

Study of the Densities of Some R₄N⁺ - Solutions in Water - Isopropyl Alcohol Solvent Mixtures at 313.15 K by Magnetic Float Densitometerz and Then Study Masson's Equation from Φ_v Data

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Abstract— Based on Masson's equation we study the molecular interactions between the compositions of the binary solution mixtures for different (%) compositions of Water– Isopropyl alcohol by adding tetraalkyl ammonium iodide at 313.15K. The densities of the solution mixtures (ρ_s) have been measured very accurately by using Magnetic float Densitometer. The densitometer works on the electrostatic attraction force developed by the passage of current through a solenoid .using this technique, the densities (d_0) of Water – Isopropyl alcohol solvent and mixtures of some tetra alkyl ammonium iodide, viz. Et₄NI, Pr₄NI, But₄NI, Pen₄NI at 0, 20, 40, 60, 80, 100% compositions (v/v) have been determined experimentally. The apparent molar volumes have been calculated from density data using Masson's equation and graph plotted between ϕ_v vs \sqrt{c} . The slopes of curves shows that in low dielectric constant medium (i.e, 20% water, $\epsilon=30.76$ and 40% water, $\epsilon=42.74$ for all the four tetraalkyl ammonium iodide salts have positive slope. But as the dielectric constant of the solvent medium is increased by adding Water – Isopropyl alcohol, further additions of salts in the solution will start contributing towards the volume so the volume will increase on increasing the salt concentration therefore the plot $\phi_v + vs \sqrt{c}$ curves will give a positive and negative slope the data have been explained on the basis of dielectric constant of the solvent mixtures and size of the electrolyte ion.

Keywords— Interactions, Tetra alkyl ammonium iodides, Isopropyl alcohol – Water.

I. INTRODUCTION

Ion –ion and ion – solvent interaction studies have in aqueous and non aqueous solvent mixtures at different dielectric constant (ϵ) with tetraalkyl ammonium iodide salts have attached many researchers in resent years. It was assumed that the structure of water is enforced around the R₄N⁺ ions on account of the water – hating influence of the

long alkyl chains. The R₄N⁺ ions are thus encaged inside the cavities forced by water molecules and so, hence the fugacity of the solvent and of R₄N⁺ ions is lowered; and that of ions is boosted. Thus in water the large R₄N⁺ ions, inspite of their large size give illusion of salvation on account of the hydrophobic enforcement of water structure. Thus the ion – solvent interaction studies in Isopropyl alcohol - Water solution of tetra alkyl ammonium iodide salts showed that the apparent molar volume decrease with increase of concentration for higher alkyl chain salts at different of compositions 0, 20, 40, 60, 80, 100% (v/v) when a solution is prepared there is either increase or decrease of volume of solvent due to addition of salt to it. The volume change while preparing the solutions can be measured in terms of the apparent molar volume ϕ_v which can be defined as “the net change in volume of solvent by the addition of pre mole of electrolyte”[4,5,7,8].

The dependence of apparent molar volume or concentration was explained by Frank on the basis of his hypothesis. According to him the water structure is enforced around the alkyl chains of R₄N⁺ ions. The decrease of the apparent molar volume ϕ_v , with increase in concentration is due to the accommodation of R₄N⁺ ions inside the cage of water molecules of the enforced water structure system. Hence the R₄N⁺ ions do not contribute fully to the increase in volume of the system when R₄NX salt is added and this leads to a decrease in volume when concentration increase; the result would be a negative slope in the ϕ_v vs \sqrt{c} curves. When all the water molecules have been used up, no void spaces are now available, the slope becomes positive and curve starts rising. The apparent molar volume ϕ_v of the electrolytes in solutions is given by Masson's equation namely

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

The ϕ_v , were then calculated using d and d_0 value for each electrolyte and for solvent composition by using

$$\phi_v = [1000(d_0-d)] / cdd_0 + M/d_0 \quad (2)$$

Here M is the molecular weight and C is the molal concentration of the electrolyte. The ϕ_v vs \sqrt{c} curves were drawn for all the four electrolytes in each four solvent composition 0, 20, 40, 60, 80 and 100% isopropyl alcohol in water shown in Figures. The curves were found to be straight line so the Masson's equation is applicable for all the salts for entire concentration selected the positive slope S_v in ϕ_v vs \sqrt{c} curves is observed in case of electrolytes containing small and compact ions. This is due to dielectric constant of the medium, which encourages the dissociation of the salts. Especially in dilute solution and high charge density of the ions gives rise to strong electrostatic ion solvent dipole interaction[1,2,3]. As concentration increase, ion - ion interaction also increase, on the other hand, ion solvent interaction or solvation per mole of ion decrease. This would give rise to increase in volume of solution and so the apparent molar volume of electrolyte would increase with the rise of concentration. This implies a positive slope in ϕ_v vs \sqrt{c} curves. Thus these electrolyte solutions give positive slope.

II. EXPERIMENT

2.1 CHEMICAL

BDH isopropyl alcohol is used choosing one composition of the solvent mixture at a time, different solutions of Et₄NI, Pr₄NI, Bu₄NI, Pen₄NI were prepared in it, on molar basis using 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14M concentration of each electrolyte.

2.2 APPARATUS AND PROCEDURE

The tetra alkyl ammonium iodide used in the present work were analytical reagent (AR) grades with minimum assay of 99.9% obtained from S.D fine chemical (India) using isopropyl alcohol of fluka grade and conductivity water whose specific conductance is of the order of 10⁻⁶ohm⁻¹. Four mixtures of Isopropyl alcohol - Water (eg. 20, 40, 60, & 80%) water in isopropyl alcohol were prepared on volume by volume (v/v) basis, the densities (d₀) of these solvent mixtures were determined by Magnetic float densitometer[8,13,15] by taking a series of observation with different weight 'w' on the float and noting the corresponding hold current 'I' when the Pt-point of the touched the bottom of the solution container the density values (d₀) were then calculated using equation

$$d_0 \text{ or } d = (W + w + f \text{ XI}) / V + w / d_{pt} \quad (3)$$

Choosing one composition of the solvent mixture at a time, different solutions of Et₄NI, Pr₄NI, Bu₄NI, and Pen₄NI were prepared in it on molar basis using 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14 M concentration of each electrolyte. Then similar solutions were prepared in other compositions, of the solvent mixtures. The density (d) of each solution was determined exactly in the same manner as that described above for the solvent mixtures using the

same equation (replacing d₀ by d in the equation). All the above observations are taken at a constant temperature 313.15K using Toshniwal constant temperature bath having accuracy $\pm 0.01^\circ\text{C}$.

III. RESULT AND DISCUSSIONS

The densities d₀ and dielectric constant (ε) data for different (%) composition of isopropyl alcohol – water mixtures are given in Table 1. The densities (d) of difference R₄NI salts solutions (R= Et, Pr, Bu, Pen) in 0.02 - 0.14M concentration range and in 20, 40, 60, 80% water – isopropyl alcohol mixtures and corresponding calculated apparent molar volume (ϕ_v - value) have been recorded in Table 2. The apparent molar volume were calculated using following formula

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

Where d₀ and d is the density of solvent and solution respectively C is the concentration in mole dm⁻³ and M is the molecular weight of the electrolyte. ϕ_v vs. \sqrt{c} curves for all the four electrolyte Et₄NI, Pr₄NI, Bu₄NI, Pen₄NI, in the concentration range 0.02- 0.14 M and in all the four solvent mixtures the graph shows straight line, indicate that Masson relation (eq.) is applicable in all the cases. The study shows straight line, increase that Masson relation (eq.) is applicable in all the cases. The study show that ϕ_v increases with increase in concentration for all the salts in 20, 40% water in isopropyl alcohol in the entire concentration range selected also clear from that Figure 1 that leads to positive S_v value for these curves. But as the water content is increased in the isopropyl alcohol i.e. if the observations are taken in 60 and 80% water rich mixtures, only Et₄NI salts gives positive S_v values (i.e. ϕ_v increase with increase in concentration) the other salts i.e. Pr₄NI, Bu₄NI, Pen₄NI, give negative S_v values in both solvent mixture (i.e. ϕ_v decreases with increasing concentration). The negative slope goes on decreasing as size of the alkyl chain increases. it is evident for the data of the Table 3. The slope goes on decreasing as the water content is gradually increased for 20 to 80% isopropyl alcohol. Above behaviour of the slope can be explained by data of Table 3.

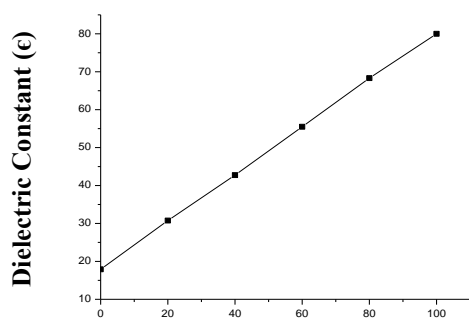
Above behaviour of slope shows that in the two low dielectric constant mixture (20% water ε = 30.76 and 40% water ε = 42.74) positive slopes are obtained. This is because low dielectric constant favours a strong ion solvent interaction which means that interaction will go on increasing as the concentration will increase. The Frank's hypothesis [9,10,12,14] of enhancement of water structure due to long alkyl chain of R₄NI salts- water hydrophobic interaction has the least effect due to very low water content in 20% & 40% water mixtures. The void space produced in the water enhanced structure will be quickly

filled up in 20% & 40% water mixtures by the long alkyl chain of R_4NI salts due to very smaller number of water molecules. Further addition of salt in the solution will start contributing towards the volume so the volume will increase on increasing the salt concentration. There four the plot ϕ_v vs \sqrt{c} curves will give a positive slope. Also since the dielectric constant of the solvent mixtures are very low i.e. in the region 20% $\epsilon = 30.76$ to 40% $\epsilon = 42.74$ the effect of low dielectric constant will lead to the strong ion solvent interactions, dominating the effect of Franks enhanced water structure[18,19,20,21].

The decrease in slope with increasing size of the salt molecule is due to the Frank's hypothesis that the larger the size of alkyl chain in the salt molecule, the greater is the repelling effect of it on the water molecule and so the larger is the enhancement of water structure. The result is that now same more R_4N^+ ions will be accommodated inside the cage of water molecule leading to lesser steepness in the lines in ϕ_v vs \sqrt{c} curves.

Table 1: Dielectric Constant (ϵ), Obtained from Graph

Composition(%) of Water – Isopropyl alcohol (v/v)	Dielectric constant (ϵ)
0% Water In Isopropyl Alcohol	17.90
20% Water In Isopropyl Alcohol	30.76
40% Water In Isopropyl Alcohol	42.74
60% Water In Isopropyl Alcohol	55.50
80% Water In Isopropyl Alcohol	68.32
100% Water In Isopropyl Alcohol	80.00



Composition % of Water in Isopropyl Alcohol

Fig.1: Graph for the Estimation of Dielectric Constant of Various Water – Isopropyl Alcohol Mixtures at 313.15K.

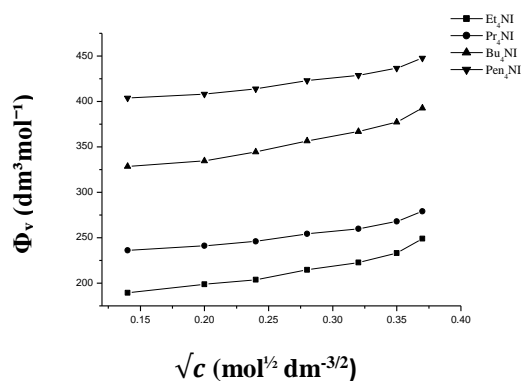


Fig. 2: Graph Between ϕ_v and \sqrt{c} for Different Electrolyte Solution in 20% Water – Isopropyl Alcohol Mixtures

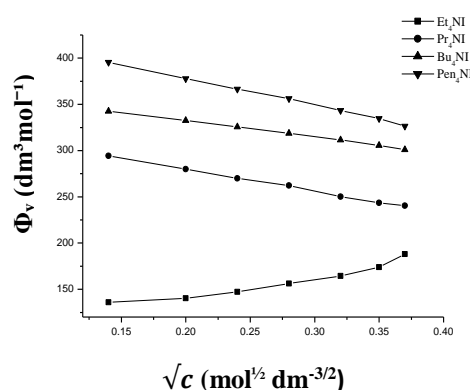


Fig. 3: Graph Between ϕ_v and \sqrt{c} for Different Electrolyte Solution in 60% Water – Isopropyl Alcohol Mixtures

Table 2: ϕ_v and \sqrt{c} Value for Different Electrolytes in Water – Isopropyl Alcohol Mixtures.

S.No.	Water in Isopropyl alcohol % composition	$(\sqrt{C})\text{mol}^{1/2}\text{dm}^{-3/2}$	Apparent Molar Volume (ϕ_v) ($\text{dm}^3\text{mol}^{-1}$)			
			Et ₄ NI,	Pr ₄ NI,	Bu ₄ NI,	Pen ₄ NI
1	20%	0.14	189.31	236.04	328.61	403.86
2	20%	0.20	198.81	241.04	334.58	408.14
3	20%	0.24	203.76	245.87	344.38	413.88
4	20%	0.28	214.64	254.23	356.52	422.94
5	20%	0.32	222.64	259.84	366.83	428.76
6	20%	0.35	233.08	267.93	377.38	436.62
7	20%	0.37	248.96	279.06	392.64	447.75
8	40%	0.14	135.85	236.42	218.06	353.86
9	40%	0.20	136.25	243.44	224.28	360.09
10	40%	0.24	139.31	250.24	232.01	369.18
12	40%	0.28	147.08	261.14	242.78	380.91
12	40%	0.32	152.78	269.82	252.60	382.72
13	40%	0.35	161.02	279.85	263.34	403.81
14	40%	0.37	169.46	294.37	279.38	421.50
15	60%	0.14	135.88	294.37	342.58	395.46
16	60%	0.20	140.19	279.85	332.56	377.82
17	60%	0.24	147.16	269.82	325.66	366.44
18	60%	0.28	156.18	262.14	318.72	356.29
19	60%	0.32	164.50	250.24	311.48	343.42
20	60%	0.35	174.04	243.44	305.68	334.62
21	60%	0.37	188.08	240.42	301.06	326.32
22	80%	0.14	111.82	180.74	316.18	396.28
23	80%	0.20	115.18	166.49	308.44	389.11
24	80%	0.24	121.18	150.95	298.06	375.58
25	80%	0.28	129.28	147.88	284.74	357.26
26	80%	0.32	136.66	138.44	272.17	348.02
27	80%	0.35	143.95	131.28	259.24	328.28
28	80%	0.37	155.46	126.09	238.80	302.92

Table.3: S_v Values for Some Tetra alkyl Ammonium Iodides in Different Water- Isopropyl Alcohol Mixtures at 313.15K

S. No.	Composition of Water in Isopropyl alcohol (v/v)	Dielectric constant (C) as computed from graph	S_v values ($\text{dm}^9/2 \text{ mole}^{-3/2} 10^{-3}$)			
			Et ₄ NI	Pr ₄ NI	But ₄ NI	Pen ₄ NI
1.	20% Water	30.76	+226.60	+207.16	+160.00	+217.00
2.	40% Water	42.74	+148.68	+109.06	+66.70	+88.17
3.	60% Water	55.50	+104.75	- 64.54	-53.80	-15.0
4.	80% Water	68.32	+86.36	- 43.38	-52.68	-85.71

IV. CONCLUSION

Ion ion and solvent interactions in different electrolyte solution using aqueous and non aqueous mixtures as the solvent as it is the easiest and simplest thermodynamic property that can be studied, in the present communication,

the apparent molar volume ϕ_v of R₄NI in isopropyl alcohol and water mixture at solvent composition 0,20,40,60,80, and 100% (v/v) have been studied and nature of ion solvent interaction is derived their basic approach was, first to find out the density data, thus obtained ; the

apparent molar volume (ϕ_v) have been calculated and plotted against $\sqrt{\text{conc.}}$. But as the dielectric constant of the solvent medium is increased by adding isopropyl alcohol in water, all the four tetraalkyl ammonium iodide salts have positive slope each of the four electrolyte gives negative slope.

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