A Study of Solute-Solvent Interaction in Solvents of Medium Dielectric Constant from the Apparent Molal Volume Data. I

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A study of the apparent molal volume (ϕ_v) of some common salts and the tetraalkylammonium iodides in DMSO has been reported in this communication. All the salts studied here, including those containing the larger R_4N^+ ions, have a positive slope in the ϕ_v *vs.* $\sqrt{C}$ curves, indicating a strong ionic interaction, apparently due to the medium dielectric constant of the solvent. This dielectric constant also promotes ion-association at higher concentrations and thus mutual penetration of the R_4N^+ ions is prevented. As a result, no negative slope in the ϕ_v *vs.* $\sqrt{C}$ curves of the larger R_4N-iodides is observed in this solvent. The effect of temperature on the limiting apparent molal volume, ϕ°, reveals that the ion-solvent interaction is comparatively stronger in the non-hydrogen bonded solvents like DMSO and DMF than that in strongly hydrogen-bonded solvents like NMA and NMP. Addition of a CH_2-group to each of the four R-chains of the R_4N^+ ion increases its volume by about 70 ml per mole in DMSO, DMF, and NMA.

Dependence of the apparent molal volume, ϕ_v, on concentration and temperature has been employed as a tool to study ion-ion and ion-solvent interactions in some non-aqueous solvents of high dielectric constant during the last few years.[1–8)] The usual idea that the salts, containing the small common ions have only a positive slope in the linear ϕ_v *vs.* $\sqrt{C}$ curves, is not universally true and the slope for some of these salts in the solvents of very high dielectric constant, like *N*-methylacetamide (NMA, $\varepsilon_{25^\circ}=171.7$) and *N*-methylpropionamide (NMP, $\varepsilon_{30^\circ}=164.3$) is negative.[5–8)] It was suggested that in such cases, perhaps, the small ions are accommodated inside the voids left in the packing of the large solvent molecules. Because of the weak ion-ion interaction, due to the very high dielectric constant of the solvents, such systems would behave, more or less, like a mixture of two molecular species widely different in size. This fact and some electrostatic ion-solvent interaction somehow combine to give a negative slope even for the salts containing small and compact ions. It was believed that the extension of studies on apparent molal volumes in solvents of medium dielectric constant[9)] should prove useful and may give a better insight into ion-ion and ion-solvent interaction in general. Hence dimethylsulphoxide ($\varepsilon_{25^\circ}=46.6$) has been chosen as the solvent for the present study in which the apparent molal volumes of some salts containing small common ions and of some tetraalkylammonium iodides have been determined and examined.[10)]

Experimental

Dimethylsulphoxide (Fluka, purum) was refluxed for several hours on freshly ignited quicklime and then distilled under reduced pressure, the middle fraction being retained; this was again distilled under reduced pressure and the middle fraction was collected. This process was continued until the electrical conductance of the sample was reduced to 10^{-7} mho or less. The purified sample was stored in dark colored

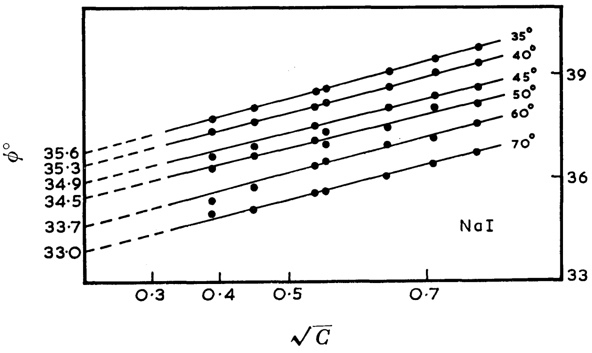

Fig. 1a. ϕ_v *vs.* $\sqrt{C}$ curves of NaI in DMSO at different temperatures.

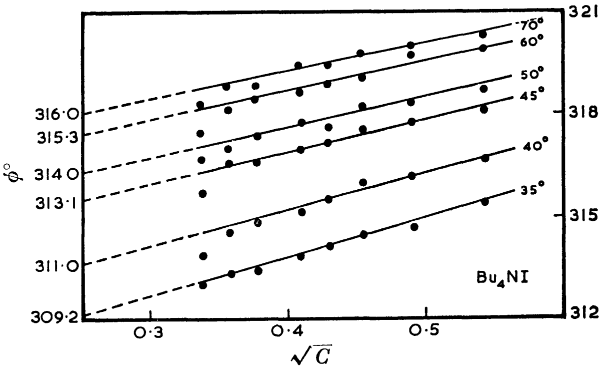

Fig. 1b. ϕ_v *vs.* $\sqrt{C}$ curves of Bu_4NI in DMSO at different temperatures.

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[1)] Ram Gopal and R. K. Srivastava, *J. Phys. Chem.*, **66**, 207 (1962).

[2)] Ram Gopal and R. K. Srivastava, *J. Indian Chem. Soc.*, **40**, 99 (1963).

[3)] Ram Gopal and M. A. Siddiqi, *J. Phys. Chem.*, **72**, 1814 (1968).

[4)] Ram Gopal and M. A. Siddiqi, *ibid.*, **73**, 3390 (1969).

[5)] Ram Goppal and M. A. Siddiqi, *Z. Phys. Chem. N. F.*, **67**, 122 (1969).

[6)] F. J. Millero, *J. Phys. Chem.*, **72**, 3209 (1968).

[7)] Ram Gopal, M. A. Siddiqi, and K. Singh, *J. Indian Chem. Soc.*, **47**, 504 (1970).

[8)] Ram Gopal, M.A. Siddiqi, and K. Singh, *Z. Phys. Chem.*, *N. F.*, **75**, 7 (1971).

[9)] K. Singh, Ph. D. Thesis, 1971, Lucknow University.

[10)] D. D. Macdonald and J. B. Hyne, *Can. J. Chem.*, **48**, 2416 (1970). Some ϕ_v-studies in DMSO–water mixtures have been reported in this paper.

bottles and kept in a dry box until used. The tetraalkylammonium iodides and the common salts, used in the present study, were purified in the usual manner, dried and kept in a vacuum desiccator. The rest of the experimental procedure for determining the density of the solutions and calculating the apparent molal volume therefrom, was the same as detailed in some earlier communications.3,4)

From the ϕ_v-data, thus obtained, ϕ_v *vs.* $\sqrt{C}$ curves were drawn and are given in Fig. 1a for NaI and in Fig. 1b for Bu_4NI. The ϕ_v *vs.* $\sqrt{C}$ curves for other salts are very much similar to those given in Figs. 1a and 1b and hence have been omitted.

From these figures it is clear that the ϕ_v *vs.* $\sqrt{C}$ curves are almost linear with a positive slope11) for all the salts studied here. Obviously, the Masson's empirical relation, namely,

$$\phi_v = \phi^\circ + S_v\sqrt{C}$$

is satisfied within the concentration range studied here. The limiting apparent molal volumes, ϕ°, obtained from extrapolation of the ϕ_v *vs.* $\sqrt{C}$ curves to infinite dilution, for various salts at different temperatures, are given in Tables 1 and 2. The ϕ°-values of some salts in DMF are also included in these Tables for the sake of comparison (quoted from Ref. 9).

TABLE 1. LIMITING APPARENT MOLAL VOLUMES OF SOME COMMON SALTS IN DMSO AND DMF (ml/mol)

Salt	ϕ° in ml per mole at					
	35 °C	40 °C	45 °C	50 °C	60 °C	70 °C
			In DMSO			
KBr	24.65	25.40	26.25	25.90	25.00	23.24
KNO_3	33.70	33.85	—	33.32	32.46	30.72
NaBr	19.14	18.82	18.55	18.20	17.22	16.54
NaI	35.65	35.42	34.92	34.40	33.72	33.15
$NaNO_3$	27.94	—	27.70	27.30	25.76	23.85
CsI	46.92	47.75	48.05	47.92	47.25	45.94
			In DMF			
$NaNO_3$	24.10	23.82	23.35	22.94	22.90	22.32
NaI	21.25	20.74	—	20.40	20.12	19.75
NH_4NO_3	41.25	40.72	—	40.12	39.45	38.90
NH_4Br	32.22	32.00	—	31.72	31.45	31.10
NH_4I	38.10	37.80	—	37.50	37.22	36.92

TABLE 2. LIMITING APPARENT MOLAL VOLUMES OF SOME R_4N-IODIDES IN DMSO AND DMF (ml/mol)

Salt	ϕ° in ml per mole at					
	35 °C	40 °C	45 °C	50 °C	60 °C	70 °C
			In DMSO			
Et_4NI	172.7	173.3	173.9	174.7	175.1	174.4
Pr_4NI	*242.2*	*243.6*	*245.6*	*246.1*	*247.2*	*248.1*
Bu_4NI	309.2	311.0	313.1	314.1	315.3	316.0
Pen_4NI	378.5	383.3	386.0	387.6	390.2	391.0
Hep_4NI	519.4	521.3	523.7	525.8	528.0	531.1
			In DMF			
Et_4NI	166.1	167.0	—	168.6	170.1	171.9
Pr_4NI	238.8	240.0	—	241.6	243.5	245.0
Bu_4NI	307.6	308.9	—	311.0	313.6	315.6
Pen_4NI	377.9	379.0	—	381.6	384.4	387.0
Hex_4NI	449.1	450.7	—	453.0	455.6	457.9
Hep_4NI	515.1	516.6	—	520.1	523.9	527.5

Note: Due to limited range of concentrations that could be studied in many cases on account of low solubility and also because of our inability to handle dilute solutions (<0.1 m) for want of proper equipment, values of ϕ° given in Tables 1 and 2 should be considered only approximate.

Discussion

Variation of the Apparent Molal Volume with Concentration. As has been pointed out earlier, both the common salts and the R_4N iodides, have a positive slope in the ϕ_v *vs.* $\sqrt{C}$ curves in DMSO and DMF11) both of which have a medium dielectric constant. It may also be recalled that the slope for some R_4N bromides ($R = CH_3$ to C_4H_9) and common salts is positive in methanol.12,13) The positive slope, even for the larger R_4N-salts in these solvents is rather surprising since the interionic penetration14) which is expected to occur when the large R_4N^+ ions are involved, should also be present in DMSO and DMF. These solvents, of course differ from solvents like water, formamide, NMA and NMP (in which negative S_v values have been reported) in having a much lower dielectric constant and negligible hydrogen bonding.

A comparison of the results obtained in DMSO and DMF on the one hand and in water, formamide, NMA and NMP on the other, suggests a possible explanation for the absence of the negative S_v values (*i.e.* the negative slope) for the R_4N-salts, in the former set of solvents. Although at infinite dilution, R_4N- and common salts are completely dissociated in all these solvents, the situation in the two types would be different at the higher concentrations. While in the solvents of high dielectric constant like water, the salts would remain completely ionized, even at fairly high concentrations, so that appreciable interionic penetration may occur and this may give rise to a negative slope in the ϕ_v *vs.* $\sqrt{C}$ curves in salts containing the larger R_4N^+ ions, the situation would be somewhat different in solvents of medium dielectric constant in which the ionic association would be quite appreciable at the higher concentrations and this would result in weakening of the ion-solvent interaction. So the ion-solvent interaction, which would be maximum at infinite dilution and would cause maximum electrostriction and contraction of the solvent, would be significantly lowered at higher concentrations. This would result in net positive volume changes per mole of the added solute since now electrostriction is less as compared to that at the lower concentrations, even if some interionic penetration, involving the large uncommitted R_4N^+ ions, occurs. As far as the common ions of small radii and compact nature are concerned,

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11) It may be mentioned that similar results, *i.e.* a positive slope in the ϕ_v *vs.* $\sqrt{C}$ curves of some common as well as tetraalkylammonium salts have been obtained in dimethylformamide (DMF); see Ref. 9.

12) J. Padova and L. Abrahamer, *J. Phys. Chem.*, **71**, 2112 (1967).

13) J. B. Stark and E. C. Gilbert, *J. Amer. Chem. Soc.*, **59**, 1818 (1937); W. C. Vosburgh, L. C. Connell, and J. A. V. Butler, *J. Chem. Soc., A*, **1933**, 933.

14) This concept has been used to explain the negative slope in the ϕ_v *vs.* $\sqrt{C}$ curves and other properties of the larger R_4N-salts in different solvents.

the question of interionic penetration does not arise; at the higher concentrations, strong electrostatic ion-ion interaction would cause ionic association and weaken the ion-solvent interaction and this would result in positive S_v values.

Variation of Limiting Apparent Molal Volume, ϕ°, with Temperature. The effect of temperature on ϕ° of the salts in DMSO is shown in Figs. 2a and 2b. Similar results have been obtained in DMF also. It may be noted that as far as the salts containing the small common ions are concerned, ϕ° *vs.* t curves pass through a maximum around 35—45°C, after which ϕ° steadily decreases with the rise in temperatures. The nature of the curves clearly suggests strong ion-solvent dipole interaction so that some of the solvent molecules remain firmly associated with the solute ions even at higher temperatures and hence are not available for expansion so that the solution expands less rapidly than the pure solvent. This behavior is somewhat similar to that in water, formamide *etc.* except that the maximum in the ϕ° *vs.* t curves occurs at lower temperatures in DMSO and DMF.

Turning now to the R_4N-iodides, it may be noted that the ϕ° *vs.* t curve for Et_4NI salt almost passes through a maximum around 60°; however, for the larger R_4N iodides, although ϕ° increases with the rise in temperature throughout the temperature range studied here, $d\phi^\circ/dt$ appears to decrease significantly, indicating the occurrence of a maximum at somewhat higher temperatures.[15] Thus the nature of the ϕ° *vs.* t curves appears to show that ion-solvent interaction is quite appreciable for the R_4N^+ ions in DMSO, the extent of interaction decreasing with increase in the radius of the R_4N^+ ion. It may be recalled that for the larger R_4N iodides, $d\phi^\circ/dt$ is almost a constant in protic solvents like formamide, NMA and NMP (not water in which ϕ° increases almost exponentially with temperature[3]), perhaps, due to release of the solvent molecules loosely bound to the R_4N^+ ions and of the solvent molecules which may be accomodated inside the larger R_4N^+ ions as well as due to uncoiling of the long coiled-up R-chains at higher temperatures. The same should be true in DMSO and DMF as well and the observed appreciable decrease in the $d\phi^\circ/dt$ values for the R_4N iodides in these solvents at higher temperatures indicates electrostatic interaction. Some other factors also appear to play an important role in controlling the general variation of ϕ° with temperature in different solvents.

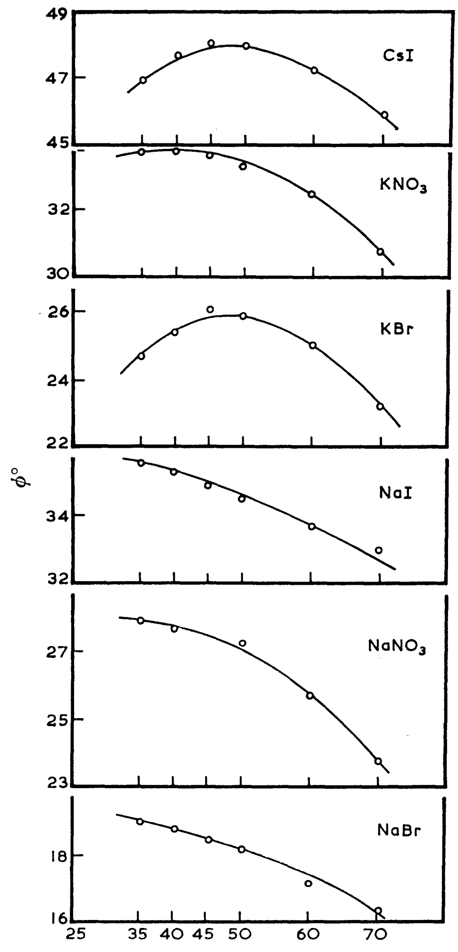

Fig. 2a. ϕ° *vs.* t curves of some common salts in DMSO.

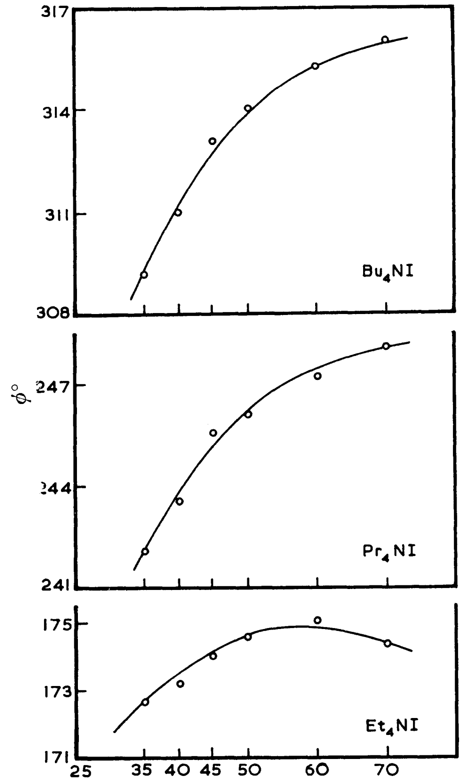

Fig. 2b. ϕ° *vs.* t curves of Et_4NI, Pr_4NI, and Bu_4NI in DMSO.

A close look into the two types of the solvents appears to suggest a solution to this riddle. While DMSO and DMF are, more or less, non-hydrogen bonded-solvents, formamide, NMA and NMP, are strongly hydrogen bonded. The ion-solvent dipole interaction energy in DMF and DMSO, in the absence of any appreciable hydrogen-bond breaking energy, would be appreciable and the attachment of the solvent molecules even to

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[15] The ϕ° *vs.* t curves for Pen_4NI and Hep_4NI are almost similar to those for Bu_4NI although slightly steeper.

the R_4N^+ ions may not be loose; at the same time, no structure formation would occur in the solvents around the ions.[16] On the other hand, in formamide, NMA and NMP, a similar ion-solvent dipole interaction will lead to the breaking of the strong intermolecular hydrogen bonds and loosening up of the solvent structure around the ions so that the attachment of the solvent molecules to the R_4N^+ ions should be weaker, on account of the competing intermolecular hydrogen-bondre formation energy. The net result will be a weaker solvation[17] and loosening of the hydrogen bonded structure of the solvent[15,16] around the ions. Now in DMF and DMSO, some solvent molecules would be associated with the R_4N^+ ions while outside the ion-sphere, the solvent structure would be almost the same as in the pure solvent; so the expansion of the solution on heating would be comparatively less than that of the pure solvent and $d\phi^\circ/dt$ would decrease with the rise in temperature. In formamide, NMA and NMP, due to net structure breaking of the solvent[16,18] in presence of the R_4N^+ ions and their comparatively weaker solvation, solution may expand more rapidly than the pure solvent and $d\phi^\circ/dt$ may remain almost a constant (if the R_4N^+ is not too small like Me_4N^+ and Et_4N^+ ions). Thus it appears that the variation of ϕ° with temperature in different solvents can be satisfactorily explained on the concept of the ion-solvent interaction alone without invoking the idea of the release of the solvent molecules locked inside the large R_4N^+ ions or of the uncoiling of the coiled up large R-chains[4,5] of the R_4N^+ ions at the higher temperatures.

Some Remarks on the Values of ϕ° of R_4N Iodides in Various Solvents. An interesting fact to which the attention may now be drawn is that the difference ($\phi^\circ_{(RR_{n+1})_4NI} - \phi^\circ_{(R_n)_4NI}$) in formamide,[5] NMA[4,8] DMF[9] and DMSO is around 70 and is almost independent of temperature. Further, this difference *i.e.* 70 ml, very nearly corresponds to the difference in the intrinsic volumes, obtained from the relation $4\pi r^4N/3$ (r being the radius of the ions in question) of the R_4N^+ ions, using the radius as given by Robinson and Stokes.[19] This observation suggests that the electrostriction in presence of the R_4N^+ ions is very little in these solvents and also that the addition of one CH_2-group to the R-chains of the R_4N^+ ions, increases the volume of the ion by about 70 ml per mole. Since our ϕ° data have been obtained by extrapolation of the ϕ_V *vs.* $\sqrt{C}$ curves from higher concentrations and in many cases, density could be measured only within a very narrow range of concentrations due to solubility restrictions, it would be safer not to make any quantative deductions. However, since the results indicate that R_4N^+-solvent interaction is very slight, one wonders whether the variation of ϕ° with temperature, in the case of the larger R_4N iodides, is only governed by I^--solvent interaction alone. It is hoped that studies on apparent molal volumes in dilute solutions would throw more light on the behavior of the R_4N^+ ions.

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16) Ram Gopal and P. P. Rastogi, *Z. Phys. Chem., N. F.*, **69**, 1 (1970).

17) Situation would be different with the small common ions with high surface charge density which would produce a much stronger ion-solvent interaction than the hydrogen bond energy. This would usually lead to strong primary and secondary solvation depending upon the radius of the ion concerned.

18) R. D. Singh, P. P. Rastogi, and Ram Gopal, *Can. J. Chem.*, **46**, 3524 (1968).

19) R. A. Robinson and R. H. Stokes, "Electrolytes Solutions," Butterworths Publishing Co., London (1959), p. 124.