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Apparent Molal Volumes of Tetraethylammonium Halides in Ethylene Glycol

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The apparent molal volumes (ϕ_v) of tetraethylammonium chloride, bromide and iodide in ethylene glycol have been calculated from the density measurements oi the respective salt solutions at concentrations less than 0·1*M* and temperatures varying from 25° to 40°. ϕ_v has been found to vary linearly with the square-root of the concentration, *C*. The effect of temperature on the limiting apparent molal volume (ϕ_v^0) of the salts in ethylene glycol has been interpreted in terms of the solute-solvent interaction. The limiting slope, S_v, of the plot of ϕ_v versus $\sqrt{C}$ is different for different salts and it has been interpreted in terms of the ion-ion and solute-solvent interactions.

RECENTLY Gopal *et al.*[1-3] and Millero[4] have used the variation of apparent molal volume (ϕ_v) with concentration and temperature as a tool for studying the solute-solvent interaction. ϕ_v varies linearly with $\sqrt{C}$, according to the Masson's[5] equation and positive slopes for various salts in the solvents of medium dielectric constants, have been observed by Gopal *et al.*[6,7]. It is found[6,7] that most of the data are obtained for the solutions of concentrations greater than 0·1*M*. In dilute solutions i.e. in solutions of concentrations less than 0·1*M*, weak ion-ion interaction is present and the solution is expected to behave like a mixture of two molecular species, widely different in size. Negative slopes for the majority of the solvents at concentrations <0·1*M* are, therefore, expected. From this point of view, the apparent molal volumes of tetraethylammonium halide solutions in ethylene glycol, have been calculated at concentrations <0·1*M*.

Materials and Methods

Ethylene glycol (commercial grade, BDH) was distilled under vacuum, after drying the sample over calcium oxide, calcium sulphate and sodium metal. The purified sample was stored in sealed bottles. The physical constants of the solvent used were comparable with the literature[8] values. Tetraethylammonium halides (AR) were kept in a vacuum desiccator and were used without further purification. All the solutions were made by weight under dry conditions. Molality and equivalent concentration were interconverted using the relationship given in literature[9]. Densities of the solutions of tetraethylammonium halides in ethylene-glycol were determined with the help of a bicapillary pycnometer[10].

Results and Discussion

Densities of the salt solutions in ethylene glycol at different temperatures have been found to fit the Root's[11] equation (Eq. 1).

$$d = d_0+AC-BC^{3/2} \qquad ...(1)$$

where *A* and *B* are constants specific to salt and *d* and d_0 are densities of salt solution and pure solvent respectively. On transforming Eq. (1), we get Eq. 2

$$d-d_0/C = A-B\sqrt{C} \qquad ...(2)$$

Thus a plot of $(d-d_0)/C$ versus $\sqrt{C}$ should be linear with *A* = the intercept and *B* = the slope of the plot. Linear plots of $(d-d_0)/C$ versus $\sqrt{C}$ have been observed for solutions of tetraethylammonium halides in ethylene glycol at all the temperatures studied presently. The values of the constants *A* and *B* of Eq. (1), estimated from these plots, are given in Table 1.

The apparent molal volume, ϕ_v, of the salt solutions in ethylene glycol, at different temperatures was calculated from their densities using Eq. 3 (ref. 12).

$$\phi_v = \frac{1000}{Cd_0}(d_0-d)+\frac{M_2}{d_0} \qquad ...(3)$$

where M_2 represents the molecular weight of the salt used.

The ϕ_v values, calculated from Eq. (3) were found to vary linearly with $\sqrt{C}$, according to the Masson's[5] equation (Eq. 4).

$$\phi_v = \phi_v^0+S_v\sqrt{C} \qquad ...(4)$$

The values of the limiting apparent molal volume, ϕ_v^0, for tetraethylammonium halides in ethylene glycol at different temperatures, obtained from the extrapolation of the plots of ϕ_v versus $\sqrt{C}$ to zero concentration are summarised in Table 2.

At all the temperatures of present study, the limiting experimental slope (S_v), of the Masson's equation is positive in the case of Et_4NI solutions suggesting strong electrostatic ion-ion interaction, whereas negative S_v values in the case of Et_4NCl solutions indicate weaker ion-ion interaction. Positive values of S_v are obtained in the case of Et_4NBr solutions at 35° and 40°, whereas a negative value of S_v is found at 30°. This observation suggests that ion — ion interaction is weak at lower temperatures in Et_4NBr but it increases with the increase in temperature.

Effect of temperature on ϕ — It has been inferred by various workers[6,7] that the maxima in the plots of ϕ_v^0 versus *t* (°C) indicate strong solute — solvent interaction while the minima suggest the presence of ion-ion interaction. In the case of Et_4NCl, the value of ϕ_v^0 remains constant from 30° to 40° (Table 2) and it may be concluded that this value of ϕ_v^0 corresponds to a maximum. Therefore, in the case of Et_4NCl solutions solute-solvent interaction is stronger than ion-ion interaction in the range 30-40°. This is in agreement with the conclusions drawn from the limiting slope, S_v, of the Masson's equation.

In the case of Et_4NBr solutions ϕ_v^0 decreases up to 35° after which it starts increasing. In the plot of ϕ_v^0 versus *t* (°C) for Et_4NBr a minimum is observed at 35° which suggests that ion-ion interaction is strongest at this temperature. Further increase in temperature results in an increase in the value of ϕ_v^0 suggesting the appearance of ion-solvent interaction. However, at 40°, ion-ion interaction dominates the ion-solvent interaction and the net resultant interaction corresponds to the ion-ion interaction which should give positive values of S_v in the order S_v (35°)$>S_v$ (40°). This is found to be true, experimentally. This also suggests that either the maximum in the plots of ϕ_v^0 versus *t* (°C) in the case of Et_4NBr should appear at a temperature much greater than 40° or at a temperature below 35°. At 30°, the value of ϕ_v^0 is greatest and the value of S_v has a negative magnitude, which suggests that ion-solvent interaction at 30° dominates in Et_4NBr solution.

In the case of Et_4NI solutions ϕ_v^0 increases from 25° to 30° and then decreases at 35°. The maximum in the plot of ϕ_v^0 versus *t* is observed at 30° suggesting that at this temperature ion-solvent interaction is stronger than ion-ion interaction. At 25° and 35°, ion-ion interaction dominates over the ion-solvent interaction. The ion-ion interaction is maximum at 25°. The order of ion-ion interaction at different temperatures in the case of Et_4NI is: ion-ion interaction (25°C)>ion-ion interaction (35°C) >ion-ion interaction (30°C).

In the case of Et_4NI the slope of Masson's equation (S_v) is positive and its magnitude is in the order: S_v (25°C)$>S_v$ (35°C)$>S_v$ (30°C).

It has been shown by various workers that Et_4N^+ remains unsolvated in most of the organic solvents[13,14]. If it is considered that the interaction of these salts with ethylene glycol is mainly due to the solvation of halide ions, the order of solvation of halide ions in ethylene glycol at 30° and 35° can be inferred from the magnitude of S_v values. Accordingly, the order of ion-solvent interaction at 30° and 35° is: $Cl^- > Br^- > I^-$.

TABLE 1 — VALUES OF THE PARAMETERS *A* AND *B* OF ROOT'S EQUATION FOR THE SOLUTIONS OF TETRAETHYLAMMONIUM HALIDES IN ETHYLENE GLYCOL AT DIFFERENT TEMPERATURES AND AT CONCENTRATION <0·1*M*

Salt	Temperature (°C)	*A*	*B*
Et_4NCl	30	0·003	0·200
	35	0·001	0·058
	40	0·002	0·012
Et_4NBr	30	0·004	0·057
	35	0·060	−0·154
	40	0·046	−0·066
Et_4NI	25	0·300	−0·800
	30	0·033	−0·060
	35	0·086	−0·250

TABLE 2 — LIMITING APPARENT MOLAL VOLUMES (ϕ_v°) OF $Et_4NX(X=Cl^-, Br^-, I^-)$ IN ETHYLENE GLYCOL AT DIFFERENT TEMPERATURES

	ϕ_v° (ml per mole) at			
	25°	30°	35°	40°
Et_4NCl	—	215·0	214·0	214·5
Et_4NBr	—	188·5	130·8	149·5
Et_4NI	−66·0	201·0	156·0	

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