

Study of the Influence of Alkyl Chain Cation - Solvent Interactions on the Slope of Φ_V vs. \sqrt{C} Curves in 1,5-Pentane Diol - DMF Solvent Mixtures by Apparent Molar Volume Measurements

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Abstract: The concept of Frank's hypothesis (that is the effect of large tetra alkyl ammonium ions on the solvent structure, especially water, in the ion-ion and ion-solvent interactions) was found to be not applicable when water was replaced by one of the organic solvents *e.g.* Dimethyl formamide (DMF), in the solvent mixture, that is, if the study involves ion-ion and ion- solvent interactions in 1,5-pentane diol - DMF solvent mixture containing large cations of tetraalkyl ammonium iodides. The densities of binary solvent mixtures and salt solutions have been measured at 298.15 K by magnetic float densitometer. The apparent molar volumes at infinite dilution, Φ_V^0 , determined by Φ_V -values in the solvent mixtures, have been utilized to estimate the partial molar volumes of transfer, $\Delta\Phi_V^0(\text{tr})$, for various tetraalkyl ammonium iodide salts from DMF to 1,5-Pentane diol.

Keywords: Ion - solvent Interactions, 1, 5-Pentane diol- DMF mixtures

Introduction

Devanathan and Fernando¹ reported abnormally high activity coefficients of aqueous solutions of tetraalkyl ammonium salts while carrying out emf measurements. Their observations were confirmed by Bower and Robinson². The abnormally high activity coefficients were also observed by Frank³ in his emf measurement work of such solutions. He explained the high activity coefficients on the basis of his hypothesis according to which the structure of water is enforced around the R_4N^+ ions on account of the water-hating influence of the large alkyl chains. This results in the formation of cavities inside the enhanced water structure and R_4N^+ ions are accommodated in the cavities so formed. So the fugacity of the solvent and the R_4N^+ ion is lowered, on the other hand the fugacity of I^- ions is increased. Because of this, even the larger R_4N^+ ions seem to be solvated on account of hydrophobic enforcement of water structure and hence large values of activity coefficients of solutions are obtained. In our earlier communication⁴ 1, 5-pentane diol- water combination was used to see the validity of Franks hypothesis in the solutions of R_4NI salts in the binary solvent mixtures, the water being one of the components. The idea was to

replace water by another non- aqueous solvent in 1, 5-Pentane diol- water combination *i.e.* 1,5-pentane diol- DMF were taken to see whether such solute- solvent hating effect is still there and the structure of any of the binary solvents is affected by the ion- solvent interactions.

In order to make sure that the behavior of enhancement of solvent structure³ is confined only either to pure aqueous solutions or the solutions in binary solvent mixtures in which one of the components should necessarily be water, the extension of the work to other similar solvent media of varying dielectric constant is very much desirable. 1, 5-Pentane diol- DMF mixtures provide such media in which water component is replaced by a non aqueous solvent, namely, DMF. These mixtures have been used as solvent media in which the dependence of the slope S_v of the Φ_v vs. \sqrt{C} curves on the structural changes, if any, in the solvent molecules with the addition of R_4NX salts has been examined in this work.

Since the apparent molar volumes and partial molar volumes of electrolytes have proved to be very useful tool in elucidating the structural interactions^{3,5-11} (*i.e.* ion-ion, ion-solvent and solvent-solvent) occurring in solution, the help of these physical parameters, has therefore, been taken in this work to study the problem.

The apparent molar volume at infinite dilution, Φ_v^0 and the apparent molar volume of transfer $\Delta\Phi_v^0(\text{tr})$ parameters have also been taken into consideration to discuss the ionic interactions in these solutions.

Experimental

The tetraalkyl ammonium iodide salts, Et_4NI , Pr_4NI , Bu_4NI and Pen_4NI which were used in present investigation were purified by the method of Conway *et al.*⁵ Dimethyl formamide (DMF) of Qualigen's Glaxo grade, after drying on freshly ignited quicklime, was purified by distilling under reduced pressure. The middle fractions of the successive distillate were redistilled under reduced pressure till the electrical conductance of the final product was of the order of $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$. The purified samples were stored in dark coloured bottles. This DMF was used to prepare 20, 40, 60 and 80% (v/v) solvent mixtures with 1, 5-pentane diol of Fluka purum grade.

The dielectric constants of these compositions have not been reported in the literature so far. Therefore the values of dielectric constants of these solvent mixtures were determined by plotting a graph assuming a linear relationship between dielectric constants and composition with the help of dielectric constant of pure 1,5-pentanediol ($\epsilon=26.3$) & of pure DMF ($\epsilon=36.7$) which are available in literature, the dielectric constants of intermediate compositions 20, 40, 60 and 80% DMF in 1,5-pentane diol were estimated by this graph and are given in Table 1.

Table 1. Estimated values of dielectric constant of 1, 5-pentane diol-DMF mixtures used as a solvent at 298.15 K

S. No.	Composition of mixtures (v/v)	Dielectric constant (ϵ)
1	20% DMF in 1,5-pentanediol	28.4
2	40% DMF in 1,5-pentanediol	30.4
3	60% DMF in 1,5-pentanediol	32.5
4	80% DMF in 1,5-pentanediol	34.6

The density, d_0 , of these solvent mixtures were determined by Magnetic Float Densitometer at 298.15 K, using Eq. 1

$$d_0 = (W + w + f.I) / (V + w/d_{pt}) \quad (1)$$

The terms involved in this equation have their usual meanings. The data of solvent mixtures, *i.e.*, weight, *w* used, current, *I*, passing in the circuit and the corresponding values of d_0 calculated by Eq.1 are recorded in Table 2.

Table 2. Density data of 1, 5-pentane diol -DMF mixtures used as solvent at 298.15 K

Solvent mixture (v/v)	Weight <i>w</i> kg.10 ⁻³	Current <i>I</i> Amp.10 ⁻³	Density d_0 kg.m ⁻³
20% DMF in 1,5-pentanediol	2.30	785	982.327
40% DMF in 1,5-pentanediol	1.80	660	974.048
60% DMF in 1,5-pentanediol	1.00	608	963.743
80% DMF in 1,5-pentanediol	0.200	590	954.108

The solutions of 0.02, 0.04, 0.06, 0.08, 0.10, 0.12 and 0.14 M concentrations of the tetraalkyl ammonium iodides, namely, Et₄NI, Pr₄NI, Bu₄NI and Pen₄NI were prepared in above selected four compositions of 1,5-pentane diol – DMF mixture, one by one taking one composition at a time. The densities, *d*, of these solutions were measured by Magnetic Float Densitometer at 298.15 K using Eq.1 replacing d_0 by *d i.e.*

$$d = (W + w + f.I) / (V + w/d_{pt}) \quad (2)$$

Me₄NI salt could not be studied due to its solubility restrictions. Using the density, d_0 , of solvent mixtures and the densities, *d*, of solutions, the apparent molar volumes, Φ_V , were calculated for each solution using following equation;

$$\Phi_V = [1000(d_0 - d) / C d_0] + [M / d_0] \quad (3)$$

The terms used in this equation have their usual meanings. Φ_V vs. \sqrt{C} curves were drawn for each salts in each composition of 1, 5-pentane diol- DMF mixture and are shown in Figure 1-4. Then slopes *S_v* of these curves were calculated for each salt and are shown in Table 3 along with solvent mixture composition.

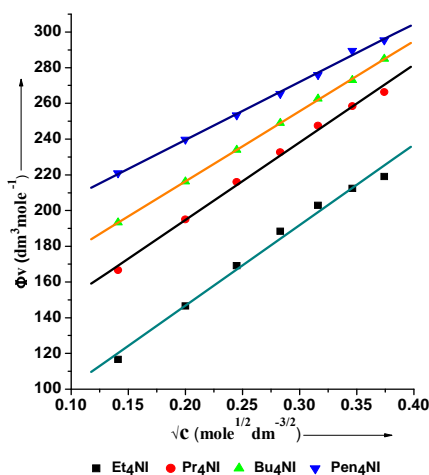


Figure 1. Graph between Φ_V and \sqrt{C} for different electrolyte solutions in 20% DMF in 1,5-pentane diol mixture, 298.15 K

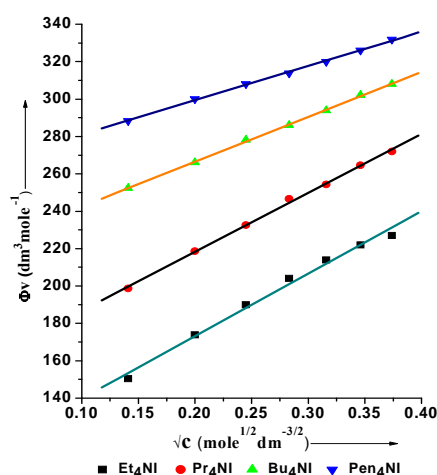


Figure 2. Graph between Φ_V and \sqrt{C} for different electrolyte solutions in 40% DMF in 1,5-pentane diol(v/v) (v/v) at mixture at 298.15 K

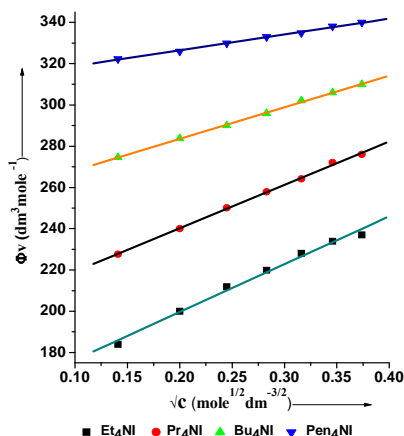


Figure 3. Graph between Φ_v and \sqrt{C} for different electrolyte solutions in 60% DMF in 1,5-pentane diol(v/v) at mixture 298.15 K

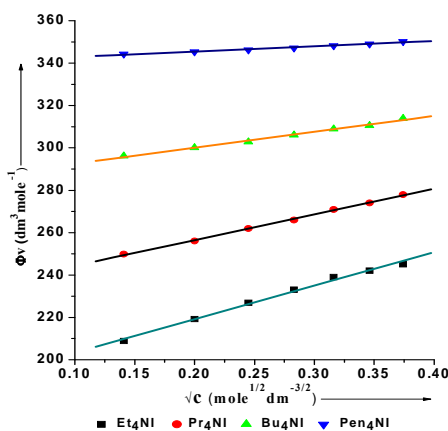


Figure 4. Graph between Φ_v and \sqrt{C} for different electrolyte solutions in 80% DMF in 1,5-pentane diol, (v/v) at mixture 298.15 K

Φ_v^0 values for each salt are also calculated from Figure 1-4 by extrapolating the Φ_v vs. \sqrt{C} curve to $C = 0$ axis (y-axis). The intercepts on y-axis will give the values of Φ_v^0 . These values are assumed as Φ_v^0 (MS) values (*i.e.* apparent molar volume of salts at infinite dilution in mixed solvent system). The apparent molar volumes of transfer, $\Delta\Phi_v^0(\text{tr})$, are calculated using the relation

$$\Delta\Phi_v^0(\text{tr}) = \Phi_v^0(\text{MS}) - \Phi_v^0(\text{S}) \quad (4)$$

Here $\Phi_v^0(\text{S})$ is the apparent molar volume of salts at infinite dilution in pure solvent⁶ (in this case DMF). $\Phi_v^0(\text{MS})$ and $\Delta\Phi_v^0(\text{tr})$ data are shown in Table 4.

Results and Discussion

The dielectric constant of pure 1, 5-pentane diol ($\epsilon=26.3$) can be gradually increased by adding DMF ($\epsilon=36.7$) to it. Thus four types of 1,5-pentane diol- DMF mixtures of varying dielectric constants, were prepared, namely, 20% DMF ($\epsilon=28.4$), 40% DMF ($\epsilon=30.4$), 60% DMF ($\epsilon=32.5$) and 80% DMF ($\epsilon=34.6$) in 1,5-pentane diol (v/v). Density measurements of some $R_4\text{NI}$ salt solutions in these solvent mixtures were done experimentally and Φ_v values then calculated with molar conc. C for each salt. Then Φ_v vs. \sqrt{C} curves were drawn for each salt in various composition and S_v values were calculated.

After, the study of curves in Figure 1-4, it is seen that the apparent molar volume Φ_v increases with increasing concentration of salt for all the cases, hence slopes were found positive for each salt and in each solvent mixture. This is also evident from Figure 1-4 in which the straight lines show the increasing trend of Φ_v values with increasing concentration. As the Φ_v vs. \sqrt{C} curves are found to be straight lines it is clear that the Masson's equation is valid for all the salts in the entire range of concentration selected.

$$\Phi_v = \Phi_v^0 + S_v\sqrt{C} \quad (5)$$

If we examine the S_v data of Table 3, it is quite clear that S_v values are all positive whether the composition of solvent mixture is changed or the salt species is changed. Since no negative value of S_v is found, the hydrophobic alkyl chain- solvent interactions are found to be absent here. No enforcement of solvent structure (either of 1,5-pentane diol or dimethyl formamide) is seen in this system. Thus the Frank's hypothesis of enforcement of

water structure³ does not seem to be applicable when the water component of 1,5- pentane diol- water system is replaced by organic solvent, DMF.

Table 3. Sv- values of Tetra alkyl ammonium iodide salt solutions in different compositions of 1,5-Pentanediol - DMF mixtures

Composition of solvent mixtures (v/v)	Sv- Values			
	Et ₄ NI	Pr ₄ NI	Bu ₄ NI	Pen ₄ NI
20%DMF in 1,5-pentanediol ($\epsilon=28.40$)	450.93	434.08	392.93	324.58
40% DMF in 1,5-pentanediol ($\epsilon=30.40$)	333.99	315.32	240.07	183.05
60% DMF in 1,5-pentanediol ($\epsilon=32.50$)	231.94	210.29	153.21	76.87
80% DMF in 1,5-pentanediol ($\epsilon=34.60$)	158.29	121.40	75.11	25.12

The decreasing trend of Sv, in moving row wise from Et₄NI to Pen₄NI in the Table 3, for a fixed solvent composition, shows that there is a marked effect of the size of electrolyte molecule on the magnitude of slope. The slope goes on decreasing as the smaller molecule is replaced by a bigger molecule successively. This happens in each binary solvent- mixture composition. This trend can easily be interpreted by the two influencing factors. Firstly, increase of ionic size decreases the charge density on the ion which results in the weak ion- ion interaction with decreasing value of charge density. Successive weak ion- ion interactions give the decreasing values of slope, hence the magnitude of the slope is smaller for Pen₄NI than Bu₄NI and likewise the magnitude of slope is smaller for Bu₄NI than Pr₄NI and so on. Secondly, bigger size alkyl chains provide large number of cavities inside the alkyl chains than those available in smaller size alkyl chains. The molecules of solvent mixtures are accommodated inside these void spaces of alkyl chain of R₄NI. Such void spaces may be available in the long alkyl chain of 1,5- pentane diol. Thus interpenetration of ions of solute into solvent molecule and vice versa can take place which causes the reduced values of slope Sv. There will be little contribution of addition of solute to 1,5- Pentane diol – DMF mixture and so the small values of Sv. Sv values also decreases as we go down the columns from 20 to 40% DMF for a particular salt. This decreasing trend of Sv values down the columns can be explained on the basis of the effect of dielectric constant of the solvent media on the slope. It is known that electrostatic forces of attraction, F, between the ions, is inversely proportional to dielectric constant of solvent medium (*i.e.* $F \propto 1/\epsilon$). The increase in the value of dielectric constant of the solvent medium results in weak electrostatic forces of attraction between the ions and hence ion- ion interactions become weaker and weaker as there is a gradual increase of dielectric constant of the medium. In the present study, the gradual increase of dielectric constant of medium is done by increasing the DMF content in the 1,5-pentane diol – DMF mixture *i.e.* as we move from 20 to 80% DMF in the 1,5-pentane diol down the columns of Table 3. Hence the decreasing values of slopes are obtained.

Table 4. Φ_v^0 (MS) and $\Delta\Phi_v^0$ (tr) values for different electrolytes in 1,5-pentane diol – DMF mixture at 298.15 K

DMF in 1,5-Pentane diol, (v/v)	Et ₄ NI		Pr ₄ NI		Bu ₄ NI		Pen ₄ NI	
	Φ_v^0	$\Delta\Phi_v^0(\text{tr})$	Φ_v^0	$\Delta\Phi_v^0(\text{tr})$	Φ_v^0	$\Delta\Phi_v^0(\text{tr})$	Φ_v^0	$\Delta\Phi_v^0(\text{tr})$
20%	56.59	-109.51	107.94	-130.86	137.76	-169.84	174.65	-203.25
40%	106.42	-59.68	155.25	-83.55	218.44	-89.16	262.83	-115.07
60%	153.27	-12.83	198.18	-40.62	252.91	-54.69	311.11	-66.79
80%	187.54	+21.44	232.21	-6.59	285.07	-22.53	340.41	-37.49

Conclusion

The Φ_V^0 values (Table 4) are positive and large for the tetraalkyl ammonium salts in all the composition of 1, 5-pentane diol – DMF mixtures, showing, thereby, the presence of weak ion- solvent interactions. Increase in Φ_V^0 and $\Delta\Phi_V^0(\text{tr})$ values with increasing concentration of DMF in 1,5-pentane diol may be attributed to increase in electrostriction in presence of DMF in the solvent mixture. Thus the electrostriction effect, which brings about the shrinkage in the solvent is increased in pure DMF as compared with that in the mixed solvent. Since electrostriction primarily reflects electrolyte- solvent interaction, it can be inferred that electrolyte - solvent interaction increases (while ion-ion interaction decreases) with increase in DMF content in this solvent mixture.

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