Cationic Transport Numbers of Potassium Iodide & Solvation of Ions in N,N′-Dimethylformamide & Propylene Carbonate

RAM GOPAL & J. S. JHA

Department of Chemistry, Lucknow University, Lucknow

The cationic transport numbers of KI have been obtained in dimethylformamide and propylene carbonate at different temperatures and the data have been used to evaluate the ionic conductivities from the available electrolytic conductivity data in these two liquids. Using the ionic conductivities of some common electrolytes and tetraalkylammonium halides, an attempt has been made to study ion-solvent interaction and solvation of ions. The results indicate that while the common cations appear to have appreciable ion-solvent interaction and solvation, the anions and the tetraalkylammonium cations (R₄N⁺) are unsolvated.

ALTHOUGH several studies on conductivities of electrolytes in N,N′-dimethylformamide (DMF) have been reported, a detailed study of the transport number of ions is still lacking. Prue and Sherrington[1] measured the cationic transport number of KCNS in DMF at 25° while Paul and coworkers[2,3] determined the transport numbers of LiCl, KCl, KCNS and NaCNS in DMF at 25° and obtained limiting transport numbers simply by intrapolating the t_+ versus $\sqrt{C}$ curves to zero concentration; this is rather an unusual procedure for the data at higher concentrations.

Propylene carbonate (PC) is a liquid of recent interest in which ion-solvent interaction and solvation studies appear to have received only scanty attention. Conductivities of a few common electrolytes in propylene carbonate (PC, $D=64.92$; ref. 4), a solvent having a wide liquid range ($-49.2°$ to $241.7°$), have been determined by a number of workers[5-9]. Mukherji et al. reported[7] the cationic transport number of LiClO₄ in PC at 25° from EMF measurements.

From this brief survey, it appears worthwhile to undertake a systematic study of the transport numbers in these two liquids in order to obtain reliable ionic conductivities of some common electrolyte and of tetraalkylammonium halides from the available electrolytic conductance data and an insight into ion-solvent interaction and solvation of ions in them. The present paper reports the cationic transport numbers of KI at different concentrations and temperatures in DMF and PC. Potassium iodide was found to be a suitable electrolyte for the present transport number studies on account of the availability of the limiting electrolytic conductivity data in DMF[10,11] and PC[7,9,12].

Materials and Methods

AR grade KI was recrystallized twice from conductivity water and dried in a vacuum desiccator. DMF (Fluka, purum) was purified as per standard procedure[10] and kept in dark-coloured bottles.

Electrical conductivity and density (30°) of the purified sample were found to be 10^{-7} ohm⁻¹ cm² and 0·9436 g cm⁻³ respectively (literature value[12]: $d_{30}=0.9445$ g cm⁻³).

PC (Fluka, purum) was dried over freshly ignited quicklime for several hours and then distilled under reduced pressure, the middle fraction of the distillate being retained. The process was repeated until the electrical conductivity of the purified sample was reduced to about 10^{-7} ohm⁻¹ cm²; $d_{25}=1.198$ g cm⁻³ (literature value[13]: $d_{25}=1.999$ g cm⁻³).

The transport number cell was similar to that of MacInnes and Dole[14]; electrodes used were of about 1 mm thick silver wire. Other equipment and the experimental procedure were the same as described earlier[15]. Solutions were prepared in freshly distilled solvents and kept overnight; a current of 2-5 mA was passed for 7-10 hr from a 90 V battery of dry cells. Changes in concentration of the iodide ion were determined by conductometric titration against silver nitrate solution. Due to slight solubility of silver iodide in DMF, formed at the anode during electrolysis, changes in concentration of the middle and cathode compartments were determined separately and inter-checked. From the experimental data, thus obtained, the anionic transport number of KI was obtained in the usual manner from which that of K⁺ ion was deduced. Using the values of the transport number of K⁺ ion at different concentrations, the limiting transport numbers, at different temperatures were obtained employing well known Longsworth's procedure[15]. For evaluating the Longsworth function, molality was converted into molarity from the density data determined side by side. The limiting conductivity data and viscosity for DMF[9] for PC[11] were taken from literature. Viscosities of PC used were: $\eta_{25}=0.0248$ (ref. 8), $\lambda_{40}=0.0228$, $\eta_{35}=0.0205$ and $\eta_{45}=0.0170$ poise; the latter three were obtained in this laboratory. The dielectric constant values used were of Bass et al.[16] for DNF and of Pyne and Theodorou[4] for PC.

Results and Discussion

The transport numbers of K^+ at different concentrations and temperatures are given in Table 1. Although the transport number determination presented no special difficulty in either of the solvents, KI was found to dissolve with difficulty in PC and only dilute solutions could be prepared.

In both the solvents the transport number (t_+) increased with the rise in temperature and decreased with the increase in concentration. The effect of temperature was consistent with Kohlrausch's law.

Ionic conductivities — The limiting cationic transport number data, given in Table 1, have been used to calculate the limiting ionic conductivities of K^+ and I^+ from the available electrolytic conductance data in DMF[9,10] and PC[6,8,11]. The ionic conductivities along with those reported by other workers (at 25° only; no such data are available at other temperatures) are given in Table 2, which includes data on some common electrolytes and tetraalkylammonium halides.

The ionic conductivities at 25° obtained here, agree closely with those of other workers in most cases and hence require no further comments.

TABLE 1 — CATIONIC TRANSPORT NUMBERS OF KI IN DMF AND PC

Molality m	Transport number (t_+) of K^+ ion at			
	25°	30°	35°	45°
IN DMF				
0·000	0·369	0·372	0·375	0·382
0·100	0·3315	0·3380	0·3436	0·3539
0·150	0·3290	0·3342	0·3398	0·3505
0·200	0·3259	0·3320	0·3365	0·3472
0·250	0·3227	0·3275	0·3322	0·3442
0·300	0·3186	0·3240	0·3281	0·3403
0·350	0·3160	0·3203	0·3248	0·3368
IN PC				
0·000	0·396	0·398	0·401	0·405
0·050	0·3750	0·3791	0·3802	0·3857
0·075	0·3706	0·3732	0·3758	0·3812
0·100	0·3660	0·3686	0·3711	0·3764
0·125	0·3615	0·3641	0·3668	0·3722
0·150	0·3572	0·3593	0·3624	0·3679

Limiting transport numbers are given only up to three decimal places due to long intrapolation of the Longsworth function versus concentration curves in different cases.

TABLE 2 — IONIC CONDUCTIVITIES IN DMF AND PC AT VARIOUS TEMPERATURES

Ion	DMF				PC			
	25°	30°	35°	45°	25°	30°	35°	45°
Me_4N^+	38·37	41·64	44·68	51·69	14·14 (14·16)[9]	15·58	17·35	21·05
Et_4N^+	35·39	38·09	40·43	46·38	13·18 (13·18)[9] (13·28)[6]	14·50	16·13	19·58
Pr_4N^+	28·89	31·41	33·54	38·39	10·44 (10·46)[9]	11·41	12·85	16·65
Bu_4N^+	25·67	27·69	30·13	34·19	8·99 (8·98)[9] (9·39)[6]	9·82	11·13	13·42
Pen_4N^+	19·53	20·69	22·52	26·04	8·18 (8·17)[9] (8·18)[7]	9·40	10·55	12·49
Hex_4N^+	13·39	14·18	15·51	18·78	—	3·72	4·42	5·53
Hep_4N^+	12·73	13·82	14·91	17·90	—	3·02	3·51	4·41
Li^+	24·73 (25·00)[1]	—	—	—	8·88 (8·89)[9] (7·30)[6]	9·68	10·55	12·89
Na^+	29·81 (29·98)[2] (29·90)[1]	30·07	34·16	39·29	9·43 (9·45)[6]	10·47	11·62	14·19
K^+	30·53 (31·90)[2] (3·80)[1]	32·35	35·11	40·59	12·05 (11·17)[9] (11·97)[6]	13·32	14·78	17·88
Rb^+	32·13 (32·40)[1]	—	—	—	12·74 (11·90)[9]	13·67	15·05	18·26
Cs^+	34·23 (34·50)[1]	—	—	—	13·51 (12·66)[9]	13·92	15·58	18·79
Cl^-	—	—	—	—	20·12 (20·20)[6]	22·17	24·50	29·31
Br^-	53·58 (53·60)[1]	—	—	—	18·91 (18·91)[9] (19·26)[6]	20·74	22·39	26·73
I^-	52·11 (51·17)[2] (52·30)[1]	—	—	—	18·38 (18·35)[9] (18·78)[6]	20·28	22·00	26·26
ClO_4^-	52·67 (52·40)[1]	—	—	—	18·70 (18·44)[9] (18·78)[6,7]	—	—	—
CNS^-	59·67 (59·50)[2]	—	—	—	21·26 (22·12)[9]	—	—	—

81
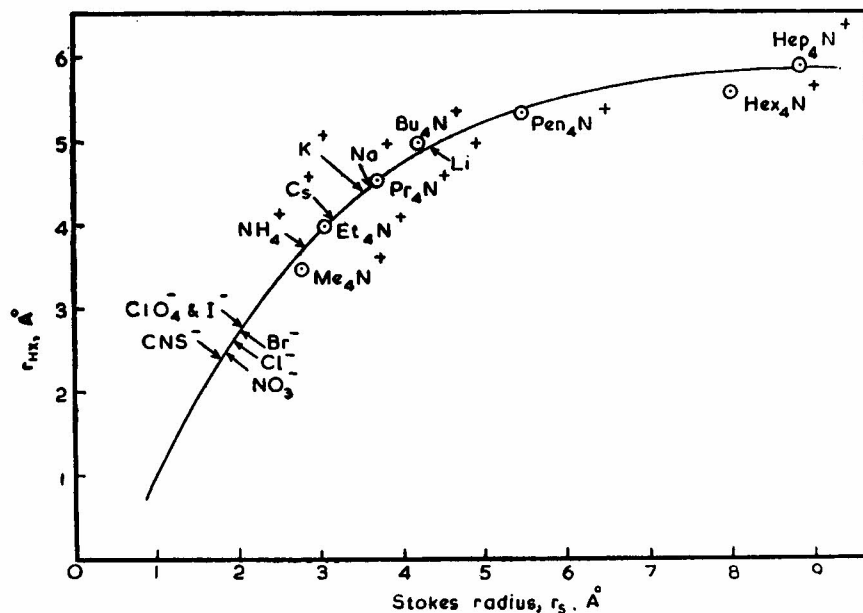
Fig. 1 — Plot of r_s against solvated ion radius in DMF

Solvation of ions in DMF and PC — Some attempts have been made earlier[2,6,17] to estimate the solvation number of ions in these solvents, the ionic conductivity data of Table 2 may be used to study the solvation of ions in a somewhat more reliable manner. The method of Robinson and Stokes[18], as modified by Nightingale[19], has been used here for estimating the solvation number of ions. Assuming that the tetraalkylammonium ions are unsolvated in DMF and PC, the Stokes radius r_s ($=0.82|z|\lambda_0\eta_0$) of these ions is plotted against the corresponding crystal radius* r_c of the R_4N^+ ions. The curves so obtained in DMF and PC are given in Figs. 1 and 2 respectively. The actual radius r_{HX} of any smaller ion in solution can be read off from the knowledge of its r_s-value on the intrapolated part of the curve concerned. Positions of some ions are shown on the two curves; further details of the method are given elsewhere[15,19]. The molecular volumes of DMF and PC are taken as 115 and 127 $Å^3$ respectively. The solvation numbers of some ions (which give an idea of the extent of ion-solvent interaction in solution) along with the respective r_s and r_{HX} values, are given in Table 3.

Table 3 clearly shows that, in general, the smaller common cations are appreciably solvated but the anions (and the R_4N^+ ions) are very little, if at all, solvated. This insignificant solvation of anions in DMF and PC, in spite of the large dipole moment ($>4D$) of the solvent molecules, calls for some

---

*Some workers[20-23] have estimated the radii (r_c) of the R_4N^+ ions which differ from those obtained by Robinson and Stokes. Validity of the Stokes law in many aqueous and non-aqueous solvents has also been called into question by others[24-27]. However, in view of the lack of agreement in the r_c values reported by different workers[20-23] and also because the r_c values given by Robinson and Stokes yield reasonable and comparable solvation of ions, these values are still being used by workers[15,28] in this field.
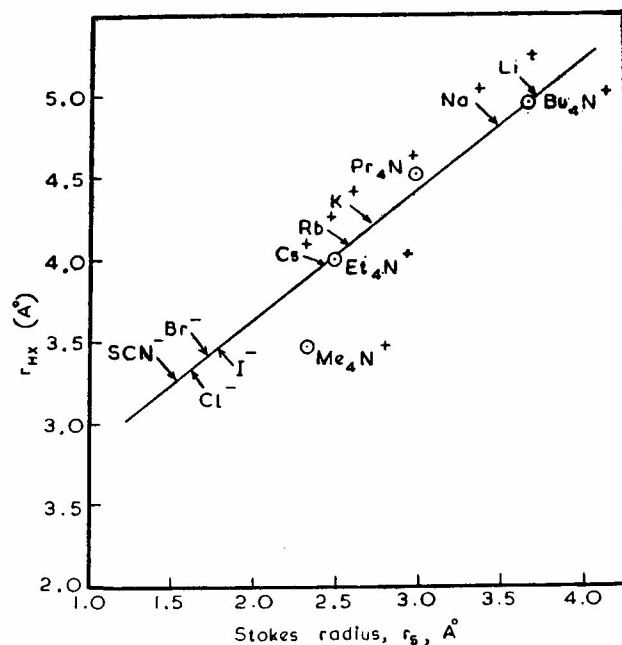
Fig. 2 — Plot of r_s against solvated ion radius in PC

explanation. It may be remarked that in all non-aqueous, protic and aprotic solvents of high dielectric constants, investigated so far, the positive end of the solvent dipole is invariably located inside the molecule and thus it is almost completely shielded from direct interaction with the negatively charged anions. In such protic solvents, however, the electrostatic ion-solvent interaction with anions could occur through hydrogen bonds or hydrogen ions which would be present in these liquids, these would react strongly with the anions on the one hand and with the exposed negative end of the

TABLE 3 — SOLVATION NUMBERS OF SOME COMMON IONS IN DMF AND PC

Ion	DMF			PC		
	r_s (Å)	r_{HX} (Å)	Solvation number	r_s (Å)	r_{HX} (Å)	Solvation number
Li+	4·36	4·94	4·4	3·75	5·00	4·1
Na+	3·62	4·46	3·2	3·51	4·73	2·7
			(2·9a, 2·4b)			
K+	3·53	4·39	3·0	2·75	4·23	2·4
			(2·27a, 2·4b)			
Rb+	—	—	—	2·58	4·10	2·2
Cs+	3·15	4·05	2·2	2·45	3·98	1·9
NH4+	2·81	3·72	1·8	—	—	—
Cl-	1·96	2·60	0·4	1·64	3·48	1·1
Br-	2·02	2·67	0·4	1·75	3·45	1·1
I-	2·07	2·75	0·4	1·80	3·35	1·1
			(0·87a, 1·3b)			
ClO4-	2·07	2·75	0·2	—	—	—

(a) ref. 2; (b) ref. 18.

solvent dipole on the other. In the aprotic solvents like DMF and PC, both the protons and the hydrogen bonding would be, more or less, missing. Thus the factors which could induce anion-solvent dipole interaction would be almost completely lacking in both these liquids and this results in weak solvation of anions. Strong electrostatic interaction between the cations and the exposed negative end of the solvent dipole, situated on the oxygen atom of the $>C=O$ group, leads to strong solvation of the common cations; however, the R_4N^+ ions are too large to react strongly with the solvent molecules.

Acknowledgement

References

1. SHEREINGTON, P. J. & PRUE, J. E., Trans. Faraday Soc., 57 (1961), 1795.
2. PAUL, R. C., SINGLA, J. P. & NARULA, S. P., Indian J. Chem., 8 (1970), 63.
3. PAUL, R. C., SINGLA, J. P. & NARULA, S. P., J. phys. Chem., 73 (1969), 741.
4. PAYNE, R. & THEODROU, I. E., J. phys. Chem., 76 (1972), 2892.
5. FUOSS, R. M., BERKOWITZ, J. B., HIRSCH, E. & PETTRICCI, S., Proc. natn. acad. Sci. (US), 27 (1958), 44.
6. MUKERJI, L. M. & BODEN, D. P., J. phys. Chem., 73 (1969), 3968.
7. MUKERJI, L. M., BODEN, D. P. & LINDAUER, R., J. phys. Chem., 74 (1970), 1942.
8. JANSEN, M. L. & YEAGER, H. L., J. phys. Chem., 77 (1973), 3089.
9. SINGH, R. D. & GOPAL, R., Z. phys. Chem., 83 (1973), 25.
10. AMES, D. P. & SEARS, P. G., J. phys. Chem., 59 (1955), 16.
11. SINGH, S., JHA, J. S. & GOPAL, R., Indian J. Chem., 14 (1976), 127.
12. WEAST, R. C., SELBY, S. M. & HODGMAN, C. D., Handbook of chemistry and physics (Chemical Rubber Co., Cleveland, Ohio), 1964, C-327.
13. LARRY, S. & AMERY, R. L., J. phys. Chem., 74 (1970), 1443.
14. MACINNES, D. A. & DOLE, M., J. Am. chem. Soc., 53 (1931), 1357.
15. GOPAL, R. & JHA, J. S., J. phys. Chem., 78 (1974), 2405.
16. BASS, S. J., NATHAN, W. I., MEIGHAN, R. M. & COLE, R. H., J. phys. Chem., 68 (1964), 50.
17. GOPAL, R. & HUSAIN, M. M., J. Indian chem. Soc., 40 (1963), 981.
18. ROBINSON, R. A. & STOKES, R. H., Electrolyte solutions (Butterworths, London), 1959, 124.
19. NIGHTINGALE, E. R. (Jr), J. phys. Chem., 63 (1959), 1384.
20. MASTERTON, W. L., BOLOCOFSKY, D. & LEE, T. P., J. phys. Chem., 75 (1971), 2814.
21. HEPLER, L. G., STOKES, J. M. & STOKES, R. H., Trans. Faraday Soc., 61 (1965), 20.
22. MUKERJI, P., J. phys. Chem., 65 (1961), 740.
23. GLUECKAUF, E., Trans. Faraday Soc., 61 (1965), 914.
24. ZWANZIG, R., J. chem. Phys., 38 (1963), 1603.
25. FRANK, H. S., Chemical physics of ionic solutions (Wiley, New York), 1966, 61.
26. KAY, R. L., CUNNINGHAM, J. P. & EVANS, D. P., Hydrogen bonded solvent systems (Taylor & Francis, London), 1968, 265.
27. KAY, R. L. & VIDULICH, G. A., J. phys. Chem., 74 (1970), 2718.
28. MONICA, D. M. & SENATORE, L., J. phys. Chem., 74 (1970), 205.