



Study of the Influence of Alkyl Chain Cation-Solvent Interactions on Water Structure in 1,3-Butanediol-Water Mixture by Apparent Molar Volume Data

R. N. PATHAK*, INDU SAXENA, ARCHNA and ANOOP KUMAR MISHRA

Department of Chemistry
Lucknow University, Lucknow -226007, India
mpk@sify.com

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Abstract: The densities of 1,3-butanediol-water mixtures and some tetraalkylammonium iodide salt solutions in these solvent mixtures at different concentrations (0.02 M-0.14 M) have been determined at 298.15 K using magnetic float densitometer technique. Then apparent molar volumes Φ_V of the electrolytes in above solvent mixtures were calculated. The apparent molar volumes of transfer $\Delta\Phi_V^0$ (tr) were also calculated and the ion-ion / ion- solvent interactions are then discussed on the basis of changes in the Masson's slope and apparent molar volumes of transfer data.

Keywords: Interactions, Tetraalkylammonium iodides, 1,3- Butanediol-water mixtures

Introduction

The knowledge of apparent molar and partial molar volumes of electrolyte has been utilized to study ion-ion and ion-solvent interactions in aqueous and non-aqueous solvents of different dielectric constant by a number of scientists¹⁻⁶. Masson⁷ found that the apparent molar volumes of electrolytes, Φ_V , vary with the square root of molar concentration, \sqrt{c} , (over a wide concentration range) by the linear relation.

$$\Phi_V = \Phi_V^0 + S_V\sqrt{c} \quad (1)$$

Where, S_V is the experimental slope.

The discovery of negative slope of R_4NI - type salts in aqueous solutions by Frank⁸ and then by Wen and Saito⁹ could lead to findings that there were R_4N^+ ion-water hydrophobic interactions present in such solutions. The negative slope was explained by Frank on the basis of his hypothesis according to which the water structure is enforced around the alkyl chains of the R_4N^+ ions. The decrease of the apparent molar volume Φ_V with increase in concentration is due to accommodation of the R_4N^+ ions inside the cages of water molecules of the enforced water structure system. The scientists, in the past, working on apparent molar volumes¹⁻¹⁵ attempted to find out the nature of Masson's slope (S_V). The change in slope shows the change in volume of solution. Positive slope corresponds to the increase in

volume while negative slope corresponds to the decrease in volume on increasing the salt concentration. The increase or decrease in volume occurs due to structural changes in solvent molecules on addition of salts. It stuck in our curious mind to see what type of changes may occur in solution and what would be the possible reasons which are responsible for these changes.

We have examined the behaviour of different tetra alkyl ammonium iodide salts in 1,5-pentanediol- water mixtures in our earlier communication¹⁵. In order to establish a definite picture of the influence of tetraalkyl chain- water interactions, it became necessary to carry out the similar studies in, another some what similar system, 1,3-butanediol-water mixture. In this communication, therefore, 1,3-butanediol-water binary solvent mixtures, having different water contents, have been selected for the study of effect of ion solvent interactions in solution of R₄NI salts.

The density data have been analysed by means of Massons's equation. The apparent molar volume, Φ_V , apparent molar volume at infinite dilution, Φ_V^0 and slopes Sv have been interpreted in terms of ion-ion and ion-solvent interactions.

The Φ_V^0 determined by Φ_V values have been utilized to estimate apparent molar volumes of transfer at infinite dilution, $\Delta\Phi_V^0$ (tr) for various tetraalkylammonium iodide salts from water to aqueous solutions of 1,3- butanediol.

Experimental

The binary solvent mixture of 1,3-butanediol-water, having 20, 40, 60 and 80% water (v/v) were prepared using conductivity water. The dielectric constants of these solvent mixtures of specified compositions have not been reported in the literature. Therefore, these were determined graphically, by plotting dielectric constants against composition (0% and 100% composition selecting as the two extreme points and then joining these two points by a straight line). The estimated values of dielectric constant of intermediate compositions were noted and are given in Table 1.

Table 1. Estimated values of dielectric constant of 1,3- butane diol-water mixtures used as a solvent at 298.15 K

S.No.	Composition of mixtures, v/v	Dielectric constant, ϵ
1	20% Water in 1,3-Butanediol	38.5
2	40% Water in 1,3-Butanediol	48.5
3	60% Water in 1,3-Butanediol	58.5
4	80% Water in 1,3-Butanediol	68.5

The densities d_0 of these solvent mixtures were measured at 298.15 K by magnetic float densitometer using equation

$$d_0 = (W + w + f \cdot I) / (V + w / d_{Pt}) \quad (2)$$

Here W = weight of float, w = weight put on the float, f = weight equivalent current (g/Ampere), V = vol. of float, d_{Pt} = density of platinum. The d_0 data have been summarized in Table 2.

Table 2. Density data of 1,3- butanediol-water mixtures used as solvent at 298.15 K

Solvent Mi xture, v/v	Weight W Kg.10 ⁻³	Current I Amp.10 ⁻³	Density d_0 Kg.m ⁻³
20% Water in 1,3-butanediol	4.800	200	999.568
40% Water in 1,3-butanediol	4.500	345	998.991
60% Water in 1,3-butanediol	4.400	370	998.334
80% Water in 1,3-butane diol	4.300	395	997.677

The solutions of Et₄Ni, Pr₄Ni, Bu₄Ni and Pen₄Ni of 0.02, 0.04, 0.06, 0.08, 0.100, 0.12, and 0.14 M were prepared in 20, 40, 60 and 80% water in 1,3- butanediol mixtures one by one taking one electrolyte and one solvent composition at a time. Me₄Ni salt was excluded due to solubility restrictions. The density, *d*, of these solutions were also measured at 298.15 K using Eq.2. The volumes of transfer parameters $\Delta\Phi_V^0$ (tr) have also been calculated for this system by using the formula:

$$\Delta\Phi_V^0(\text{tr}) = \Phi_V^0(\text{MS}) - \Phi_V^0(\text{W}) \quad (3)$$

Where Φ_V^0 (MS) is the apparent molar volume at infinite dilution in the mixed solvent and Φ_V^0 (W) is the apparent molar volume, at infinite dilution, in pure solvent (in this case water). Φ_V^0 (W) data have been taken from the literature¹⁰. The $\Delta\Phi_V^0$ (tr) values are summarized in Table 4. The interactions have also been discussed on the basis of this property at the end.

Results and Discussion

The apparent molar volumes, Φ_V , were then calculated using *d* and *d*₀ values for each electrolyte and for each concentration by using the equation:

$$\Phi_V = [1000 (d_0 - d) / cd_0] + [M / d_0] \quad (4)$$

Here *M* is the molecular weight and *c* is the molar concentration of the electrolyte. Then Φ_V vs. \sqrt{c} curves were drawn for all the four electrolytes in each four solvent composition. These curves are shown in Figure 1 to Figure 4. The curves were found to be all straight lines so the Masson's equation is applicable for all the salts for entire range of concentration selected.

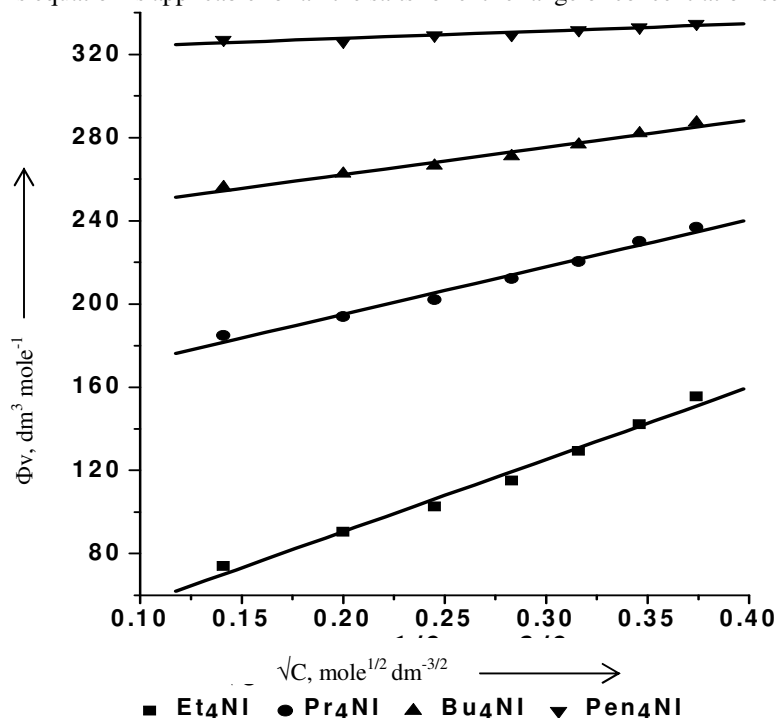


Figure 1. Graph between Φ_V and \sqrt{c} for different electrolyte solutions in 20% water in 1,3-butanol mixture, (v/v) at 298.15 K

The experimental slope S_v as given in the Masson's Eq.1 was also calculated for each curve. If Φ_V increases with increases in concentration, the slope comes out to be positive while the slope assumes the negative value if Φ_V decreases on increasing the solute concentration. The S_v -data with their sign (+ve or -ve) have been summarized along with the solvent composition in Table 3. From the Figure 1, the trend of Φ_V indicates that the apparent molar volume increases with increase in electrolyte concentration for all the four electrolytes, eg, Et_4NI , Pr_4NI , Bu_4NI and Pen_4NI in the 20% solvent mixture. Hence S_v is positive for each of them.

Table 3. S_v - values of tetraalkylammonium iodide salt solutions in different compositions of 1,3- butanediol- water mixtures

Composition of solvent mixtures (water in 1,3 0 - butanediol), v/v	S_v - Values			
	Et_4NI	Pr_4NI	Bu_4NI	Pen_4NI
20% Water ($\epsilon = 38.5$)	+346.8	+227.6	+131.6	+35.6
40% Water ($\epsilon = 48.5$)	+253.7	+132.7	+82.3	-81.7
60% Water ($\epsilon = 58.5$)	+180.1	+89.1	-40.7	-157.1
80% Water ($\epsilon = 68.5$)	+94.7	+46.1	-124.1	-250.8

As the water content is increased to 40% in 1,3-butanediol the apparent molar volume decreases with increasing electrolyte concentration in case of Pen_4NI , therefore the slope becomes negative in this case of Pen_4NI while the other salts Et_4NI , Pr_4NI and Bu_4NI , still give positive value of slope (Figure 2).

If the water content is further increased to 60 or even 80%, the Φ_V values of two higher tetraalkylammonium salts Bu_4NI and Pen_4NI show a decreasing trend. Hence they give negative slope while the two lower tetra alkyl ammonium salts Et_4NI and Pr_4NI give positive slope (Figure 3 & 4). The overall picture is very much clear if one observes the data of Table 3 carefully.

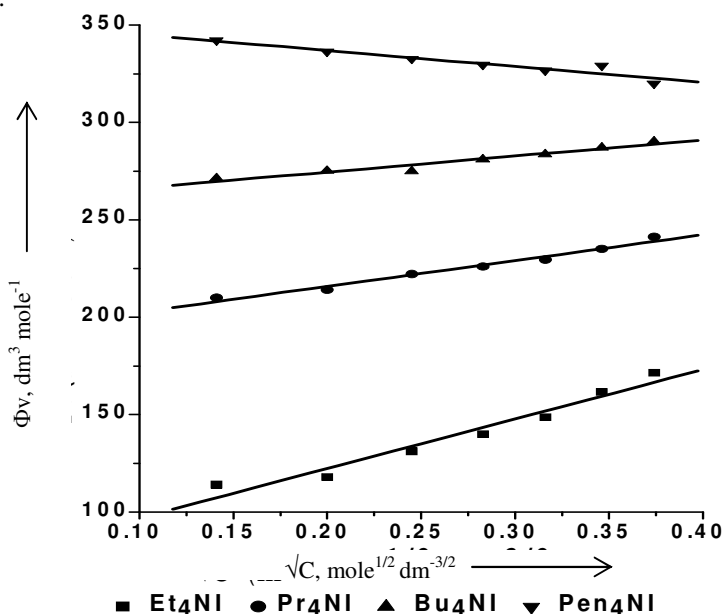


Figure 2. Graph between Φ_V and \sqrt{c} for different electrolyte solutions in 40% water in 1,3-butanediol mixture, (v/v) at 298.15 K

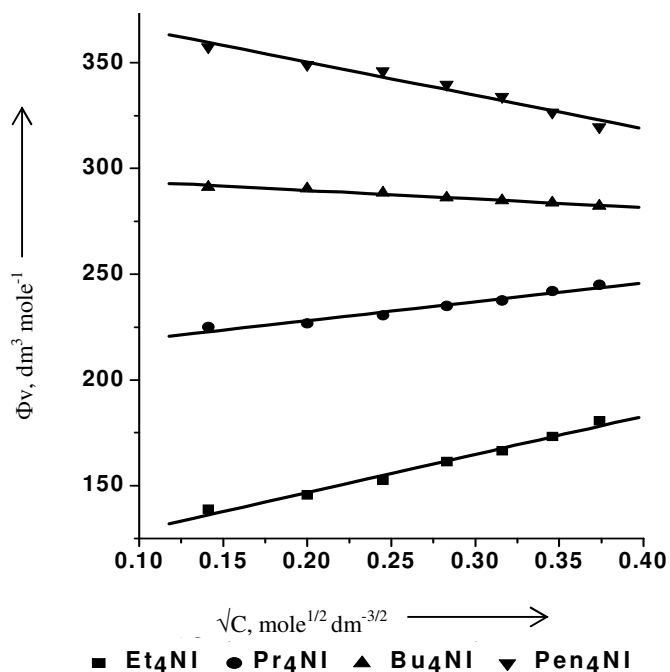


Figure 3. Graph between Φ_v and \sqrt{c} for different electrolyte solutions in 60% water in 1,3-butanediol mixture, (v/v) at 298.15 K

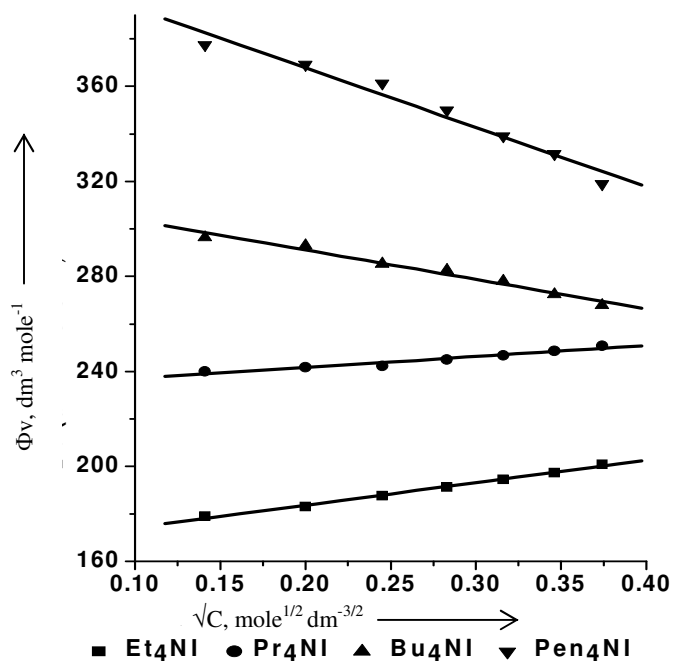
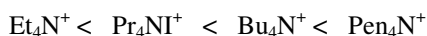


Figure 4. Graph between Φ_v and \sqrt{c} for different electrolyte solutions in 80% water in 1,3-butanediol mixture, (v/v) at 298.15 K

If this Table is examined critically, it is evident that the slopes go on decreasing, row-wise from Et₄NI to Pen₄NI and also down the column from 20 to 80% water in 1,3-butanediol mixture. By increasing the higher percentage of water content in the mixtures the slopes even change sign from positive to negative in case of Bu₄NI and Pen₄NI.

This type of behaviour shown by the slope, S_v , may be explained as below

The higher tetraalkylammonium ions enforce the structure of water more than the lower tetraalkylammonium ions *i.e.* the relative power of enforcement of water structure in cation-water hydrophobic ion- solvent interactions is



Thus Pen₄NI salt has greater influence on water molecules and elongates the water structure more than the Bu₄NI salt does. Similarly Bu₄NI salt has greater influence on water molecules and elongates the water structure more than the Pr₄NI salt does. But the effect of Bu₄NI salt is less than that of Pen₄NI on the water solvent molecules and so on. The effect of enforcement of water molecule structure is least in case of Et₄NI salt. The more stretching of the water molecules means the more cavities or void spaces formed in the solvent molecules.

In 20% water, since the water content is very small, only a few cavities are available which are filled up instantly as the salt concentration is increased and the addition of salt increases the volume hence Φ_v increases with increase in concentration of salt resulting the positive S_v values in all the four electrolytes. As the water content further increased from 20 to 40% in the solvent mixture, hence more water molecules are available. In such a mixture, three salts Et₄NI, Pr₄NI and Bu₄NI are not able to enforce the water structure much due to lesser amount of water present and so the increase of electrolyte concentration increases the Φ_v values and so a positive slope is obtained in these cases also. The fourth salt Pen₄NI has greater influence, owing to its largest size, on the structure of water molecule in cation-water hydrophobic ion- solvent interactions. So comparatively water molecules form a network of structure consisting of more void spaces. Thus the addition of Pen₄NI salt in 40% water solvent mixture does not contribute towards the volume. The molecules of Pen₄NI, because of large number of cavities inside the water structure network, hide themselves in the cavities and thus there is no contribution of it toward the volume. So the Φ_v decreases on the addition of salt. Hence the negative S_v value is obtained in case of Pen₄NI in 40% water mixture.

In 60 and 80% water rich mixtures, the plenty of water molecules are available. The higher tetraalkylammonium ions, namely Bu₄NI and Pen₄NI exert the greater influence on the water molecules and hence the structure of water molecules is enforced to the extent that the addition of salt does not fill up all the void spaces created inside the water structure network in dilute solutions. Thus the increase in concentration in case of these two salts does not increase the volume and hence Φ_v decreases with increase in the electrolyte concentration in case of Bu₄NI and Pen₄NI salts. Therefore S_v values are found to be negative in these cases. The effect is much more stronger in case of Pen₄NI than Bu₄NI. So the value of S_v is more negative in the former case than in the later case. The values of S_v down the columns go on decreasing, it is because of little enhancement in the values of dielectric constant which is responsible in weaker ion-ion interactions (Low dielectric constant of the medium favours strong ion-ion interaction while the high dielectric constant favours weak ion-ion interaction).

Conclusion

The Φ_v^0 values (Table 4) are +ve and large for the tetraalkylammonium salts in all the composition of aqueous solution of 1,3- butanediol, showing, thereby, the presence of weak ion- solvent interactions. Increase in Φ_v^0 and $\Delta\Phi_v^0$ (tr) values with decreasing concentration of 1,3-butanediol (or increasing concentration of water) may be attributed to increase in electrostriction in presence of water in the solvent mixture.

Table 4. Φ_v^0 and $\Delta\Phi_v^0$ (tr) values for different electrolytes at 298.15 K

(Water in 1,3-butanediol) v/v	Et ₄ NI		Pr ₄ NI		Bu ₄ NI		Pen ₄ NI	
	Φ_v^0	$\Delta\Phi_v^0$ (tr)	Φ_v^0	$\Delta\Phi_v^0$ (tr)	Φ_v^0	$\Delta\Phi_v^0$ (tr)	Φ_v^0	$\Delta\Phi_v^0$ (tr)
20%	21.2	-164.1	149.5	-101.1	235.8	-76.0	320.5	-89.8
40%	71.6	-113.8	189.2	-122.7	258.0	-53.9	353.2	-57.1
60%	110.8	-74.6	210.3	-40.4	297.8	-14.1	381.7	-28.6
80%	164.8	-20.6	232.5	-18.2	316.0	+4.1	418.0	-7.7

Thus the electrostriction effect, which brings about the shrinkage in the volume of the solvent is increased in pure water 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 decrease in 1,3- butanediol content (or increase in water content) in the solvent mixture. From the above discussion, it is evident that the Frank's hypothesis of enforcement of water structure by large tetraalkylammonium salts not only is applicable in pure water solutions but seems to be applicable in non- aqueous - water mixture system also.

References

1. Gopal R and Siddiqi M A, *J Phys Chem.*, 1968, **72**, 1814.
2. Gopal R and Singh K, *Z Physik Chem (NF)*, 1974, **91**, 98.
3. Gopal R, Siddiqi M A and Singh K, *Z Physik Chem (NF)*, 1971, **75**, 7.
4. Gopal R and Siddiqi M A, *J Phys Chem.*, 1969, **73**, 3390
5. Rohankar P G and Aswar A S, *Indian J Chem.*, 2002, **41**, 312.
6. Millero F J, *J Phys Chem.*, 1968, **72**, 3209..
7. Masson D O, *Phil Mag.*, 1929, **8(7)**, 218.
8. Frank H S, *J Phys Chem.*, 1963, **67**, 1554.
9. Wen W Y and Saito S, *J Phys Chem.*, 1964, **68**, 2639.
10. Millero F J, "Structure and Transport Process in Water and Aqueous Solutions" Sharma R A, Ed., Wiley- Inter Science, New York W.Y.,1971, Chapter 15,
11. Bhattarai A and Das B, *J Nepal Chem Soc.*, 2008 / 2009, **23**, 82.
12. Parmar M L, Sharma P and Guleria M K, *Indian J Chem.*, 2009, **48A**, 806.
13. Romero Carmen M and Paez Manuel S, *J Solution Chem.*, 2007, **36**, 237-245.
14. Kandpal K, Joshi B K, Joshi S K and Kandpal N D, *E- J Chem.*, 2007, **4(4)**, 574-580.
15. Pathak R N, Saxena I, Archana and Mishra A K, *J Indian Council Chem.*, 2009, **26**, 170.



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