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Apparent Molal Volume of Tetraalkylammonium Iodides in Dioxane-Water Mixtures of Varying Dielectric Constants

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Dependence of the slope (S_v) of the plots of apparent molal volume (ϕ_v) versus $\sqrt{C}$ for some tetraalkylammonium salts on the dielectric constant has been examined in water-dioxane mixtures of different dielectric constants. The results indicate that the nature of slope (positive or negative) mainly depends on the dielectric constant of the medium. A high dielectric constant and the large size of R_4N^+ ions favour a negative slope.

IN an earlier study[1] we observed that the slope (S_v) of the Mason's empirical equation

$$\phi_v = \phi_0 + S_v\sqrt{C} \qquad ...(1)$$

in the case of some tetraalkylammonium iodides in water-methanol mixtures depends on the dielectric constant of the solvent medium. The study has now been extended to dioxane-water mixtures in order to see if a similar dependence of S_v on the dielectric constant of the solvent medium is valid.

Conductivity water and doubly distilled AR dioxane were used for preparing solvent mixtures. Due to rapid decrease in solubility of the R_4N iodides with the increase in dioxane content of the mixture, only mixtures containing 2, 6 and 10% dioxane (by weight) could be used in the present study. Tetraalkylammonium iodides (M/s Distillation Products Industries, USA) were purified in the usual manner[2]. Rest of the experimental procedure was the same as described elsewhere[5,12,13]. The density data thus obtained were used to calculate the apparent molal volume (ϕ_v).

TABLE 1 — VALUES OF THE SLOPE (S_v) FOR SOME R_4NI SALTS IN WATER-DIOXANE MIXTURES

Weight % of dioxane in mixture	Dielectric constant at 40°C	S_v at 40°C for			
		Me_4NI	Et_4NI	Pr_4NI	Bu_4NI
0	73·1	5·1	−0·2	−1·0	−6·3
2	71·5	5·8	0·8	−0·4	−5·8
6	68·1	7·2	1·8	0·6	−4·5
10	64·4	8·4	3·0	1·7	−3·2

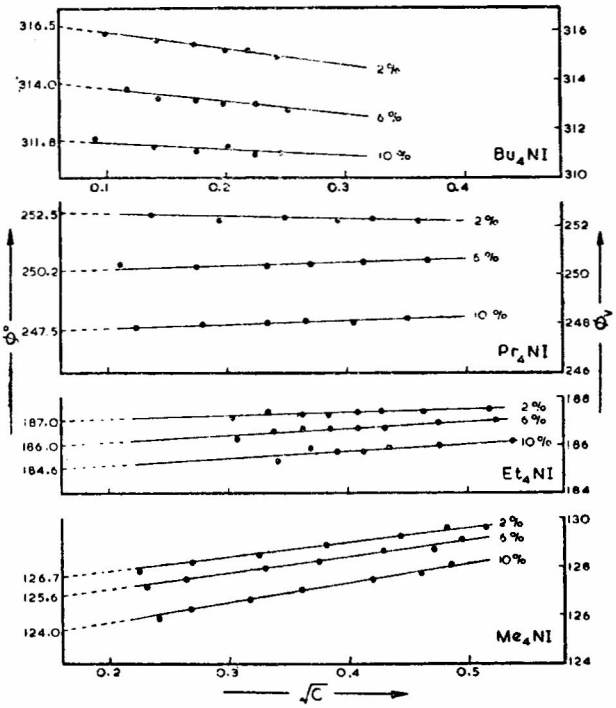

Fig 1 — Plots of ϕ_v versus $\sqrt{C}$ for different salts at 40°

Using the ϕ_v values, as obtained above, the plots of ϕ_v versus $\sqrt{C}$ for different salts at 40° were drawn (Fig. 1). These plots were almost linear indicating applicability of the Mason's empirical relation (1) within the concentration range studied presently. It may also be noted from Fig. 1 that the slope S_v is positive for Me_4NI and Et_4NI salts in all the three mixtures. However, for Pr_4NI, it is slightly negative in a mixture containing 2% dioxane ($\epsilon = 71{\cdot}5$) but becomes positive in a mixture containing 6% ($\epsilon = 68{\cdot}1$) and 10% ($\epsilon = 64{\cdot}7$) dioxane. The slope remains negative in all the three solvent systems for Bu_4NI and the intrapolation procedure suggests that S_v in this case would become positive when the dielectric constant is reduced further. Since a lower dielectric constant enhances electrostatic interionic attraction, it a ppears reasonable to infer that the positive slope is due to this effect. For the negative slope, as found in the case of higher homologues (R_4NX) and some common salts in solvents of high dielectric constants, various explanations have been suggested[6-11] and need not be discussed here. It may be emphasized, however, that the factors responsible for the negative slope are non-electrostatic ion-solvent interactions and depend on the shape and size of the solvent molecules and ions.

The dependence of the nature of slope on the dielectric constant of the medium may be examined a little more closely. The S_v values are given in Table 1 along with the corresponding values in water for different salts for the sake of comparison.

It may be noted from Table 1 that S_v increases with the decrease in dielectric constant of the medium. It remains positive for Me_4NI in all the solvent systems. However, for Et_4NI, S_v changes from negative to a positive value at about $\epsilon \approx 74$,

for Pr_4NI at $\epsilon \approx 68$ and for Bu_4NI at about $\epsilon = 57$ (intrapolated value). It, therefore, appears that S_v may change from negative to a positive value provided the dielectric constant of the medium is appropriately reduced. It may be mentioned here that these conclusions are based on density data for higher concentrations and may not be applicable in very dilute solutions in which the limiting slope has been reported to be positive in some R_4NX salts even though the S_v is negative at higher concentrations[12,13].

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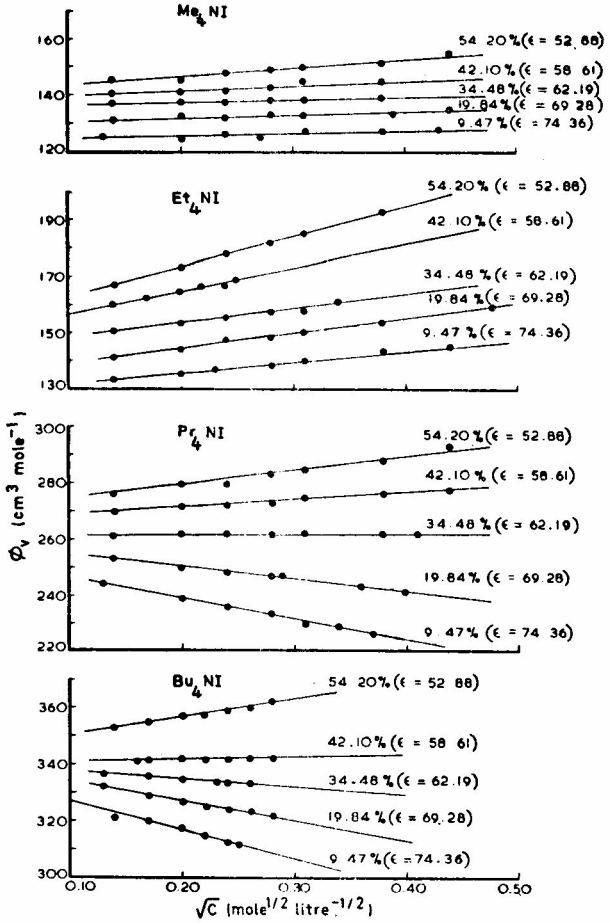

Fig. 1 — Variation of apparent molal volume with concentration of some R_4NI salts in methanol-water mixtures at 40°

Apparent Molal Volume of Tetraalkylammonium Iodides in Water-Methanol Mixtures of Varying Dielectric Constants

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Dependence of the slope S_v of the empirical Mason's equation, $\phi_v = \phi_o + S_v\sqrt{C}$, on the dielectric constant of the medium has been examined in methanol-water mixtures. The data obtained suggest a dependence of S_v on dielectric constant of medium.

STUDIES[1] on the variation of apparent molal volume (ϕ_v) on dielectric constant in water-dioxane mixtures[1] indicate a dominant role of the dielectric constant of the medium on the nature (positive or negative) of the limiting slope (S_v) of the ϕ_v versus $\sqrt{C}$ plots. According to Debye-Hückel theory[2], the slope (S_v) is expected to be positive and this is supported by the experimental data in water[3,4] and formamide[5,6] for common electrolytes. However, difficulties arise, at least at the higher concentrations, in the case of tetraalkylammonium ions* for which the slope has been found to be negative not only in water but in several other solvents of high dielectric constant investigated so far. Similar studies in solvents of lower dielectric constant like methanol[7], dimethylsuplphoxide[8], dimethylformamide[8] and propylene carbonate[9], indicate that even these salts give a positive slope in these solvents. It may be noted with interest that studies in dioxane-water mixtures[1] indicate that the negative slope in pure water becomes positive as the dielectric constant of the mixture is reduced. In order to ascertain if the elecrolytes behave similarly in some other solvent systems, the slope (S_v) of ϕ_v versus $\sqrt{C}$ curves of tetraalkylammonium iodides in methanol-water mixtures of varying dielectric constants have now been obtained. The dielectric constants of water-methanol mixtures have been reported recently[10] and used in this study.

Methanol (AR, BDH) was distilled twice, the middle fraction being retained each time. Conductivity water was used for preparing methanol-water mixtures containing 9·47 ($\epsilon_{25°} = 74{\cdot}36$), 19·84 ($\epsilon_{25°} = 69{\cdot}28$), 34·48 ($\epsilon_{25°} = 62{\cdot}19$), 42·10 ($\epsilon_{25°} = 58{\cdot}61$) and 54·20% ($\epsilon_{25°} = 52{\cdot}88$) methanol by weight.

*Some common salts have a negative slope in N-methylacetamide [Z. *phys. Chem.*, **75** (1971), 7] and in N-methypropionamide [Z. *phys. Chem.*, **91** (1974), 98; *J. phys. Chem.*, **72** (1968), 3209].