



# Study of Ionic Interactions in Solution and Influence of Alkyl Chain Cation – Solvent on Water Structure in Ethanol – Water Mixture by Magnetic Float Densitometer

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## Authors' contributions

This work was carried out in collaboration between all authors. Author IS designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author RD managed the analyses of the study. Authors VK and SG managed the literature searches. All authors read and approved the final manuscript.

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## ABSTRACT

The densities of the binary solvent mixtures and its salt solutions have been measured by one of the recently modified techniques, namely Magnetic Float Densitometer. The partial molar volume or apparent molar volume  $\phi_v$  and at infinite dilution are determined by  $\phi_v^0$  values of solution mixtures for some tetra alkyl ammonium iodide salts from aqueous to non aqueous binary solvent mixture of Water – Ethanol system. The  $\phi_v$  values showed positive and large for all the tetra alkyl ammonium salts in all the compositions of binary mixture solution. This is due to, the presence of weak ion-ion interactions between the components of the mixtures. The value of  $\phi_v$  increases on decreasing the concentration of ethanol. The value of slope  $S_v$  also showed positive for  $\text{Et}_4\text{NI}$  and  $\text{Pr}_4\text{NI}$  salt solution whereas it is negative for  $\text{Bu}_4\text{NI}$  and  $\text{Pen}_4\text{NI}$  salts solution. This is due to the presence of specific molecular interactions that will lead to increase in electrostriction with the presence of water in the solution mixture.

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## 1. INTRODUCTION

The basic approach of ion –ion and ion –solvent interactions in different electrolyte solution using aqueous and non- aqueous mixtures as the solvent of different dielectric constant ( $\epsilon$ ) of the medium by a number of researchers [1,2] was first to find the density data, using Magnetic Float Densitometer and then by using Masson's equation [3-6] these data were used to calculate the apparent molar volume ( $\phi_v$ ). It was found by Masson that apparent molar volume of electrolytes ( $\phi_v$ ) varies with the square root of molar concentration,  $\sqrt{C}$ . by the linear relation

$$\phi_v = \phi_v^0 + S_v \sqrt{C} \quad (1)$$

Where,  $S_v$  is the experimental slope. The molecular interaction such as ion – ion and ion - solvent interactions can be explained with the help Masson's equation. Further, by knowing the value of slope  $S_v$  - values of Masson's equation after Plotting a graph between  $\phi_v$  versus  $\sqrt{C}$ , we shall predict the clear picture of molecular structure of the binary liquid system, which are formed due to molecular rearrangement, and molecular or ionic interactions between the solute and solvent molecules.

The negative slope of  $R_4NI$  type of salts in aqueous solutions was discovered by Frank, Wen and Saito [2,7-9], by this they could find that there is  $R_4N^+ I^-$  ion –water hydrophobic interactions which are present in such solvents. Frank explained the negative slope on the basis of his hypothesis which states that the water structure is enforced around the  $R_4N^+$  ion and alkyl chains. The decrease of the apparent molar volume ( $\phi_v$ ) with increase in concentration is due to accommodation of  $R_4N^+$  ions inside the cages of water molecules of the enforced water structure system. The accuracy of the measurements of  $\phi_v$  for different electrolytes depend on the accuracy of densities of the electrolyte solutions and it is measured in the following manner [6,10,11],

$$\phi_v = [1000(d_0-d) / cd_0] + [M/d_0] \quad (2)$$

Where,

$d$  = density of solution  
 $d_0$  = density of solvent mixture  
 $M$  = molecular weight And  
 $C$  = concentration. (In  $\text{mol.dm}^{-3}$  of an electrolyte)

In the past year, the researchers have worked on apparent molar volumes [5,6] and attempted to find out the nature of Masson's slope ( $S_v$ ). The changes in slope showed the change in volume of solution. Positive slope corresponds to the increase in volume while negative slope corresponds to the decrease in volume with increasing the salts concentrations. The increase or decrease in volume occurs due to structural changes in solvent molecules on addition of salts. To see what would be the possible reasons which are responsible for these changes. We have examined the behavior of different tetra alkyl ammonium iodide salts in water – ethanol solvent mixtures, having different water content, and our aim is the study the effect of bigger size of  $R_4N^+$  cation on solvent interaction in binary salts solution mixture. The values of  $\phi_v$ ,  $\phi_v^0$  and  $S_v$  have been interpreted in terms of ion - ion and ion - solvent interactions.

## 2. MATERIALS AND METHODS

### 2.1 Instruments Use

Magnetic Float Densitometer, Dilatometer.

The binary solvent mixture of ethanol water, having 20, 40, 60, and 80% water (v/v) were prepared using distilled water. The dielectric constants ( $\epsilon$ ) of this solvent mixture of specified composition have not been reported in the literatures so far. Therefore the value of dielectric constants of different % compositions were determined graphically, assuming a linear relationship between the value of dielectric constants ( $\epsilon$ ) and % compositions by taking the value of dielectric constant of pure water ( $\epsilon = 80.0$ ) & of pure Ethanol ( $\epsilon = 24.5$ ) which are available in the literature, the dielectric constant of intermediate compositions 20, 40, 60, 80% Ethanol in water estimated by the graph, (Fig. 1) and the values are given in Table 1.

The densities,  $d_0$ , of these solvent mixtures were measured at 303.15 K by Magnetic Float Densitometer by using equation [8,12],

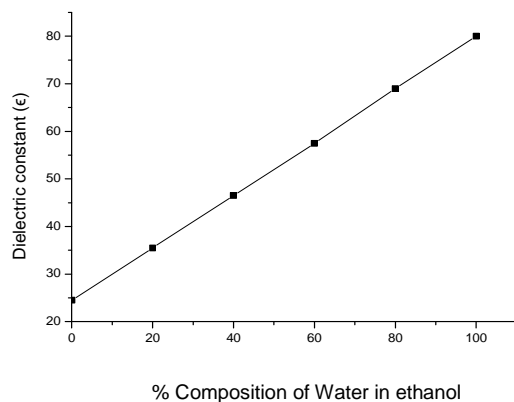
$$d_0 = (W + w + f.l) / (V + w/d_{pt}) \quad (3)$$

Here,  $W$  = weight of float,  $w$  = weight of platinum (Pt) on the float,  $f$  = weight equivalent current (g/amp),  $V$  = volume of float,  $d_{pt}$  = density of platinum and  $I$  = current, passing in the circuit.

The solutions of Et<sub>4</sub>NI, Pr<sub>4</sub>NI, Bu<sub>4</sub>NI, Pen<sub>4</sub>NI of 0.02, 0.04, 0.06, 0.08, 0.10, 0.12 and 0.14 mol.dm<sup>-3</sup> concentrations were prepared in 20, 40, 60, and 80% water in ethanol mixtures, one by one, taking one electrolyte and solvent composition at a time. Me<sub>4</sub>NI salt was excluded due to solubility restrictions. The densities, of these solutions were also been measured at 303.15 K using equation (3).

**Table 1. Estimated values of dielectric constant ( $\epsilon$ ) of water – ethanol solvent mixtures at 303.15 K**

S. no.	% compositions of binary liquid mixtures (v/v)		Dielectric constant ( $\epsilon$ )
	Water	Ethanol	
1	0	100	24.5
2	20	80	35.6
3	40	60	46.7
4	60	40	57.8
5	80	20	68.9
6	100	0	80.0



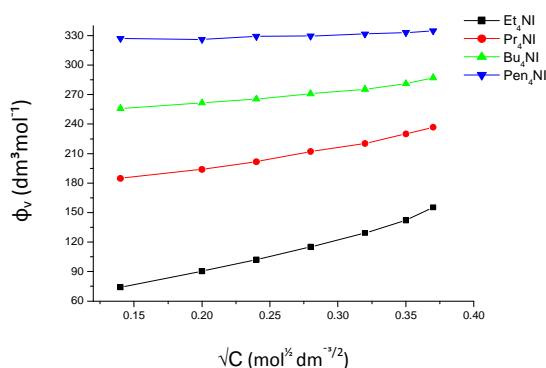
**Fig. 1. Graph plotted between dielectric constant ( $\epsilon$ ) and % composition of water – ethanol solvent mixtures**

### 3. RESULTS AND DISCUSSION

The apparent molar volumes  $\phi_v$ , were calculated using  $d$  and  $d_0$  values for each electrolyte and for each solvent composition using the equation (2).

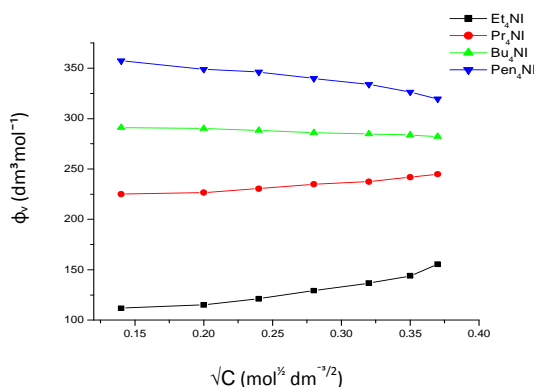
These  $\phi_v$  values have been shown in Table 2 and graph is plotted between  $\phi_v$  versus  $\sqrt{C}$  curves were drawn for all the four electrolytes in each four solvent composition (20, 40, 60, and 80% water in ethanol) which are shown in Fig. 2. The curves were found to be straight lines; hence the

Masson's equation is applicable [5,7,13] for all the salts for entire range of concentration selected. The experimental slope  $S_v$  – values as given in the Masson's equation 1 was also calculated for each curve. If  $\phi_v$  increases with increase in concentration, the slope comes out to be positive while the slope appeared as negative value if  $\phi_v$  decrease on increase of the solute concentration. The  $S_v$  – values with their sign (positive or negative) have been summarized along with the solvent composition in Table 3.



**Fig. 2. Graph plotted between  $\phi_v$  and  $\sqrt{C}$  for different electrolyte solution in 20% water – ethanol mixtures at 303.15 K**

From the Figs. 2 & 3, the trend of  $\phi_v$  indicates that the apparent molar volume ( $\phi_v$ ) increases with increase in electrolyte concentration for all the four electrolytes e.g. Et<sub>4</sub>NI, Pr<sub>4</sub>NI, Bu<sub>4</sub>NI and Pen<sub>4</sub>NI in the 20% and 60% water in ethanol solvent. Hence  $S_v$  – values is positive for each of them.



**Fig. 3. Graph plotted between  $\phi_v$  and  $\sqrt{C}$  for different electrolyte solution in 60% water – ethanol mixtures at 303.15 K**

**Table 2. Apparent molar volume ( $\phi_v$ ) and  $\sqrt{C}$  values for different electrolytes in different % compositions of water-ethanol mixtures at 303.15 K**

S. no.	% Composition of water in ethanol	$\sqrt{C}$ $\text{mol}^{1/2} \text{dm}^{-3/2}$	Apparent molar volume ( $\phi_v$ ) $\text{dm}^3 \text{mol}^{-1}$			
			$\text{Et}_4\text{NI}$ ,	$\text{Pr}_4\text{NI}$ ,	$\text{Bu}_4\text{NI}$ ,	$\text{Pen}_4\text{NI}$
1	20%	0.14	74.04	184.94	255.90	327.08
2	20%	0.20	90.50	194.00	261.59	326.20
3	20%	0.24	102.14	201.80	265.40	329.22
4	20%	0.28	115.03	212.20	270.85	329.48
5	20%	0.32	129.30	220.90	275.50	331.64
6	20%	0.35	142.15	229.90	281.12	333.64
7	20%	0.37	155.34	236.75	287.20	333.08
8	40%	0.14	113.93	209.89	271.10	334.81
9	40%	0.20	118.00	213.99	275.18	342.19
10	40%	0.24	131.01	222.00	274.89	336.33
12	40%	0.28	139.99	226.01	280.96	332.71
12	40%	0.32	148.62	229.41	283.62	329.17
13	40%	0.35	161.53	234.99	287.05	326.83
14	40%	0.37	171.30	241.12	290.13	320.01
15	60%	0.14	111.82	225.05	291.22	357.39
16	60%	0.20	115.18	226.65	290.31	349.02
17	60%	0.24	121.28	230.49	288.36	346.23
18	60%	0.28	129.28	234.91	286.13	339.84
19	60%	0.32	136.66	237.57	284.79	334.03
20	60%	0.35	143.95	241.83	283.68	326.53
21	60%	0.37	155.46	244.88	282.20	319.53
22	80%	0.14	178.93	240.00	296.01	377.57
23	80%	0.20	183.01	241.76	229.01	369.20
24	80%	0.24	187.71	242.28	285.23	361.41
25	80%	0.28	191.30	245.05	282.57	350.04
26	80%	0.32	194.45	246.70	278.04	339.23
27	80%	0.35	197.39	248.64	272.46	331.73
28	80%	0.37	200.91	250.74	272.77	319.05

**Table 3.  $S_v$  values for some tetra alkyl ammonium iodides in different water- ethanol mixtures**

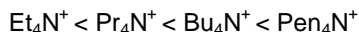
S. no.	% compositions		Dielectric constant ( $\epsilon$ )	$S_v$ -values ( $\text{dm}^{9/2} \text{mol}^{-3/2} \times 10^{-3}$ ) in different % compositions of water in ethanol			
	Water	Ethanol		$\text{Et}_4\text{NI}$	$\text{Pr}_4\text{NI}$	$\text{Bu}_4\text{NI}$	$\text{Pen}_4\text{NI}$
1	20	80	35.6	+346.8	+227.6	+131.6	+35.6
2	40	60	46.7	+253.7	+132.7	+82.3	-81.7
3	60	40	57.8	+180.1	+89.1	-40.7	-157.1
4	80	20	68.9	+94.7	+46.1	-124.1	-250.08

As the water content is increased to 40% in ethanol then apparent molar volume decreases with increase in electrolyte concentration in case of  $\text{Bu}_4\text{NI}$  &  $\text{Pen}_4\text{NI}$  and the slope becomes negative, But for the other salts  $\text{Et}_4\text{NI}$  &  $\text{Pr}_4\text{NI}$  still gives positive value of slope if the water content is further increased to 60% or 80%. The  $\phi_v$  values of two higher tetra alkyl ammonium salts  $\text{Bu}_4\text{NI}$  and  $\text{Pen}_4\text{NI}$  shows a decreasing trend. Hence they give negative slopes while the two lower tetra alkyl ammonium iodide salts  $\text{Et}_4\text{NI}$  and  $\text{Pr}_4\text{NI}$  give positive slopes. The overall picture is very much clear if one analyses the data from the

Table 3. If this table is examined critically, it is evident that the slope goes on decreasing, row wise from  $\text{Et}_4\text{NI}$  to  $\text{Pen}_4\text{NI}$  and also down column from 20% to 80% water in ethanol solution. By increasing the water content further in the mixture the slope even changes sign from positive to negative in case of  $\text{Bu}_4\text{NI}$  and  $\text{Pen}_4\text{NI}$ . This type of behavior shown by the slope  $S_v$  may be explained as below.

The higher tetra alkyl ammonium ions enforced greater to the structure of water than the lower tetra alkyl ammonium ions. The relative power of

enforcement of water structure in  $R_4N^+$  – water hydrophobic ion solvent interactions depends on the size of alkyl chain in the following manner<sup>4</sup>,



Thus  $Pen_4NI$  salt has greater influence on water molecules and the water structure more is elongated than the  $Bu_4NI$  salt but less than that of  $Pen_4NI$  on the water solvent molecules and so on. The effect of enforcement of water molecule structure is least in case of  $Et_4NI$  salts. The more stretching of the water molecules i.e. the more cavities or void spaces formed in the solvent molecules in the presence of  $Bu_4N^+$  and  $Pen_4N^+$  ions. If water content (say 20%) 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  $\phi_v$  - values are increased with increase in concentration of salt and resulting the positive values of  $S_v$  for all the four electrolytes.

Further as the water content is increased from 20% to 40% in the solvent mixtures then more water molecules are available in such a mixtures and salts  $Et_4NI$  and  $Pr_4NI$  are not able to enforce the water structure much due to lesser amount of water present, and the increase of electrolyte concentrations, also increases the  $\phi_v$  values and have positive slope  $S_v$  – values. The fourth salt  $Pen_4NI$  has greater influence, owing to its larger size, on the structures of water molecule due to  $R_4N^+$  - water hydrophobic ionic interactions. So, comparatively water molecules form a network like structure consisting of more void spaces and thus the addition of  $Pen_4NI$  salt in 40% water solvent mixture does not contribute towards the volume. The molecules of  $Pen_4NI$  hide themselves in the cavities due to large number of cavities present inside the water network structure which decreases  $\phi_v$  - value. Hence the negative  $S_v$  - value is obtained in case of  $Pen_4NI$  in 40% water mixture. In 60% and 80% water rich mixtures, the plenty of water molecules are available and the higher tetra alkyl ammonium ions, namely  $Bu_4NI$  and  $Pen_4NI$  start exerting the greater influence [2,8] on the water molecule 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 structures network in dilute solution. Thus the increase in concentration in case of these two salts does not increase the volume and so  $\phi_v$  decreases with increase in the

electrolyte concentration in case of  $Bu_4NI$  and  $Pen_4NI$  salts. Therefore  $S_v$  values are found to be negative in these cases. The effect is much stronger in case of  $Pen_4NI$  than  $Bu_4NI$ . So the value of  $S_v$  is more negative in the former case than in the latter case. The values of  $S_v$  down the columns goes on decreasing due to little enhancement in the values of dielectric constant which is responsible in weaker ion – ion interactions [6,11,13-15].

The  $\phi_v$  values are positive and large for the tetra alkyl ammonium salts in all the composition of aqueous solution of ethanol due to the presence of weak ion- ion interactions. This may be attributed to increase in electrostriction in presence of water in the solvent mixture. Thus the electrostriction effect, which brings about the shrinkage in the volume of the solvent, is more in pure water as compared with that of the mixed solvent. Since electrostriction primarily reflects electrolyte - solvent interaction, it can be inferred that electrolyte - solvent increases (while ion - ion interaction decrease) with decrease of ethanol content (or increase of water content) in the solvent mixture.

#### 4. CONCLUSION

The  $\phi_v$  values (Table 2) are positive and large for the tetra alkyl ammonium iodide salts in all the compositions of Water- Ethanol mixtures showing thereby, the presence of weak ion – solvent interactions. The apparent molar volumes ( $\phi_v$ 's) have been calculated by using Masson's equation and plotted against  $\sqrt{C}$ . The slopes  $S_v$  - values (Table 3) of these curves showed positive values in low dielectric constant of medium (20% Water,  $\epsilon = 35.6$ ) for all the four tetra alkyl ammonium salts. But as the dielectric constant of the medium is increased by adding water in Ethanol,  $Et_4NI$  and  $Pr_4NI$  salts showed positive  $S_v$  values while  $Bu_4NI$  and  $Pen_4NI$  showed negative values. This is may be attributed to increase in electrostriction in presence of water in the solvent mixtures. Such trend of  $S_v$  values can be understood on the bases of increase of ionic size decrease in charge density of the ions and bigger size of alkyl chains. This causes the negative values of slope  $S_v$ .

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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