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The Acoustical investigation on intermolecular interaction of Tetrabutylammonium iodide with Ethanol and Water at Various Temperatures

Indu Saxena,*Onkar Nath Mishra, Syed Mohd. Ejaz, Aditya Gupta, Divyanshi Mishra, and Preeti Yadav

ABSTRACT

The densities of the binary solvent mixtures and their salt solutions have been measured by one of the recently modified techniques, namely the Magnetic Float Densitometer. The partial molar volume or apparent molar volume φ_v at infinite dilute are determined by φ_v^0 values of solution mixtures for tetra butyl ammonium iodide salt from aqueous to non-aqueous solvent mixture of the Water-Ethanol system. The φ_v values showed large and positive values, due to weak ion-ion interactions between the components of mixtures. It increases by decreasing the concentration of ethanol. However, the value of slope S_v showed a negative value for Bu_4NI salt solutions. This is due to the presence of specific molecular interactions that will lead to an increase in electrostriction with the presence of water in the solution mixture.

Keywords- Apparent molar volume, Magnetic Float Densitometer, ion-ion interactions, Dielectric constant

Introduction

Many researchers have found a basic approach to studying the ion-ion and ion-solvent interactions [1] in a different electrolyte solution, which was prepared using aqueous or non-aqueous mixtures having solvents of different dielectric constant ε. The first step is to find the density data using the "Magnetic Float Densitometer"[14] and then by using Masson's equation calculated the apparent molar volume (ϕ_v). It was Masson who found that the molar volume (ϕ_v) varies with the square root of molar concentration 'C'[11]

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

It is a linear form of the equation of the type y = mx + c where S_v is the experimental slope.
The credit for discovering the negative slope of the R_4NI type of salt in an aqueous solution goes to Frank, Wen Saito. They found that there is an ion of type R_4N^+ I^- water hydrophobic interaction in such solvents. Based on the hypothesis made by Frank, he explained the reason behind the negative slope. He mentioned that water structure is enforced around R_4N^+ ions and an alkyl chain. So, in such solvents, there is a decrease in apparent molar volume(φ_v) with an increase in concentration due to cages formed by water molecules around R_4N^+ ions.

The ethanol-water dimer is an excellent model system for hydrogen bonding, as it exhibits both a strong O–H···O hydrogen bond, as well as a weak C–H···O hydrogen bond. The energy landscape of the dimer is thus an interplay between the relative donor/acceptor strengths of water and ethanol, as well as the gauche/trans conformations of the ethanol monomer. The strong hydrogen bond between ethanol and water makes the largest contribution to the relative energies of the structures. Since ethanol is a better hydrogen bond acceptor than the donor, the water donor structures are lower in energy than the water acceptor structures [2,3]. The ethanol molecule can exist in the trans or gauche conformation, which dictates the position of the strong hydrogen bond.

Weaker interactions in the dimer lead to further energy separations between conformers.

The polarity of the water molecule plays a major part in the dissolution of ionic compounds during the formation of aqueous solutions. When ionic solid dissolves in water, the positive ends of the water molecules are attracted toward anions, while their negative ends are to the cations. This process is called ***hydration***. The hydration of its ions tends to cause salt to break apart (dissolve) in the water. In the dissolving process, the strong forces present between the positive and negative ions of the solid are replaced by strong water-ion interactions.

One of the interesting topics to investigate is the behavior of salt-containing partially and completely alkyl-substituted ammonium ions in aqueous and non-aqueous solutions. The interest was to create, to begin with, some unusual properties of these salts in aqueous and non-aqueous solutions caused by their large size and hydrophobic alkyl chain interaction. In a study of the concentration dependence of the apparent and partial molar volume, since volume properties are easy to measure and interpret so, interaction in a solution of the salts can thus be easily obtained [4].

Experiment

When a solution is prepared it is unknown whether the volume of the solvent after the addition of the salts remains the same, increasing or decreasing from its initial volume.

The binary solvent mixture of Ethanol-Water having 0, 40, 50, 60, and 100% composition of ethanol(v/v) was prepared using conductivity water. The values of dielectric constants of such compositions have been determined graphically by plotting dielectric constants(ϵ) against the composition of mixtures.

The densities were measured using the formula:

$$\mathbf{d = (W + w + f \times I)/(V + w/d_{Pt})}$$

where W is the weight of the float, w is the weight on the float, f is weight equivalent current (g/amp), V is the volume of the float, d_{Pt} is the density of the platinum, and I the current flows.

Now moving toward our objective was to calculate the densities of the mixture of solute tetrabutylammonium iodide in the solvent of an aqueous-nonaqueous mixture of Ethanol-Water solvent mixture for certain concentrations of salt in certain percentages of a solvent mixture of ethanol in water at two specified temperatures. Table 1 shows the density and apparent molar volume for 40% ethanol at 35 and 45^0C

Table 1

40% Ethanol in water (v/v) for Bu_4NI(369.37 g/mol)

Density(d_0)= 941.67 kg/m^{-3}, ϵ= 57.5

S.No	M Mol.dm^{-3}	d(at 35^0) kg.m^{-3}	d(at 45^0) kg.m^{-3}	√C √(mol dm^{-3})	ϕ_v(at 35^0) dm^{3}mol^{-1}	ϕ_v (at 45^0) dm^{3}mol^{-1}
1	0.02	943.58	938.0	0.1374	291.22	295.82
2	0.04	944.1	936.5	0.1943	290.31	290.31
3	0.06	945.7	939.1	0.2382	288.36	282.36
4	0.08	944.07	938.7	0.2748	286.13	263.13

- **For 50% ethanol in water at 35°and 45^0C**

Table 2

50% Ethanol in water (v/v) for Bu_4NI(369.37 g/mol)

Density(d_0)= 925.8 kg/m^{-3}, ϵ= 52.0

S.No	M Mol.dm^{-3}	d(at 35^0) $kg.m^{-3}$	d(at 45^0) $kg.m^{-3}$	√C √(mol dm^{-3})	ϕ_v(at 35^0) dm^3mol^{-1}	ϕ_v (at 45^0) dm^3mol^{-1}
1	0.02	927.4	921.2	0.1362	225.05	235.05
2	0.04	929.9	922.4	0.1928	226.65	236.65
3	0.06	925.9	918.9	0.2357	230.49	240.49
4	0.08	923.8	915.3	0.2718	234.91	244.91

- **For 60% ethanol in water at 35°and 45^0C**

Table 3

60% Ethanol in water (v/v) for Bu_4NI(369.37 g/mol)

Density(d_0)= 909.4 kg/m^{-3}, ϵ= 46.5

S.No	M Mol.dm^{-3}	d(at 35^0) $kg.m^{-3}$	d(at 45^0) $kg.m^{-3}$	√C √(mol dm^{-3})	ϕ_v(at 35^0) dm^3mol^{-1}	ϕ_v (at 45^0) dm^3mol^{-1}
1	0.02	910.44	904.16	0.1362	271.10	277.10
2	0.04	911.62	905.25	0.1928	274.18	284.18
3	0.06	914.33	906.98	0.2357	275.89	287.89
4	0.08	913.43	904.18	0.2718	280.96	292.96

TABLE 4

S_V values for some tetra butyl ammonium iodide

indifferent Ethanol-Water mixture

S.No.	Composition of Ethanol in Water (v/v)	Dielectric constant (∈) as computed from the graph	S_V -values ($dm^{9/2}$ $mole^{-3/2} \times 10^{-3}$)in different compositions of Water in Ethanol
			Bu_4NI
1.	40% Ethanol	57.5	-66.70
2.	50% Ethanol	52.0	53.80
3.	60% Ethanol	46.5	52.68

Result and Discussion

The apparent molar volume [6], ϕ_v, was calculated using d and d_0 values for electrolyte and each solvent composition by using the equation

$$\phi_v = [1000(d_0 - d)]/Cd_0 + M/d_0$$

Here M is the molecular weight and C is the molar concentration of the electrolyte. These ϕ_v values have been shown in Tables 1 to 3[12]. Then ϕ_v vs $\sqrt{C}$ curves were drawn for the electrolyte in each of the three solvent compositions (40, 50, and 60% ethanol in water) shown in Figures 1 to 3. The curves were found to be straight lines; hence Masson's equation is applicable for the salt for the entire range of concentrations selected. The experimental slope S_v as given in Masson's equation was also calculated for each curve. If ϕ_v increases with an increase in concentration, the slope comes out positive while the slope assumes the negative value if ϕ_v decreases on increasing the solute concentration. The S_v – data with their sign (positive or negative) have been summarized along with the solvent composition in Table -4.[15]

Table 1 to 3 indicates,

As the water content is 40% in ethanol the apparent molar volume increases with increasing electrolyte concentration giving the positive value of the slope. If the water content is further increased to 60%, the ϕ_v value of Bu_4NI salt shows a decreasing trend, giving negative slopes.

Bu_4NI salt has a greater influence on water molecules and elongates the water structure. The more stretching of the water molecules means more cavities or void spaces formed in the solvent molecules.

When the water content is 40% in the solvent mixture, the Bu_4NI salt is not able to enforce the water structure much due to the lesser amount of water present and so the increase of electrolyte concentration increases the ϕ_v value, as a result, the positive slope is obtained.

In 60% water-rich mixtures, plenty of water molecules are available. The higher tetra butyl ammonium ion starts exerting a 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 does not increase the volume, and hence ϕ_v decreases with an increase in the electrolyte concentration. Therefore, S_v values are found to be negative in these cases.

SUMMARY AND CONCLUSION:

The general definition of interactions says that there is an interplay of two substances with each other that reflects changes in them. Here we have tried to study the interactions between tetrabutylammonium iodide and a binary mixture of ethanol and water at certain compositions and specific temperatures. Since the binary mixtures have different dielectric constant ε values, that led to variations in the values of apparent molar volume.

While experimenting, the interaction that exists between the salt acts as an electrolyte and binary mixture is weak-ionic.

The calculated values for apparent molar volume ϕ_v for various concentrations of salts for different ethanol-water mixture percentages are large, which thereby depicts that there is a presence of weak ion-solvent solution; where the weak ion is Bu_4N^+ and ethanol-water mixture is the respective solvent.

By graph, it was observed that the slope calculated for 60% water and 40% ethanol solvent, came to be negative. That means as the water content rose to 60% slope S_v was negative due to the high dielectric constant of water. This is may be attributed to an increase in electrostriction in presence of water in the solvent mixtures. Such a trend of S_v values can be understood based on the increase of ionic size, decrease in charge density of the ions, and bigger size of alkyl chains. This causes the negative slope of S_v.

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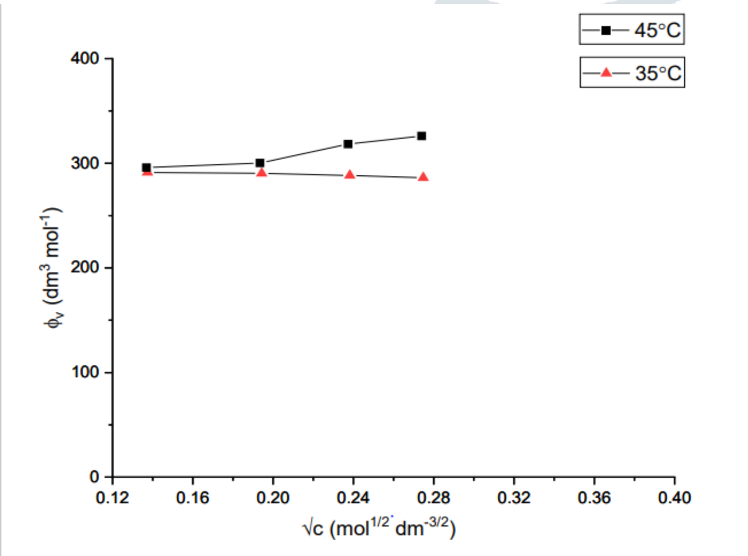
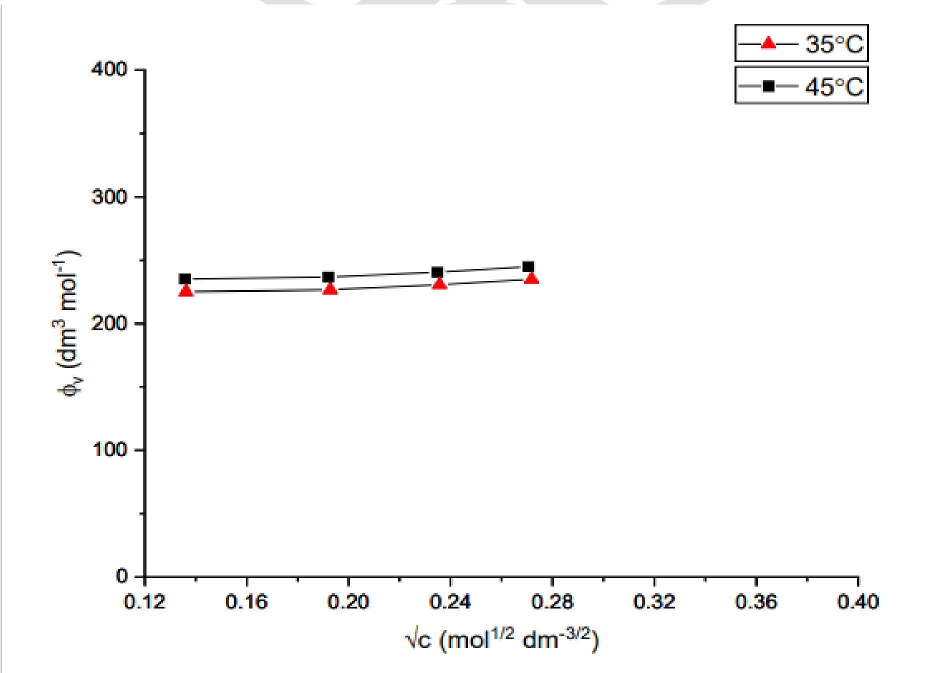
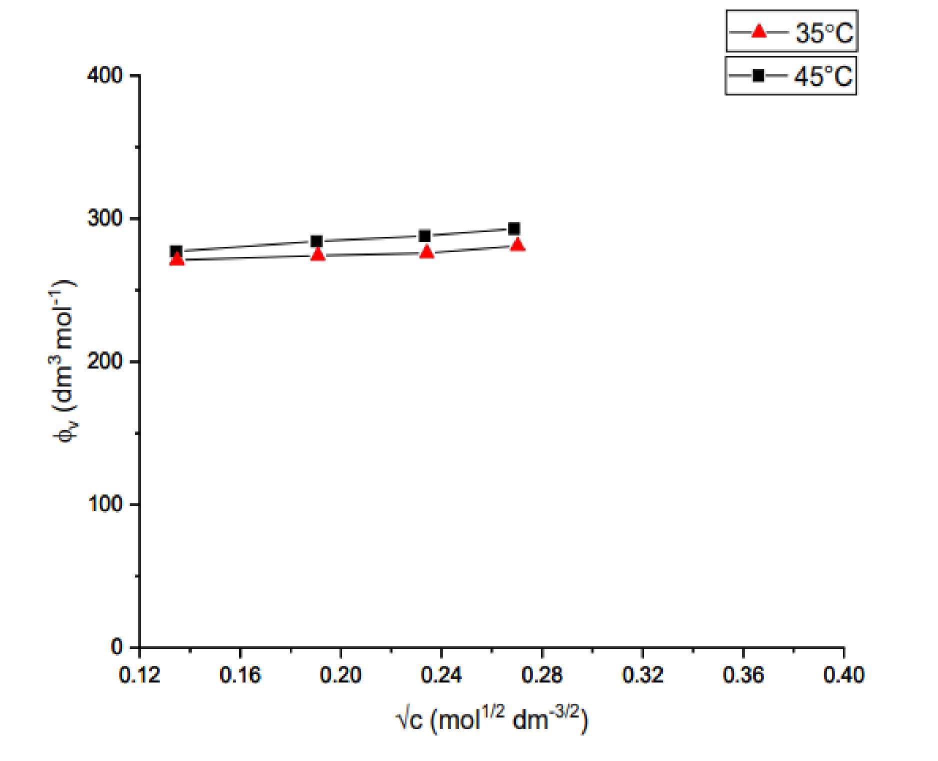


The graph between φ_v and √C for different electrolyte solutions Bu_4NI in 40% ethanol in water mixtures



The graph between φ_v and √C for different electrolyte solutions Bu_4NI in 50% ethanol in water mixtures



The graph between φ_v and √C for different electrolyte solutions Bu_4NI in 60% ethanol in water mixtures

TABLE 10

S_V values for some tetra butyl ammonium iodide indifferent Water- Ethanol mixture

S.No.	Composition of Ethanol in Water (v/v)	Dielectric constant (∈) as computed from the graph	SV -values ($dm^{9/2}$ $mole^{-3/2}\times 10^{-3}$) in different compositions of Water in Ethanol
			Bu_4NI
1.	40% Ethanol	57.5	-66.70
2.	50% Ethanol	52.0	53.80
3.	60% Ethanol	46.5	52.68