Verification of Masson's Equation by the Density and Apparent Molar Volume Prediction in Some Ternary Electrolyte Solutions

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Abstract

Density (ρ) and Apparent Molar volume (ϕ_v) are reported for ternary liquid mixtures of 1, 4-Dioxane, DMSO (Dimethyl Sulphoxide) and Water with some tetra alkyl ammonium iodide (R_4NI) salts over entire range of mole fractions at 303.15K and atmospheric pressure. The density for ternary liquid mixtures can be measured by using Magnetic Float Densitometer. Apparent molar volume has been calculated and estimated, the slope (S_v) is obtained by plotting the graph ϕ_v vs $\sqrt{C}$. This paper investigates the theoretical aspects of the nature of molecular interactions to see the validity of Masson's equation in ternary liquid mixtures. These observations were explained on the basis of slope (S_v) value by varying the dielectric constant (ϵ) of the selected components of the liquid mixtures.

Keywords: Masson's equation, Density, Dielectric constant, Molecular interaction, Sv-value, Ternary liquid mixture.

Introduction

Thermodynamic is a fundamental subject that is significantly valuable in the area of Chemical Engineering and Physical Chemistry. Focusing our work on the thermodynamic of the ternary liquid system (i.e. 1, 4-Dioxane + Dimethyl Sulphoxide + Water) containing four different types of tetra alkyl ammonium iodide salts separately namely Et_4NI, Pr_4NI, Bu_4NI and Pen_4NI at different % composition. Many industrial processes utilize aqueous and non-aqueous solutions containing several solute components[1]. The paper presents the nature of molecular interaction of aqueous/non-aqueous electrolytic system in terms of apparent molar volume, (ϕ_v) measurement. The parameter can be calculated from the direct measurement of density (ρ). The densities have been determined by Magnetic Float Densitometer[2]. These data are useful in process engineering, design applications and other related area[3-7].

The effect of a salt dissolved in a ternary mixed solvent has potential application in the molecular rearrangement, packing density, free volume or radial distribution function. However, the molecular interactions depend on forces between the molecules, their forms and volume of molecules. The apparent molar volume (ϕ_v) of the electrolytes in solution is given by Masson's equation[8] namely,

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

The ϕ_v's, were calculated using ρ and ρ_0 value for each electrolyte by using equation,

$$\phi_v = [1000(\rho_0-\rho)] /c\rho\rho_0 + M/\rho_0 \qquad (2)$$

Here, M is the molecular weight and C is the molar concentration of the electrolyte. The slope S_v may be positive or negative for common electrolytes and R_4NI salts for aqueous solution at ordinary concentrations, in which smaller chain of R_4N^+ cations have positive and larger chain of R_4N^+ cations have negative values of S_v[9]. In 1968 Millero[10-11] observed a negative Sv-value for $NaNO_3$ and NaBr in N-Methyl Propanamide and the explanation has been given on the basis of dependence of Sv-values on the dielectric constant of the solvent media.

Frank[12] explained the high activity coefficient 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. These observations confirm the formation of void space inside the enhanced water structure and R_4N^+ ions are accommodated in the void so formed. The fugacity of I^- ion is increased because fugacity of solvent and R_4N^+ ion is lowered. Therefore, the larger R_4N^+ ions seem to be solvated on account of hydrophobic enforcement of water structure, the extent values of activity coefficient of solution are obtained.

In our previous work[13-14], we have studied the validity of Frank's hypothesis in the solution of some R_4NI salts in binary solvent mixtures of Water + Isopropyl Alcohol, Water + 1, 5-Pentane Diol and DMF + 1, 5-Pentane Diol systems. These studies were done in aqueous – non-aqueous and non-aqueous- non-aqueous system at different temperatures to see whether such solute-solvent hating effect is still there and the structure of any selected binary solvents is influenced by ion-solvent interactions. From these observations, it confirms that the nature of enhancement of solvent structure is done by pure aqueous solutions or the binary solution mixtures in which water is necessarily to be used as one of the component.

Further extending the work to ternary liquid solution mixtures (i.e. 1, 4-Dioxane + DMSO + Water + R_4NI salts) of four different % compositions such as 0, 20, 40 and 60% DMSO (v/v) in which water is taken to be 40% constant at each time. The component of ternary liquid mixtures of varying dielectric constant (ε) plays a significant role in investigation. The aim of this work is to test the particular methods for density prediction and calculate the apparent molar volume of mixed aqueous/non-aqueous electrolyte solutions separately of selected different salts. These solution 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 change observed.

Experimental and Theoretical Methods

Materials:

The solvents, DMSO and 1, 4-Dioxane was of Qualigen's Glaxo grade, supplied by SD Fine Chem. Ltd. (Mumbai India) and it was purified, after drying on freshly ignited quicklime, 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} ohm^{-1} cm^{-1}. The purity of DMSO and Dioxane was checked by GC –MS (Shimadzu Model no. QP2010) and as found to be 99.2% and 99.4% respectively. The purified samples were stored in dark coloured bottles. All the tetra alkyl ammonium iodide salts, Et_4NI, Pr_4NI, Bu_4NI and Pen_4NI have been purchased from Sigma Aldrich, Mumbai (India), which were used in present investigation were purified by the method of Conway[15].

Methods:

The densities of selected ternary system were determined at different temperatures by magnetic float densitometer and calculated by using eq. 1.

$$\text{Density } (\rho) = (W+w+f\times I)/(V+w/\rho_{pt}) \tag{1}$$

The terms involved in this equation have their usual meanings. The data of solution mixtures, *i.e.*, weight, w used, current, I, passing in the circuit, ρ_{pt}, density of pt and V, volume of float. Before measuring the density of the solution, the dilatometer is calibrated with pure water using equation,

$$w = - [f / (1- \rho_{Water}/ \rho_{Pt}) \times I + (\rho_{Water} V-W)/ (1- \rho_{Water}/ \rho_{Pt}) \tag{2}$$

This equation now resembles with $Y = mX + C$, Where $m = - [f / (1- \rho_{Water}/ \rho_{Pt})$ = Slope of the line and $C = (\rho_{Water} V-W) / (1- \rho_{Water}/ \rho_{Pt})$ = Intercept of the line on Y-axis

The system is calibrated[2] at 25^0C by measuring hold down current (I), when various platinum weights were added to the float so that it just immersed in pure water. An attractive force is then exerted by passing current through the main solenoid so that the platinum point of the float touches the bottom of the solution container. A graph is then plotted between the weights, w and the corresponding hold down current, I. Using the known value of the density of water and the density of platinum at 25^0C, the value of the weight equivalent of current, f, is calculated by using the slope of the line. Similarly using weight of the float (W=77.4240g and intercept of the line, the volume of the float V at 25^0C is calculated. Now the densitometer is run in the solution of unknown density and various weights and corresponding hold down currents are noted. The density of the solution is, then, calculated by using eq. (1). We have measured the values of dielectric constant (ϵ) values were measured for different % compositions of 1, 4-Dioxane in binary liquid mixtures (DMSO + Water) with the help of BI-870 dielectric constant meter (absolute accuracy to ± 2%). By inserting the probe in the desired liquid and adjusting the two controls on the front panel accurate measurement of low and high dielectric constant, including mixed liquid & solutions. The dielectric constant (ϵ) of the liquid's sample is determined by measuring the current between the outer and inner cylinders of the probe. With a stable voltage source

and precisely known probe parameters, it is possible to display the dielectric constant directly. Calibration is simply done using the back panel adjustment with a liquid of known dielectric constant (ϵ).

Results and Discussion

The dielectric constants of binary solvent mixtures DMSO + Water ($\varepsilon = 66.4$) can be gradually decreased by adding 1, 4 – Dioxane ($\varepsilon = 2.25$) shown in Table 1. Water is taken to be constant (i.e. 40%) for all the selected components of ternary liquid mixtures and calculated the values of apparent molar volume (ϕ_v) at 303.15K were calculated. Thus, four types of Dioxane + DMSO + Water mixtures of varying dielectric constant were prepared namely, 0% Dioxane ($\varepsilon = 66.4$), 20% Dioxane ($\varepsilon = 61.5$), 40% Dioxane ($\varepsilon = 54.7$) and 60% Dioxane ($\varepsilon = 48.5$) in DMSO and Water (v/v).

Density of some R_4NI salt solutions in those solvent mixtures were measured experimentally and ϕ_v values were then calculated with molar concentration for each salt, ϕ_v vs. $\sqrt{C}$ curves were drawn for each salt in various compositions and S_v –values were calculated. The nature of curve in Fig. 1-4, shows that the apparent molar volume (ϕ_v) increases/decreases as well as gives straight trend with increasing molar concentration of all selected salts for different % compositions (v/v) in ternary liquid mixtures at 303.15K shown in Table 2.

From the experimental observations, it is clear that apparent molar volume (ϕ_v) increases at 0% and 20% DMSO in binary liquid mixtures (Dioxane + Water) with increasing concentration in all the cases of selected quaternary alkyl ammonium iodide salts, hence slopes were found to be positive at these percentage compositions. But at 40% and 60% DMSO, apparent molar volume (ϕ_v) decreases with increasing concentration of salts for all the cases, hence slopes were found negative for each salt. Such variations in the ϕ_v curves are shown in figure 1-2 in which straight lines show the increasing trends of ϕ_v values with increasing concentration, suggesting strong solute-solvent interactions. These were plotted against the square root of molar concentration of salt solution and data were regressed linearly according to equation.

Table 1: Measured values of dielectric constants (ϵ) by BI–870 Dielectric Constant Meter (absolute accuracy to ± 2%) for ternary liquid mixtures of 1, 4 – Dioxane + DMSO + Water at 313.15K

S.N.	% Compositions of Solvents			Dielectric Constants (ϵ)
	Dioxane	DMSO	Water	
1.	0	60	40	66.4
2.	20	40	40	61.5
3.	40	20	40	54.7
4.	60	0	40	48.5

Table 2: Summary of experimental data: % compositions, dielectric constant (ε), density (ρ), root square concentration (√C), and apparent molar volume (ϕ$_v$) calculated parameters for ternary liquid mixtures of at 313.15K.

0% DMSO + 60% 1, 4-Dioxane + 40% Water + Et$_4$NI salt				20% DMSO + 40% 1, 4-Dioxane + 40% Water + Et$_4$NI salt			
M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ$_v$ dm^3 mol^{-1}	M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ$_v$ dm^3 mol^{-1}
0.02	1036.6	0.1402	140.52	0.02	1053.8	0.1402	180.36
0.04	1038.8	0.2000	148.68	0.04	1055.2	0.2000	183.77
0.06	1040.4	0.2404	154.52	0.06	1056.0	0.2404	187.72
0.08	1041.8	0.2802	159.94	0.08	1056.8	0.2802	192.44
0.10	1043.0	0.3200	166.70	0.10	1057.6	0.3200	196.72
0.12	1044.2	0.3550	170.10	0.12	1058.2	0.3550	200.46
0.14	1044.8	0.3720	175.00	0.14	1058.8	0.3720	202.96
40% DMSO + 20% 1, 4-Dioxane + 40% Water + Et$_4$NI salt				**60% DMSO + 0% 1, 4-Dioxane + 40% Water + Et$_4$NI salt**			
M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ$_v$ dm^3 mol^{-1}	M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ$_v$ dm^3 mol^{-1}
0.02	1066.8	0.1402	129.14	0.02	1082.0	0.1402	200.66
0.04	1068.2	0.2000	126.76	0.04	1082.6	0.2000	197.70
0.06	1071.4	0.2404	124.24	0.06	1083.8	0.2404	195.58
0.08	1073.4	0.2802	122.42	0.08	1085.0	0.2802	194.68
0.10	1075.8	0.3200	120.34	0.10	1086.8	0.3200	192.10
0.12	1078.2	0.3550	119.62	0.12	1089.8	0.3550	191.90
0.14	1080.2	0.3720	117.76	0.14	1092.0	0.3720	190.24
0% DMSO + 60% 1, 4-Dioxane + 40% Water + Pr$_4$NI salt				**20% DMSO + 40% 1, 4-Dioxane + 40% Water + Pr$_4$NI salt**			
M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ$_v$ dm^3 mol^{-1}	M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ$_v$ dm^3 mol^{-1}
0.02	1039.2	0.1402	226.42	0.02	1053.2	0.1402	220.10
0.04	1041.2	0.2000	226.98	0.04	1056.4	0.2000	222.64
0.06	1044.0	0.2404	227.18	0.06	1059.6	0.2404	225.26
0.08	1046.4	0.2802	227.90	0.08	1060.0	0.2802	227.68
0.10	1048.8	0.3200	228.28	0.10	1061.2	0.3200	231.50

M moldm^{-3}	ρ kgm^{-3}	$\sqrt{C}$ mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}	M moldm^{-3}	ρ kgm^{-3}	$\sqrt{C}$ mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}
0.12	1051.0	0.3550	230.14	0.12	1062.8	0.3550	233.15
0.14	1052.8	0.3720	232.34	0.14	1063.6	0.3720	234.10

40% DMSO + 20% 1, 4-Dioxane + 40% Water + Pr$_4$NI salt				60% DMSO + 0% 1, 4-Dioxane + 40% Water + Pr$_4$NI salt			
M moldm^{-3}	ρ kgm^{-3}	$\sqrt{C}$ mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}	M moldm^{-3}	ρ kgm^{-3}	$\sqrt{C}$ mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}
0.02	1064.2	0.1402	199.20	0.02	1090.0	0.1402	239.40
0.04	1066.8	0.2000	197.72	0.04	1090.8	0.2000	234.60
0.06	1070.4	0.2404	195.88	0.06	1091.4	0.2404	229.98
0.08	1071.6	0.2802	192.42	0.08	1092.0	0.2802	225.58
0.10	1072.8	0.3200	190.98	0.10	1093.4	0.3200	220.10
0.12	1075.2	0.3550	187.20	0.12	1095.0	0.3550	215.82
0.14	1078.0	0.3720	185.68	0.14	1096.4	0.3720	212.94

0% DMSO + 60% 1, 4-Dioxane + 40% Water + Bu$_4$NI salt				20% DMSO + 40% 1, 4-Dioxane + 40% Water + Bu$_4$NI salt			
M moldm^{-3}	ρ kgm^{-3}	$\sqrt{C}$ mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}	M moldm^{-3}	ρ kgm^{-3}	$\sqrt{C}$ mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}
0.02	1039.4	0.1402	276.18	0.02	1053.4	0.1402	280.14
0.04	1041.4	0.2000	277.42	0.04	1056.8	0.2000	284.26
0.06	1044.4	0.2404	278.10	0.06	1059.2	0.2404	290.32
0.08	1046.8	0.2802	279.82	0.08	1060.8	0.2802	293.12
0.10	1049.0	0.3200	278.16	0.10	1061.4	0.3200	298.04
0.12	1050.0	0.3550	281.68	0.12	1062.2	0.3550	302.48
0.14	1052.2	0.3720	282.14	0.14	1062.8	0.3720	303.58

40% DMSO + 20% 1, 4-Dioxane + 40% Water + Bu$_4$NI salt				60% DMSO + 0% 1, 4-Dioxane + 40% Water + Bu$_4$NI salt			
M moldm^{-3}	ρ kgm^{-3}	$\sqrt{C}$ mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}	M moldm^{-3}	ρ kgm^{-3}	$\sqrt{C}$ mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}
0.02	1063.2	0.1402	285.64	0.02	1082.4	0.1402	318.66
0.04	1064.6	0.2000	283.82	0.04	1083.8	0.2000	311.20
0.06	1066.2	0.2404	280.80	0.06	1085.5	0.2404	302.75
0.08	1067.4	0.2802	278.18	0.08	1087.2	0.2802	295.90
0.10	1069.2	0.3200	275.60	0.10	1089.8	0.3200	288.18

| 0.12 | 1070.2 | 0.3550 | 273.64 | 0.12 | 1091.2 | 0.3550 | 281.06 |
| 0.14 | 1072.6 | 0.3720 | 270.92 | 0.14 | 1092.8 | 0.3720 | 272.80 |

0% DMSO + 60% 1, 4-Dioxane + 40% Water + Pen$_4$NI salt				20% DMSO + 40% 1, 4-Dioxane + 40% Water + Pen$_4$NI salt			
M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}	M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}
0.02	1040.0	0.1402	326.5	0.02	1053.6	0.1402	325.12
0.04	1041.6	0.2000	329.4	0.04	1056.9	0.2000	328.24
0.06	1045.2	0.2404	332.64	0.06	1059.0	0.2404	333.24
0.08	1048.2	0.2802	336.28	0.08	1060.4	0.2802	337.06
0.10	1051.0	0.3200	340.1	0.10	1061.2	0.3200	339.00
0.12	1052.8	0.3550	342.2	0.12	1062.0	0.3550	340.62
0.14	1054.0	0.3720	348.28	0.14	1061.6	0.3720	342.04

40% DMSO + 20% 1, 4-Dioxane + 40% Water + Pen$_4$NI salt				60% DMSO + 0% 1, 4-Dioxane + 40% Water + Pen$_4$NI salt			
M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}	M moldm^{-3}	ρ kgm^{-3}	√C mol$^{1/2}$dm$^{-3/2}$	Φ_v dm^3 mol^{-1}
0.02	1062.4	0.1402	371.46	0.02	1083.4	0.1402	350.62
0.04	1063.4	0.2000	367.62	0.04	1085.2	0.2000	345.20
0.06	1064.6	0.2404	364.58	0.06	1086.8	0.2404	339.46
0.08	1065.6	0.2802	359.22	0.08	1088.0	0.2802	331.94
0.10	1066.8	0.3200	357.74	0.10	1089.6	0.3200	327.21
0.12	1068.0	0.3550	354.62	0.12	1091.0	0.3550	320.44
0.14	1069.4	0.3720	351.60	0.14	1093.2	0.3720	313.50

For apparent molar volume at infinite dilution (ϕ^0_v) the experimental slope (S_v) is determined using least square fitting of ϕ_v values to Masson's equation. As the ϕ_v vs √C curves were found to be straight lines, it is clear that the Masson's equation is valid for all the salts at 0% and 20% DMSO in binary liquid mixtures (Dioxane + Water). But at 40% and 60% DMSO (figure 3-4), by seeing the nature of ϕ_v it decreases with increasing concentration of each salt, hence it is clear that Masson's equation is not applicable in that.
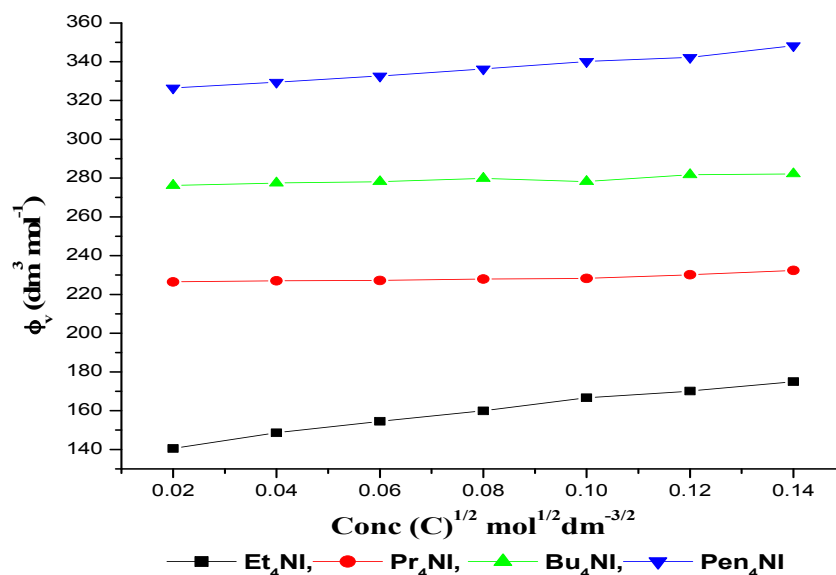
Fig. 1: Graph plotted between ϕ_v and $\sqrt{C}$ for different electrolyte solution in 0% DMSO + 60% Dioxane + 40% Water mixtures.
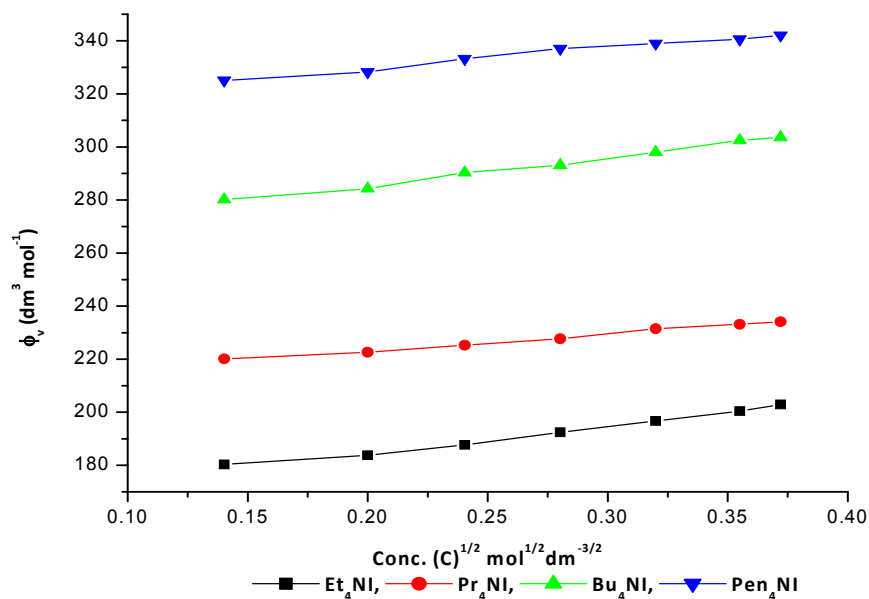

Fig. 2: Graph plotted between ϕ_v and $\sqrt{C}$ for different electrolyte solution in 20% DMSO + 40% Dioxane + 40% Water mixtures.
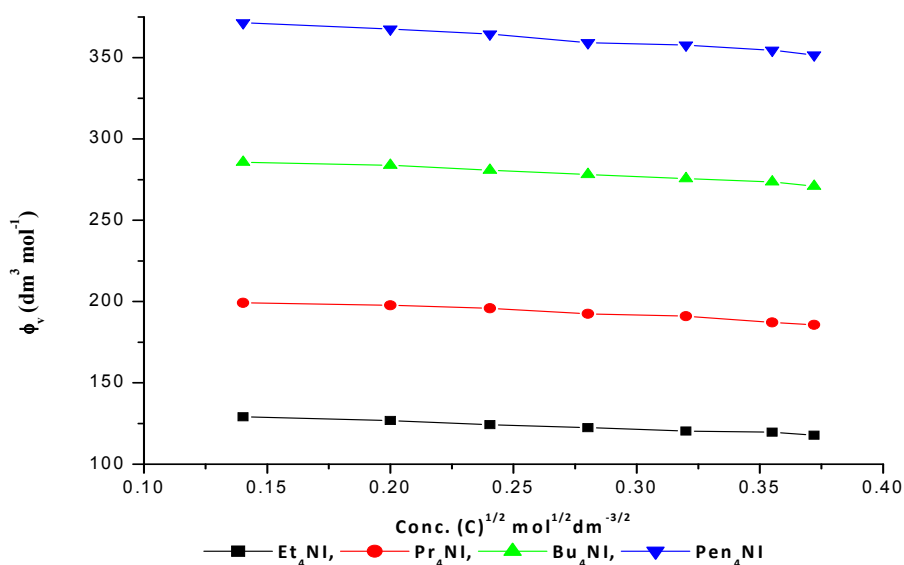
Fig. 3: Graph plotted between ϕ_v and $\sqrt{C}$ for different electrolyte solution in 40% DMSO + 20% Dioxane + 40% Water mixtures.
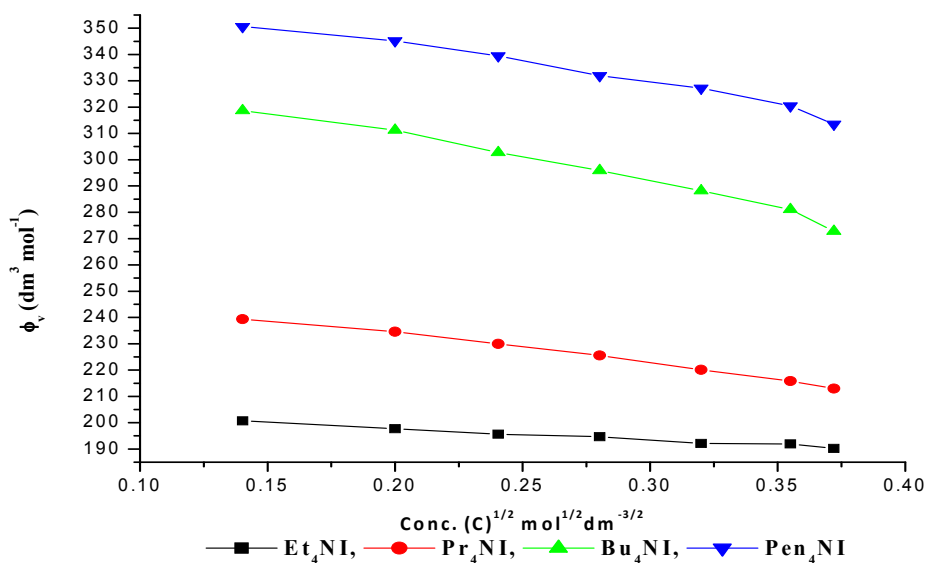

Fig. 4: Graph plotted between ϕ_v and $\sqrt{C}$ for different electrolyte solution in 60% DMSO + 0% Dioxane + 40% Water mixtures.

For understanding the molecular interaction between solute and solvent molecules and the packing efficiency of solute as well as solvent molecule studied in which solvent molecules were surrounded around the structure of Et_4N^+ and Pr_4N^+ cation while in the case of Bu_4N^+ and Pen_4N^+ cation solvent molecules are inserted into the vacant space of large alkyl chain length. Therefore, Bu_4N^+ and

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Pen_4N^+ cation form more compact packed structures than Et_4N^+ and Pr_4N^+ cation and also have more thermal stability.

For Et_4NI, Pr_4NI, Bu_4NI and Pen_4NI salts, ϕ_v is found to be positive at 0 and 20% DMSO while it shows negative value at 40 and 60% DMSO. From these observations, it is clear that the molecular interactions are very weak and very strong at 0% -20% and 40%-60% respectively for each salt selected in the given system. It is very interesting observation from the thermo-dynamical point of view, in which specific types of molecular interactions are involved.

Table 3: Estimated Slope (Sv) – values for some tetra alkyl ammonium iodides in ternary liquid mixtures of 1, 4 – Dioxane + DMSO + Water.

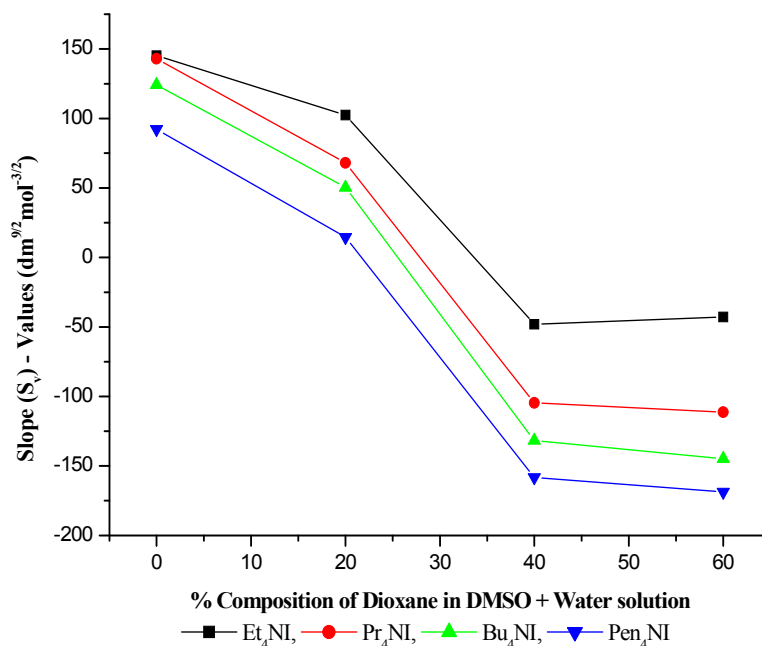| S. N.	% Compositions of Solvents			Dielectric Constants	Slope (S_v) – Values $dm^{9/2}mol^{-3/2}$			
	Dioxane	DMSO	Water	(ϵ)	Et_4NI	Pr_4NI	Bu_4NI	Pen_4NI
1.	0	60	40	2.25	+145.2	+142.98	+124.16	+92.22
2.	20	40	40	17.26	+102.5	+68.14	+50.32	+14.58
3.	40	20	40	31.48	-48.01	-104.64	-131.72	-158.20
5.	60	0	40	46.7	-42.8	-111.24	-144.85	-168.68

Fig. 5: Graph plotted between Slope (S_v) and % composition of Dioxane in DMSO +Water for different electrolyte solution.

By examining the S_v data of Table 3, it is quite clear that S_v values are positive as well as negative when the compositions of solvent mixture on the salt species are changed. Positive slopes are obtained for 0%-20% Dioxane while negative slopes for 40%-60% Dioxane in binary solvent system (DMSO+Water) for all the selected tetra alkyl ammonium cation are shown in figure 5. Positive as well as negative values of S_v indicate that the hydrophobic alkyl chain-solvent interactions are absent in positive slopes and present in negative slopes, because negative slopes (S_v), enforcement of solvent structure (i.e. 1, 4-Dioxane) are seen in ternary liquid mixtures at 0% and 20% DMSO for all the salts. Thus, the Frank's hypothesis of enforcement of water structure is seen to be applicable in selected ternary liquid mixture (i.e. DMSO + Dioxane + Water).

For a fixed solvent composition, S_v shows decreasing order when moving row wise from Et_4NI to Pen_4NI salt (Table 3), shows significant effect of size of solute molecule on the nature of molecular interactions. The S_v values decreases as the smaller molecule of solute are replaced by a large molecule successively. Such observations are found in each ternary solvent mixture composition. This trend can easily be interpreted by the two influencing factors – Firstly, increase of ionic size decreases the charge density of ion, which results in the weak ion-ion interaction with decreasing value of charge density and secondly, larger size alkyl chains provide large number of cavities inside them in comparison to smaller size alkyl chains.

Thus, interpretation of solvent molecules into bigger alkyl chain cation of Bu_4NI and Pen_4NI salts can take place which causes the reduced values of slope S_v. This decreasing trend of S_v-values can be explained on the basis of the effect of dielectric constant (ε) of the solvent media. It is known that electrostatic force of attraction, F, between the ions, is inversely proportional to dielectric constant of solvent medium (*i.e*. F α $1/\varepsilon$), The decrease in the value of dielectric constant of the solvent medium (i.e. from 0% Dioxane to 60% Dioxane in binary liquid mixture) results in strong electrostatic forces of attraction between the ions and hence ion - ion interactions become stronger and stronger as there is a gradual decrease of dielectric constant of the medium, thereby decreasing values of slopes are obtained. These observations also confirm, that the maximum number of solvent molecules of Dioxane which are inserted into the cavities of bigger size of alkyl cation results the negative value of S_v.

Conclusions

Following conclusions are drawn from the above discussion:

i. ϕ_v-values increases for all the selected quaternary alkyl ammonium iodide salts only at 0% and 20% DMSO while it decreases at 40% and 60% DMSO.

ii. Shows the validity of the Masson's equation for selected components of the ternary liquid mixtures at 0%-20%, which is verified.

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iii.   At 40% and 60% DMSO, Masson's equation is not applicable for any salt.

iv.   Presence of specific strong as well as weak dipolar type molecular interactions.

v.   Mostly, straight lines of ϕ_v-values are found for Et_4NI and Pr_4NI salt which is responsible for the very weak type of molecular interaction.

vi.   For Et_4NI and Pr_4NI salts, found positive values slope (Sv) and negative values for Bu_4NI and Pen_4NI salts are found.

vii.   The negative slopes values (Sv) indicate hydrophobic type of molecular interaction.

viii.   The solvent molecules are inserted into void space of large tetra alkyl ammonium ion (i.e, Bu_4N^+ and Pen_4N^+ cation) but such properties are not available in the case of small tetra alkyl ammonium ion (i.e. Et_4N^+ and Pr_4N^+ cation)

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