr_4N^+	0.3690	0.3570	0.3492	0.3214	0.3060
n-Bu_4N^+	0.3329	0.3178	0.3145	0.2941	0.2660
n-Pen_4N^+	0.3009	0.2785	0.2528	0.2260	0.2094
n-Hex_4N^+	0.2453	0.2436	0.2251	0.2158	0.1926
n-Hep_4N^+	0.1989	0.2348	0.2066	0.1818	0.1598
Cl^-	0.9451	0.8887	0.8449	0.8191	0.7945
Br^-	0.8761	0.8241	0.8002	0.7721	0.7426
I^-	0.6823	0.6469	0.6414	0.6182	0.6156
NO_3^-	0.6741	0.6303	0.6044	0.6012	0.5828
BF_4^-	0.5648	0.5421	0.5232	0.5188	0.4981
PF_6^-	0.6102	0.5823	0.5751	0.5665	0.5559
BPh_4^-	0.3329	0.3178	0.3145	0.2941	0.2660

[a] Walden product.

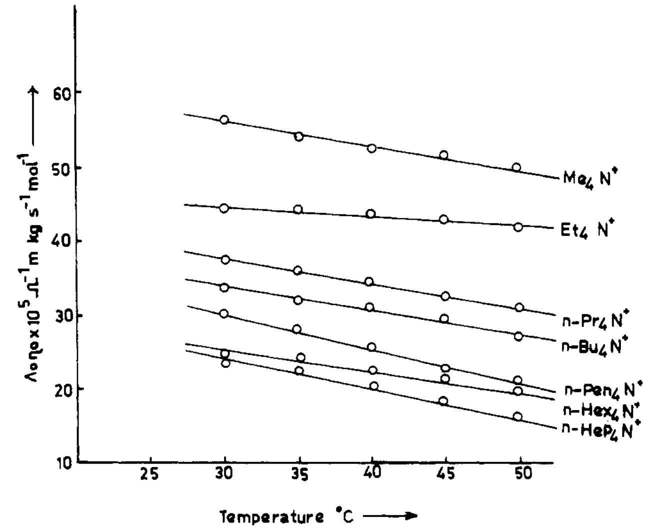

Figure 4. Plots of $\Lambda_0^{\pm}\eta^0$ vs. temperature in sulfolane.

Although the temperature dependence of the Walden product may be examined from these data, the plots of $\Lambda_0^{\pm}\eta_0$ vs. t^0, given in Figures 4 and 5, make it more explicit. A decrease in the Walden product of all the ions studied, with rise in temperature, is similar to the behavior in water (*15*) and certain nonaqueous protic solvents (*16*) like formamide, *N*-methylformamide (NMF), *N*-methylacetamide (NMA), and *N*-methylpropionamide (NMP), but contrary to the normal behavior of R_4N^+ ions in aprotic solvents. The cations appear to be net structure breakers giving rise to disruption of solvent structure around them; this results in a rearrangement of the solvents molecules beyond this region in which the structure is broken (*17*). The similarity of behavior of R_4N^+ and alkali metal ions in nonaqueous solvents is clear since the special structure formation feature (hydrophobic solvation as in water) of R_4N^+ ions would be missing in such nonaqueous solvents because of the similarity of the building constituents (*18*) (e.g., the presence of the alkyl group) of the R_4N^+ ions and the solvent

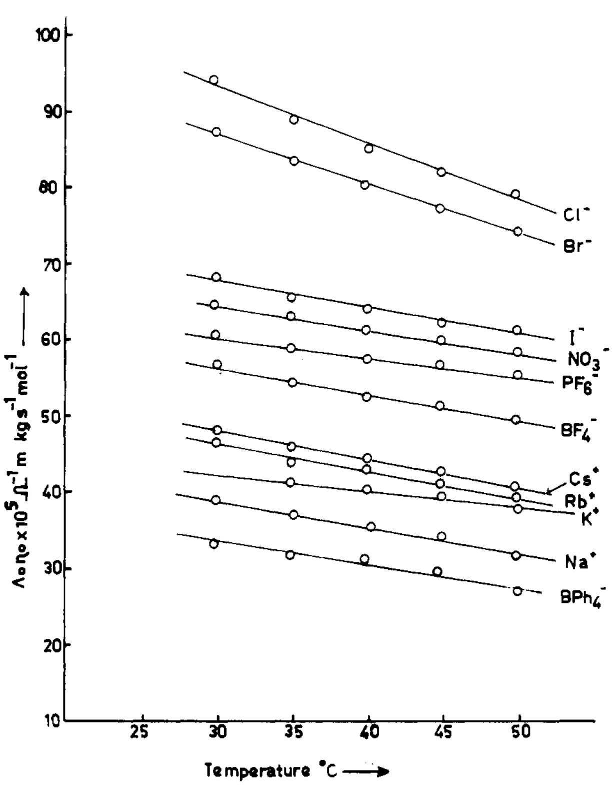

Figure 5. Plots of $\Lambda_0{}^{\pm}\eta_0$ vs. temperature in sulfolane.

molecules of sulfolane and of other nonaqueous organic solvents (*14*) (even protic ones). Such a structure-breaking feature of tetraalkylammonium ions in sulfolane has also been suggested by the conductance studies of Bruno et al. (*19*).

A better insight into the ion–solvent interaction in such systems can be obtained if the relative position of $\Lambda_0{}^{\pm}\eta_0$ vs. temperature curves for different ions, as given in Figures 4 and 5 are examined. It may be noted that, for R_4N^+ ions, the $\Lambda_0{}^{+}\eta_0$ is larger the smaller the size of the ion, thus indicating that the electrostatic R_4N^+–solvent interaction, if any, is very weak in these cases. These ions thus appear to remain completely bare in solution so that the smaller the ion, the faster is its movement under electrical potential and thus the large $\Lambda_0{}^{+}\eta_0$ values. The same is possibly true for Cl^-, Br^-, and I^- ions as well. However, the reverse is the case with the common alkali metal ions, which are comparatively much smaller as compared to the R_4N^+ ions. The $\Lambda_0{}^{+}\eta_0$, in these cases, tend to increase with an increase in the crystal radius of the cation. The role of high electrostatic charge density on the alkali metal ions thus favors a strong ion–solvent interaction and ionic solvation. The smaller ion, coupled with a higher charge density, thus favors a stronger ion–solvent dipole interaction, which results in a larger size of the solvodynamic unit. The result is the radii of the solvated alkali metal cations would be in the order $Na^+ > K^+ > Rb^+ > Cs^+$, in spite of the reverse order of their crystallographic radii. It may be recalled in this connection that these ions in water, formamide, NMA, and NMP behave in a similar manner and the size of the solvodynamic unit varies inversely as the crystal radius of the ion, although in these solvents $\Lambda_0{}^{+}\eta_0$ of these ions varies with temperature. This is in contrast to its behavior in propylene carbonate (*20*) and sulfolane.

In sulfolane, the common anions behave like large R_4N^+ ions and do not appear to be solvated to any appreciable extent. It is interesting to note that although cations like Rb^+ and Cs^+ are close in size to the halide anions, the ion–solvent interaction in the latter is weak. The absence of hydrogen-bonding interaction in this solvent may be a plausible reason, which could have favored anion solvation and is considered to be responsible for the solvation of anions in dipolar protic solvents in which the positive end of the solvent dipole is embedded somewhere inside the solvent molecule. Hence any direct interaction between the anion and the solvent dipole could only be very weak; the anion could only interact strongly with the exposed negative end of the dipole through hydrogen bonding.

To conclude, it appears that, in sulfolane, the common small cations are associated with some solvent molecules but the R_4N^+ ions and the anions are more or less bare, in agreement with ionic solvation studies in this solvent by Della Monica (*8*).

Registry No. KI, 7681-11-0; Et_4NI, 68-05-3; $Bu_4N^+BPh_4^-$, 15522-59-5; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2; Me_4N^+, 51-92-3; Et_4N^+, 66-40-0; *n*-Pr_4N^+, 13010-31-6; *n*-Bu_4N^+, 10549-76-5; *n*-Pen_4N^+, 15959-61-2; *n*-Hex_4N^+, 20256-54-6; *n*-Hep_4N^+, 35414-25-6; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; No_3^-, 14797-55-8; BF_4^-, 14874-70-5; PF_6^-, 16919-18-9; BPh_4^-, 4538-26-3; sulfolane, 126-33-0.

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