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Physical Chemistry

A STUDY OF ION-SOLVENT INTERACTION OF SOME TETRA-ALKYL-AMMONIUM AND COMMON IONS IN POLAR, HYDROGEN-BONDED AND NON-HYDROGEN-BONDED SOLVENTS*

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The tetra-alkylammonium ions, R_4N^+, have a special interest in view of their large size and symmetrical shape with low surface charge and recently a number of communications have appeared reporting the behaviour of these ions in different solvents.

The reported results on viscosity *B*-coefficient and Walden product indicate that the R_4N^+ ions act as net structure breakers and common ions as net structure promoters in NMF, NMA and NMP; which was found to be absent in a non-hydrogen-bonded solvent like DMF. The exhibited abnormal behaviour of larger R_4N^+ ions like Pr_4N^+, Bu_4N^+ and Am_4N^+ in aqueous solutions has been reasonably explained in terms of ion-dipole interaction energy of these ions which surprisingly recedes the dipolar interaction energy of water molecules.

After a study of the ionic mobility of common cations and anions related to their crystallographic radii in polar hydrogen-bonded solvents like H_2O, D_2O, CH_3OH, C_2H_5OH, Formamide, NMF, NMA, NMP etc., and a non-hydrogen-bonded solvent like DMF, it has been concluded that the solvation of cations is presumably through electrostatic bonds and that of anions is definitely through hydrogen bonds. Further, it has been indicated that the hydrogen-bonding is a dominant feature of solvents and plays an important role in the theory of solvation.

The reported ionic mobility of R_4N^+ has been plotted against the reciprocal of their respective crystallographic radius in a variety of solvents. The almost linear function of the R_4N^+ ions in all the solvents of high dielectric constant like H_2O, D_2O, NMA, NMP etc., very strongly recommends their lack of solvation while the curves obtained in solvents like MeOH, EtOH, $MeNO_2$, MeCN etc., are reasonably interpreted in terms of their low dielectric constant. Finally, it has been concluded, in general, that R_4N^+ ions remain definitely 'unsolvated' in solutions of all the solvents on account of their large size and low surface charge density.

Keywords: Ion-solvent Interaction; Tetra-alkyl-ammonium; Polar, Hydrogen and Non-Hydrogen Bonded Solvents

INTRODUCTION

THE solvation of various ions like common cations, anions, tetra-alkyl-ammonium and other multivalent ions in different solvents has been thoroughly investigated through different measurements e.g., conductance (Coates & Taylor, 1936; Kay

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et al., 1963, 1966; Kay & Evans, 1965, 1966*a*, *b*; Ernesto & Lind, 1966; and Adams & Laidler, 1968*a*, *b*, *c*), partial molal volume (Wen & Saito, 1964; Wen & Nara, 1968; and Padova & Abrahamer, 1967), activity coefficient (Devanathan & Fernando, 1962; Frank, 1963; Diamond, 1963; and Wen *et al.*, 1966), transference number (Gopal & Bhatnagar, 1964, 1965, 1966), thermochemical studies (Wood *et al.*, 1967; and Boyd *et al.*, 1967), viscosity (Gurney, 1953; Kaminsky, 1957; and Kay *et al.*, 1966) etc. and some interesting anomalies have also been reported. For example, Kaminsky (1957) has pointed out that the larger common ions K^+, Rb^+, Cs^+, NO_3^-, I^- etc., are net structure breakers while the highly hydrated ones like Li^+, Be^{++}, Mg^{++}, Ce^{+++} etc., behave as long range order makers in aqueous solutions. Kay and Evans, (1966*b*) and Kay *et al.* (1966) have introduced the "hydrophobic solvation" of the larger R_4N^+ ions in aqueous solutions. They described Pr_4N^+ Bu_4N^+ to be structure makers and Me_4N^+ to be structure breaker while the opinion remains divided as for the behaviour of the Et_4N^+ ion, which is quite in contrast to their general structure breaking feature as reported in NMA (Rastogi *et al.*, 1968). The cations and anions are stated to be differently solvated in aliphatic mono-alkyl-substituted amides. Thus in view of the ambiguous statements, it appears interesting and desirable to investigate the basic phenomenon of ion solvation more extensively.

It is well known that the temperature dependence of the Walden product and Jones and Dole (1929) viscosity coefficient *B*, usually gives a good insight into the mode of ion-solvent interaction. This approach to study ion-solvation has yielded valuable information in aqueous solutions and so it has been employed to study R_4N^+-solvent interaction in some mono- and N: N-di-alkyl substituted aliphatic amides from the conductance and viscosity point of view. Further, the dipole-dipole and ion-dipole interaction energies have also been calculated for alkali metal cations, halide anions and R_4N^+ ions in a variety of solvents just to illustrate the cause of discrepancy in the behaviours of these ions in general and R_4N^+ ions in particular.

Experimental

NMF, NMA, NMP and DMF, obtained from Eastman Organic Chemicals Co., Rochester, NY, USA, were treated with freshly ignited quicklime, kept overnight, and then distilled under reduced pressure. The process of purification was continued until the electrical conductance of the middle fraction of the distillate was reduced to less than 10^{-6} mho. The samples were stored in dark amber-coloured bottles, kept inside a dry nitrogen box, and were always used immediately after distillation.

Tetra-alkyl-ammonium iodides, supplied by M/s. Distillation Products Industries, U.S.A., were recrystallized from suitable solvents of their mixtures. Me_4NI and Et_4NI were dissolved in absolute alcohol and precipitated from solution with ether. These were dried in a vacuum desiccator.

NMF, N-methylformamide; *NMA*, N-methylacetamide;
NMP, N-methylpropionamide; *DMF*, N:N-dimethylformamide;
MeOH, Methanol; *EtOH*, Ethanol; *$MeNO_2$*. Nitromethane;
MeCN, Acetonitrile.

Pr_4NI, Bu_4NI and Am_4NI were dissolved in methanol and precipitated with ether. The precipitated salts were dried in a vacuum desiccator. The Li Cl and KI were Merck's A.G. reagents and were used without further purification.

The electrical conductance was determined with a suitably grounded Kohlrausch's bridge assembly and precautions were taken to eliminate, or compensate for, the capacity and induction effects. The cationic Walden products, $\lambda_0^+\eta_0$, were calculated from the determined limiting ionic conductance, λ_0^+, of R_4N^+ ions at different temperatures.

Density was measured with a dilatometer which was provided with a graduated stem on which volume could be read up to 0.005 ml within an error of $\pm$ 0.002 ml. Modified Ubbelohde viscometer was employed for measuring viscosity. Before use, the viscometer was flushed with dry nitrogen and the required amount of solution was introduced through the wider tube. A stop watch, reading 0.1 sec was used for recording the flow time which was usually more than 600 sec. The readings differing by more than $\pm$ 0.1 to 0.2 sec were discarded.

RESULTS

The temperature dependence of the Walden product, of different R_4N^+ ions in NMA and NMP has been shown in Fig. 1, whereas the viscosity coefficient B of these R_4NI salts in NMF, NMA, NMP and DMF have been determined (Rastogi, 1970*a*; and Rastogi & Gopal, 1970) by the use of Jones-Dole equation and been summarised in Table I.

$$\eta = \eta_0(1 + A\sqrt{C} + BC) \qquad \ldots(1)$$

An estimation of dipole-dipole interaction energy, ΔE_{DD}, and that of the ion-dipole interaction energy, ΔE_{ID}, have been made from the usual relations, namely :

$$\Delta E_{DD} = -2\mu^2/r^3 \qquad \ldots(2)$$

and

$$\Delta E_{ID} = -e\mu/r^2 \qquad \ldots(3)$$

where 'μ' represents the dipole moment of the solvent molecule, 'e' the charge on the ion and, 'r' the distance between the centres of two molecules of a solvent or of an ion from a molecule of the solvent. The calculated (Rastogi, 1971) values of the E_{DD} of the six solvents i.e., water, formamide, DMF, NMF, NMA, NMP have been listed in Table II along with their dipole moments and the van der Waals' radii; whereas the estimated values of the ΔE_{ID} of alkali metal cations, halide anions and symmetrical tetra-alkyl-ammonium ions in these solvents have been tabulated in Table III along with their crystallographic radii as reported elsewhere (Pauling, 1948; and Robinson & Stokes, 1959).

The reported (Rastogi, 1970*c*) ionic mobilities of common ions like Li^+, Na^+, K^+, Rb^+, Cs^+, F^-, Cl^-, Br^-, I^- etc., in H_2O, D_2O, CH_3OH, C_2H_5OH, NMF, NMA, NMP, formamide, DMF etc., have been plotted against their crystallographic radii (Robinson & Stokes, 1959) as shown in Fig. 2 (A, B, C & D). The obtained plots are curves for the cations in H_2O, D_2O, NMF, NMA and NMP and are linear in

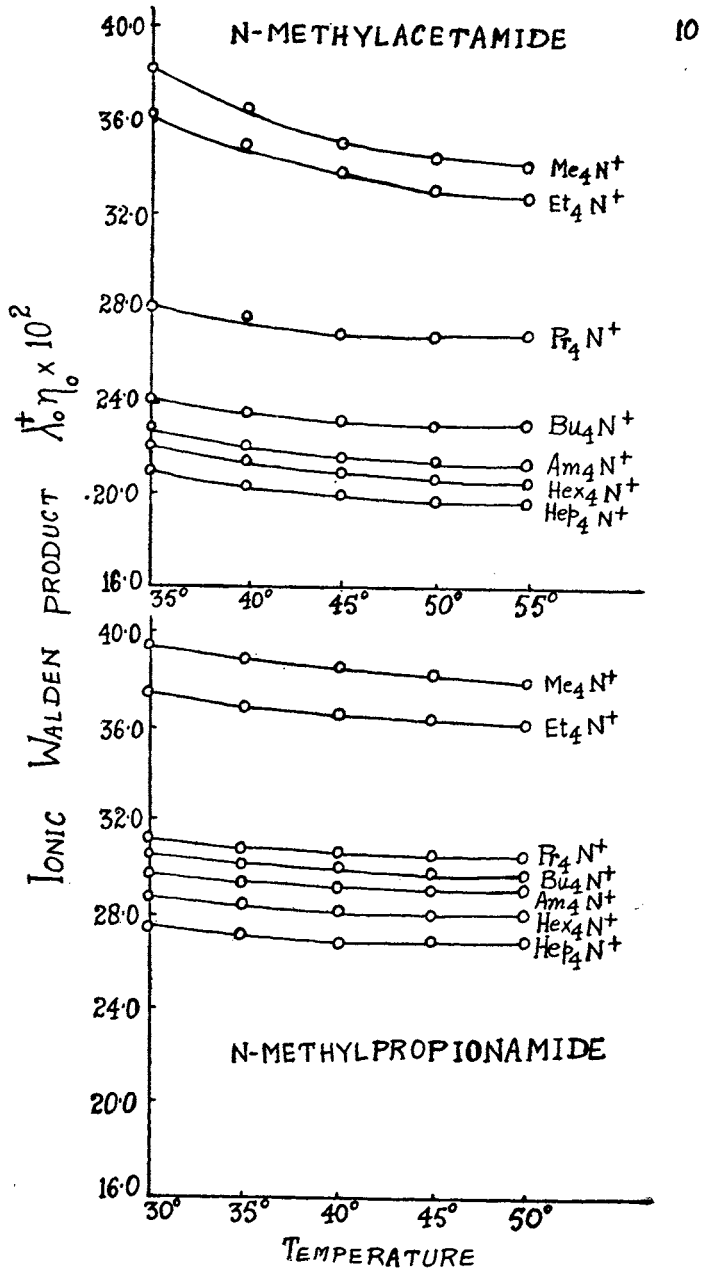

FIG. 1.

CH_3OH, C_2H_5OH, formamide and DMF: whereas the plots are linear for the anions, in general, except in H_2O and D_2O with a most remarkable feature of a negative slope in DMF.

TABLE I

Viscosity B-coefficients in NMF, NMA, NMP and DMF

Temp. (°C)	Me_4NI	Et_4NI	Pr_4NI	Bu_4NI	Am_4NI	LiCl	KI
			NMF				
25	0.38	0.49	0.68	0.81	0.97	0.59	0.56
30	0.42	0.52	0.71	0.85	1.00	0.55	0.54
35	0.48	0.57	0.75	0.88	1.03	0.53	0.51
			NMA				
35	0.61	0.80	0.99	1.16	1.31	0.97	1.01
40	0.65	0.84	1.03	1.19	1.35	0.94	0.98
45	0.68	0.89	1.05	1.23	1.38	0.90	0.96
50	0.72	0.92	1.08	1.25	1.40	0.88	0.94
55	0.77	0.96	1.12	1.28	1.44	0.84	0.91
			NMP				
20	0.53	0.74	1.05	1.35	1.61	1.29	1.33
25	0.58	0.78	1.10	1.39	1.64	1.25	1.30
30	0.62	0.81	1.13	1.42	1.68	1.22	1.28
35	0.66	0.86	1.18	1.46	1.70	1.19	1.26
40	0.71	0.92	1.22	1.49	1.73	1.15	1.25
			DMF				
25	—	1.07	1.25	1.34	1.40	0.59	1.10
30	—	1.06	1.26	1.35	1.40	0.56	1.08
35	—	1.06	1.25	1.35	1.40	0.54	1.08
40	—	1.07	1.25	1.36	1.41	0.54	1.07

The reported (Rastogi, 1973) ionic mobilities of Me_4N^+, Et_4N^+, Pr_4N^+, Bu_4N^+ and Am_4N^+ ions in H_2O, D_2O, NMA, NMP, MeOH, EtOH, $MeNO_2$, MeCN etc., have been plotted against the reciprocal of their crystallographic radii, r_x, as shown in Figs. 3 and 4. The obtained plots are almost linear in H_2O, D_2O, NMA and NMP but are curves in MeOH, EtOH, $MeNO_2$ and MeCN.

DISCUSSION

It may be noted from Fig. 1 that the Walden product of the R_4N^+ ions decreases with increase in the radius of the ion more rapidly in water than in NMA & NMP. Further, the R_4N^+ ions and the univalent common cations appear to behave similarly in NMA and NMP because all these cations give rise to 'electrostatic solvation' in these solvents due to the fact that probably both belongs to organic origin or with similar structure (e.g., presence of alkyl groups in the R_4N^+ ions and the solvent molecules). The results indicate R_4N^+ ions to be structure breakers in these solvents, quite opposite to their general behaviour in aqueous solutions. This structure breaking feature of R_4N^+ ions and the existence of some electrostatic solvation was supported by the viscosity of R_4NI salts in these solvents. It may

TABLE II

Dipole moment, van der Waals' radius and dipole-dipole interaction energy of various solvents

Solvent	Dipole moment[a] ($\mu \times 10^{18}$)	van der Waals' radius[e] (in Å)	Dipole-dipole interaction energy ($\triangle E_{DD} = -2\mu^2/r^3kT$)
H_2O	1.85[b]	1.45[b]	6.67
Formamide	3.22[c]	2.12	6.62
NMF	3.71	2.42	5.91
DMF	3.80	2.60	4.77
NMA	3.71	2.80[d]	3.81
NMP	3.59	3.35	2.08

[a]Meighan, R. M., and Cole, R. H. (1964). Dielectric properties of alkyl amides—I. Vapour phase dipole moments and polarization in benzene solution. *J. phys. Chem.*, **68**, 503.

[b]Gurney, R. W. (1953). P. 50–52.

[c]Wesson, L. G. (1948). *Tables of Electric Dipole Moments.* The Technology Press, Cambridge.

[d]Katz, J., and Post, B. (1960). The crystal structure and polymorphism of *N*-methylacetamide. *Acta crystallogra*, **13**, 624; Pimental, G. C., and McClellan, A. L. (1959). *The Hydrogen Bond.* Reinhold Publishing Corporation, N.Y., p. 361.

[e]Van der Waals' radii of Formamide, NMF, DMF and NMP have been estimated from their molar volumes.

TABLE III

Ion-dipole interaction energy of some alkali metal cations, halide anions and symmetrical tetra-alkyl ammonium ions in different solvents

Ion	Crystallographic radius (Å)	Ion-dipole interaction energy ($\triangle E_{ID} = -e\mu/r^2kT$)					
		H_2O	Formamide	NMF	DMF	NMA	NMP
Li^+	0.60	51.40	50.82	47.50	42.28	37.47	26.86
Na^+	0.95	37.51	39.90	38.15	34.43	30.81	22.67
K^+	1.33	27.95	31.59	30.81	28.15	25.40	19.14
Rb^+	1.48	25.16	29.01	28.47	26.14	23.65	17.97
Cs^+	1.69	21.92	25.90	25.65	23.67	21.49	16.50
F^-	1.36	27.36	31.05	30.32	27.73	25.03	18.90
Cl^-	1.81	20.32	24.34	24.22	22.41	20.38	15.75
Br^-	1.95	18.73	22.70	22.69	21.06	19.20	15.75
I^-	2.16	16.58	20.53	20.74	19.26	17.61	13.80
OH^-	1.76	20.96	25.23	25.03	22.92	19.28	16.05
NO_3^-	2.64	12.91	16.60	16.91	15.92	14.64	11.68
Me_4N^+	3.47	8.92	12.03	12.48	11.89	11.02	9.09
Et_4N^+	4.00	7.27	10.03	10.52	10.07	9.37	7.76
Pr_4N^+	4.52	6.06	8.53	8.99	8.66	8.09	6.77
Bu_4N^+	4.94	5.29	7.56	8.00	7.72	7.23	6.10
Am_4N^+	5.29	4.75	6.85	7.29	7.06	6.62	5.62

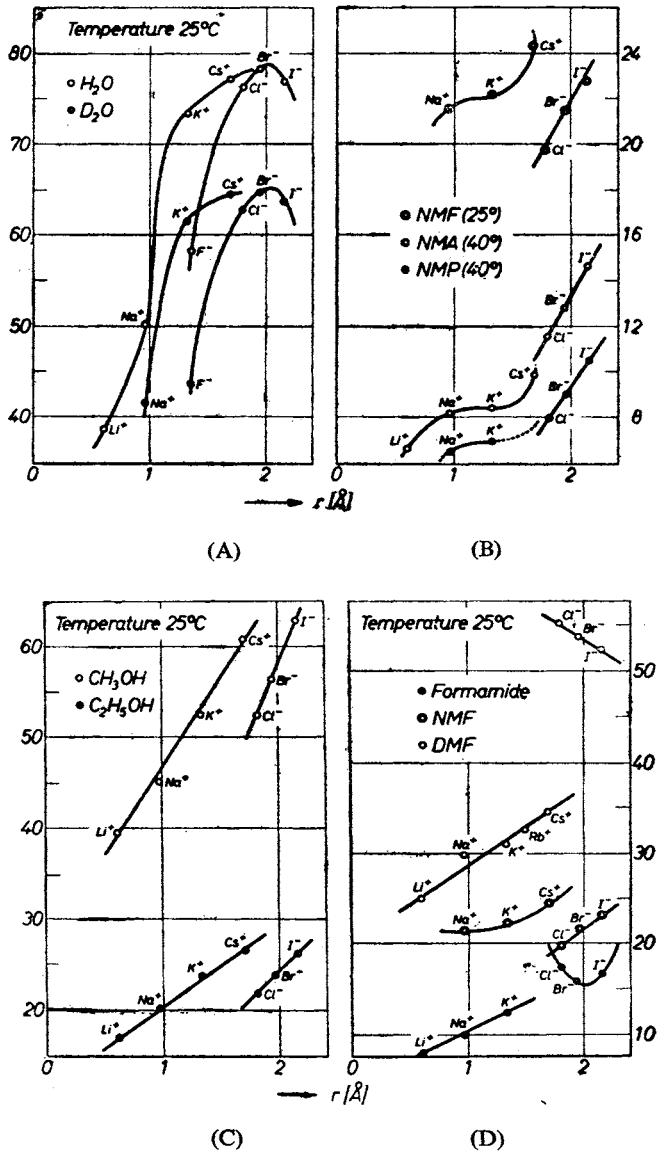

FIG. 2. Ionic mobility of cations (λ_0^+) and anions (λ_0^-) in different solvents against their crystallographic radius (r).

be observed from Table I that the viscosity-B-coefficient increases with the rise in temperature for all R_4NI salts; on the other hand, it decreases for LiCl and KI in NMF, NMA and NMP. So dB/dT is positive for the R_4N-iodides and negative for others. The positive dB/dT indicates a net structure breaking effect of the R_4N^+ ions in these solvents because the viscosity of a pure solvent decreases faster than the intrinsic viscosity of the solution. On the other hand, the negative dB/dT for the

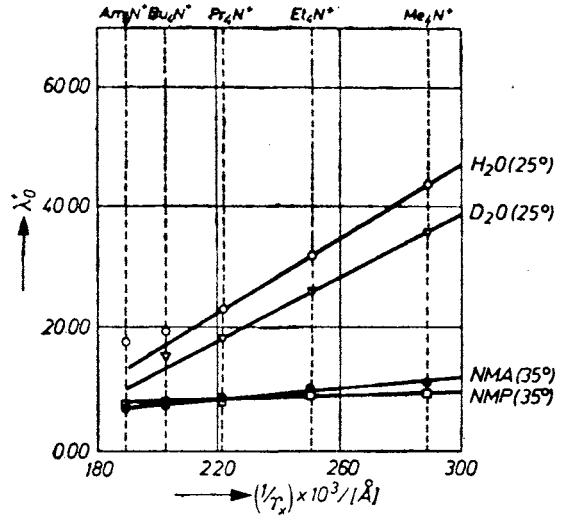

FIG. 3. Ionic mobility *vs.* reciprocal crystallographic radius in solvents of high dielectric constant.

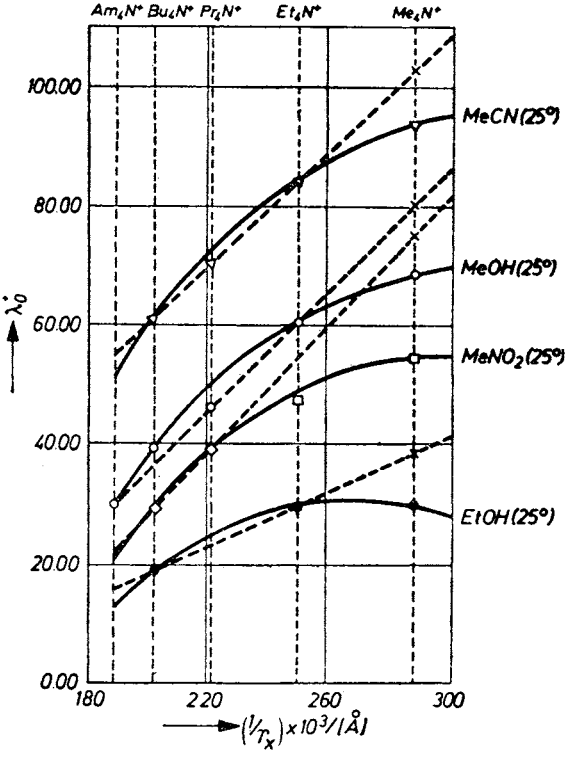

FIG. 4. Ionic probabilities *vs.* reciprocal crystallographic radius in solvents of low dielectric constant.

salts of cations are net structure promoters i.e., more structure is present in the solution than in the pure solvent and this breaks down at higher temperatures so that the decrease in the intrinsic viscosity of solution is faster than that of the pure solvent and dB/dT is negative. It thus appears that while the R_4N^+ ions are net structure breakers in NMF, NMA and NMP, the common cations like Li^+ and K^+ are structure promoters. The smaller surface charge density on the R_4N^+ ions appears to be compensated by the large dipole moment of the solvent molecules and so an appreciable solute-solvent interaction, resulting in the depolymerization of the hydrogen bonded solvent and been supported by the temperature independent values of viscosity-*B*-coefficient in a polar non-hydrogen-bonded solvent like DMF (ruling out any breaking of the structure of DMF in view of the absence of hydrogen bond).

It may be recalled that in aqueous solutions, highly hydrated cations like Li^+, Na^+, Mg^{++}, Ce^{+++} etc. can polarise water molecules, in the region beyond the first solvation layer and so they act as structure promoters while the larger ions like K^+, Rb^+, Cs^+, Cl^-, Br^-, I^- etc., with low surface charge are net structure breakers. The change in the behaviour of K^+-ion is apparently due to the lower surface charge density (as compared to that of Li^+ & Na^+) being compensated by the large dipole moments of NMF, NMA & NMP molecules.

It may be noted from Tables II and III that the ion-dipole interaction energy of R_4N^+ ions is generally higher than the dipolar interaction energy of the solvents except in H_2O particularly for the larger R_4N^+ ions like Pr_4N^+, Bu_4N^+, Am_4N^+ etc., for which it surprisingly falls to the dipolar interaction energy of the water molecules. Perhaps, on account of the above mentioned reasons, the larger R_4N^+ ions fail to promote structural orientation of the water molecules i.e., are unable to disrupt the molecular clusters of H_2O and can be reasonably described as unsolvated in aqueous solutions. This also appears to explain the abnormal behaviour of the larger R_4N^+ ions in water. The special structural promotion feature or "hydrophobic solvation" of the larger R_4N^+ ions as established by Kay and Evans (1966) and Kay *et al.* (1966*a*) in aqueous solutions has been found to be absent and almost ruled out in other solvents like NMF, NMA and NMP from our reported studies on Walden product and the viscosity coefficient *B*.

It can reasonably be concluded from the dipolar and ion-dipole interaction energy considerations that the sufficiently large values of the latter than the former cause the long-range polarisation or secondary solvation, while the moderate values leads to structure breaking or primary solvation; the lower values remarkably indicate the absence of solvation of larger R_4N^+ ions, which is also pointed out to be absent in other investigated solvents. Thus the present studies indicate an absence of the solvation of the larger R_4N^+ ions in aqueous solutions, a conclusion contrary to the reported inconvincing special "hydrophobic solvation" of these ions.

In order to discuss the solvation phenomenon more critically and clearly, the reported results have been classified into the following four categories in view of the specific features of solvents :

(*A*) *H_2O and D_2O* — It may be noted from Fig. 2A that despite almost equal anionic and cationic radii, the cations are more mobile than the anions in H_2O and D_2O which appears to indicate stronger solvation for the latter ions. Thus one may conclude that the solvation of cations and anions seems to occur through different ways in H_2O as well as D_2O.

One may also state from the plots shown in Fig. 2A that the relative order of ionic mobility is in the increasing order of their crystallographic radii i.e., $Li^+ < Na^+ < K^+ < Cs^+$ and $F^- < Cl^- (< I^-) < Br^-$, in which the mobility of the I^- ion openly deviates from the normal behaviour of common ions and is quite obvious from the fact that the tangent to the curve has a negative slope only for the I^- ion i.e., $\frac{d\lambda_0 I^-}{dr} < 0$, which appears to illustrate the reported abnormalities in aqueous solutions (Devanathan & Fernando 1962; and Frank 1963).

(*B*) *NMF, NMA and NMP* — It may be observed from Fig. 2B that the plots are linear for the anions in contrast to the curvatures for the cations in NMF, NMA and NMP. Moreover, in these solvents, the mobility of the anions is greater than that of the corresponding cations, indicating a stronger interaction for the common cations. Thus it may be concluded again that the cations are strongly solvated (presumably through the electrostatic bonds) while the anions are weakly solvated.

(*C*) *CH_3OH and C_2H_5OH* — The plots are linear for the common ions in CH_3OH and C_2H_5OH as is clear from Fig. 2C. The higher mobility of the cations as compared with the anions lead to suggest a stronger solvation of the anions than of the corresponding cations in CH_3OH and C_2H_5OH, which suggests once again that the solvation of ions occurs through different ways.

(*D*) *Formamide, NMF and DMF* — It is seen from Fig. 2D that the plot is linear for the cations in contrast to the curvature for the anions in a highly hydrogen-bonded solvent like formamide, whereas the behaviour reverses in a less hydrogen-bonded solvent like NMF. The influence of the absence of hydrogen-bonding on the mobility of common ions is that both cations and anions behave linearly in DMF, but again differently, the difference being the sign of their slopes, which is positive for the cations and negative for the anions.

Since the relative order of anionic mobility, in DMF, is in the decreasing order of their crystal radii i.e., $I^- < Br^- < Cl^-$, it is indicated very strongly that the anions are definitely left unsolvated due to the absence of hydrogen-bonding in this solvent.

Thus the hydrogen-bonding appears to dominate over the electrostatic-bonding in formamide, decreases sharply and reverses in NMF and completely vanishes in a non-hydrogen-bonded solvent like DMF. Hence, it may be finally concluded that the solvation of cations occurs presumably through electrostatic bonds and that of anions definitely through hydrogen bonds.

It is a well-known fact that the mobility of ions in solutions is inversely proportional to the size of the solvated complex which is usually explained in terms of Fajans theory (1924), i.e., the smaller the ion, the more solvated it should be on account of its higher surface charge density and consequently would be more mobile as compared to larger ones or in other words the mobility follows the Stokes Law.

However, if the ions are unsolvated then the mobilities should be inversely proportional to their crystallographic radii, r_x, which can be considered as the basis for the "assumption" of the absence of solvation.

It may be noted from Fig. 3 that the plots are almost linear for R_4N^+ ions in all the solvents of high dielectric constant like H_2O, D_2O, NMA, NMP etc., and these ions can be safely considered as "unsolvated", a conclusion contrary to that reported by Nightingale and Allam and Lee in aqueous solutions.

The deviations are greater in the case of R_4N^- salts with the largest values of Λ_0, which is in accordance with the Bjerrum theory (1926) that ionic association is more likely to take place with the ions of smaller radius, i.e., of high mobility. Therefore, the larger ions like Pr_4N^+, Bu_4N^+, Am_4N^+ etc., which comparatively remain dissociated can be taken as mean for the estimation of absolute values of λ_0^+ for the associated Me_4N^+ ions. It is clear from Fig. 4 that the deviation is more significant for the smaller ions and is the greatest for the Me_4N^+ ion (including Et_4N^+ ion in $MeNO_2$) in MeOH, EtOH and MeCN which has been stated to be associated in these solvents and, therefore, yields its partial cationic mobility. However, the absolute value can be easily estimated by the extrapolation of the graph. The curves are regular for all R_4N^+ ions in $MeNO_2$ and EtOH on account of the presence of appreciable ionic association even in larger R_4N^- salts. This appears to predominate the complete dissociation of such salts due to low dielectric constant of the solvents or solutions and, therefore, the estimation of cationic mobility is rather difficult and less reliable.

From the above discussion, it may be assessed that all the R_4N^+ ions are definitely unsolvated in solvents of high dielectric constant and convincingly remain so even in solvents of low dielectric constant. Finally, it is fair to conclude that all R_4N^+ ions, in general, are "unsolvated" in all the solvents of high and low dielectric constants on account of their large size and low surface charge density.

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References

Adams, W. A., and Laidler, K. J. (1968*a*, *b*, *c*) Electrical conductivities of quaternary ammonium salts in acetone. Parts I, II & III. *Can. J. Chem.*, **46**, pp. 1977, 1989 and 2005.

Bjerrum (1926) *Kgl Danske Videns Kabs Selsk. Math. Fys. Mess*, **7**(9), 1.

Boyd, G. E., Chase, J. W., and Vaslow, F. (1967) Enthalpy and entropy of dilution of quaternary ammonium halides. *J. phys. Chem.*, **71**, 573.

Coates, J. E., and Taylor, E. G. (1936) Studies on hydrogen cyanide Part VIII. *J. chem. Soc.*, 1245.

Devanathan, M. A. V., and Fernando, M. J. (1962) Activity coefficients of some tetra-alkyl-ammonium salts in aqueous solution. *Trans. Farad. Soc.*, **58**, 784.

Diamond, R. M. (1963) Aqueous solution behaviour of large univalent ions. *J. phys. Chem.*, **67**, 2513.

Ernesto, J. R., and Lind (Jr.), J. E. (1966) Temperature dependence of electrolytic conductance. *J. phys. Chem.*, **70**, 2876.

Fajans and Joos (1924) Molecular refraction by ions and molecules in the light of atomic structure. *Z. physik. Chem.*, **23**, 1.

Frank, H. S. (1963) Single ion activities and ion-solvent interaction in dilute aquous solutions. *J. phys. Chem.*, **67**, 1554.

Gopal, R., and Bhatnagar, O. N. (1964) Cationic transport number of potassium chloride in formamide. *J. phys. Chem.*, **68**, 3892.

——— (1965) Cationic transport number of potassium bromide in *N*-methylacetamide. *J. phys. Chem.*, **69**, 2382.

——— (1966) Cationic transport number of potassium bromide in *N*-methylpropionamide. *J. phys. Chem.*, **70**, 4070.

Gurney, R. W. (1953) *Ionic Processes in Solution.* McGraw Hill Book Co. Inc. N.Y., 159–171.

Jones, G., and Dole, M. (1929) The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J. Am. chem. Soc.*, **51**, 2950

Kaminsky, M. (1957) Ion-solvent interaction and the viscosity of strong electrolytes solutions. *Disc. Faraday Soc.*, **24**, 171

Kay, R. L., Blum, S. C., and Schiff, H. I. (1963) The electrophoretic and relaxation contribution to the conductance of several quaternary ammonium chlorides and bromide in nitromethane. *J. phys. Chem.*, **67**, 1223.

Kay, R. L., and Evans, D. F. (1965) Conductance of tetra-alkyl-ammonium halides. *J. phys. Chem.*, **69**, 4216.

——— (1966*a*) Interaction with tetra-alkyl-ammonium ion with water. *J. phys. Chem.*, **70**, 2974.

——— (1966*b*) Mobility of symmetrical ions in aqueous solutions. *J. phys. Chem.*, **70**, 2325.

Kay, R. L., Vituccio, T., Zawoyski, C., and Evans, D. F. (1966) Viscosity *B*-coefficients for tetra-alkyl-ammonium halides. *J. phys. Chem.*, **70**, 2336.

Padova, J., and Abrahmer, I. (1967) Ion-solvent interaction. VIII. *J. phys. Chem.*, **71**, 2112.

Pauling, L. (1948) *Nature of Chemical Bond.* Cornell University Press 2nd Edn., Ithaca.

Rastogi, P. P., Singh, R. D., and Gopal, R. (1968) Ion-solvent interaction. I. *Can. J. Chem.*, **46**, 2325.

Rastogi, P. P. (1970*a*) Ion solvent interaction of tetra-alkyl-ammonium and some common ions in *N*-methylformamide from viscosity data. *Bull. chem. Soc. Japan*, **43**, 2442.

——— (1970*b*) Role of hydrogen bonding in the theory of ion solvation. *Z. physik. Chem.*, **73**, 163.

——— (1971) A study of ion-dipole interaction energy. I. *Z. physik. Chem.*, **75**, 202.

——— (1973) Phenomenological theory of symmetrical tetra-alkyl-ammonium ions in solutions. *Z. physik. Chem.*, **86**, 43.

Rastogi, P. P., and Gopal, R. (1970) A study of ion-solvent interaction of some tetra-alkyl-ammonium ions. *Z. physik. Chem.*, **69**, 1.

Robinson, R. A., and Stokes, R. H. (1959) *Electrolyte Solutions.* Butterworths, London, 2nd Edn., 124–140.

Wen, W. Y., and Nara, K. (1968) Volume changes on mixing solutions of potassium halides. *J phys. Chem.*, **71**, 3907.

Wen, W. Y., and Saito, S. (1964) Partial molar volumes of tetra-alkyl-ammonium bromide solutions. *J. phys Chem.*, **68**, 2639.

Wen, W. Y., Saito, S., and Lee, W. H. (1966) Activity coefficient of tetra-alkyl-ammonium flourides. *J. phys. Chem.*, **70**, 1244.

Wood, R. H., Anderson, H. L., Beck, J. D., France, J. R., deVry, W. E., and Soltzberg, L. J. (1967) Heat of dilution of some aqueous tetra-alkyl-ammonium fluoride. *J. phys. Chem.*, **71**, 2149.