Study of the Influence of Alkyl Chain Cation Solvent Interactions on the Slope of φv v/s √C Curves in 1, 3-Butanediol-DMF Solvent Mixtures by Apparent Molar Volume Measurements

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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. Authors Archna, RD and VK managed the analyses of the study. Authors SG and JT managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The concept of Frank's hypothesis (that is the effect of large tetra alkyl ammonium iodides on the solvent structure, especially in the ion – ion and ion – solvent interactions) was found to be not applicable when water was replaced by one of organic solvent. That is, if study involves ion- ion and ion – solvent interactions in 1, 3 – Butane diol – DMF solvent mixture. The densities of these mixture and some adding tetra alkyl ammonium iodide salts solutions at different concentrations (0.02 – 0.14 M) have been determined at 298.15 K using Magnetic Float Densitometer technique. The apparent molar volume (ϕ_v) and apparent molar volumes of transfer $\Delta\phi_v^0$ (tr) of the electrolytes in above solvent mixtures were calculated. ϕ_v vs √C curves are plotted and explained the nature of molecular interactions by using slope (S_v) values. Also, the significant role of varying dielectric constants (ε) of the selected solvent mixtures in the ionic interaction is discussed.

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1. INTRODUCTION

A lot of works [1-17] has been done on the apparent and partial molar volumes of electrolytes and non electrolytes in aqueous, non aqueous and in binary solvent mixtures, eg. Aqueous – non aqueous and non aqueous- non aqueous type mixtures in the past. The work on apparent molar volumes of tetraalkyl ammonium halides in aqueous and non aqueous solvents done by several scientists in the past reveals that the slope Sv of φv vs √C curves of R_4NX salts is found to be positive in solvents of low dielectric constants medium. This slope is found negative for R_4NX salts, involving the larger of R_4N^+ ions, in solvents of high dielectric constants.

Frank [18] found special type of interactions between alkyl chain cation of R_4NX salts and water solvent which he called them as hydrophobic alkyl chain cation – water interactions. The negative slope of R_4NX salts obtained in water, according to him, is due to enforcement of water structure due to water hating nature (hydrophobic nature) of R_4NX salts. He thus proposed his hypothesis on the enforcement of water structure which is stated as the structure of water is enforced around the R_4N^+ ions on account of the water hating influence of the long alkyl chains. This result in the formation of void spaces inside the enhanced water structure and R_4N^+ ions are accommodated in these void spaces so formed. Because of this even the larger R_4N^+ ions seem to be solvated on account of hydrophobic enforcement of water structure. The addition of salt, thus, does not contribute to the volume of the solution as the cations hide themselves inside the cavities of water molecule structure and hence negative Sv values are found.

The validity of Frank's hypothesis was tested for one of the binary solvent mixtures where water is mixed with 1, 5 -pentane diol and similar studies were carried out for 1, 3 - butane diol – water was taken as the binary solvent mixture. In both these cases an attempt was made to see whether the Frank's hypothesis of enforcement of water structure by the hydrophobic alkyl chain cation-water interactions was still valid if, instead of taking pure water, it was taken as one component of the binary solvent mixture (aqueous-non aqueous).

The apparent molar volume (φv) of R_4NI salts (R = Et, Pr, Bu, Pen) were determined in 1, 5-pentane diol – DMF mixture. In this study an attempt was made to see whether the Frank's hypothesis was still applicable to a system of binary solvent mixture 1, 5-pentane diol – DMF, where component was replaced by an organic component DMF.

This paper also covers the studies of measurement of apparent molar volumes φv of R_4NI salts (R = Et, Pr, Bu, Pen) in binary solvent mixture 1, 3-butane diol – DMF to investigate whether the lyophobic alkyl chain cation – solvent interactions also exist and whether any of the structure 1, 3-butane diol or DMF is enforced by the influence of ion- solvent interaction taking place in the system.

At the end ion- solvent interaction is also interpreted in terms of apparent molar volumes of transfer parameter $\Delta\phi_v^0$ (tr).

2. MATERIALS AND METHODS

2.1 Instruments Used– Magnetic Float Densitometer, Dilatometer

The tetra alkyl ammonium iodide salts were purified by the method of Conway et al. [3]. N, N-Dimethyl Formamide (DMF) of Qualigen Glaxo grade, after drying on freshly ignited quicklime was purified by 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 purified samples were stored in the colored bottles. 20,40,60,80, % DMF (v/v) was used for preparing, 1, 3-butane diol –DMF mixtures in 1, 3-butane diol have not been reported in the literature so far. These have been determined graphically by assuming a linear relationship between % composition and dielectric constant values on y- axis, selecting first and last, as two extreme points, a straight line was drawn. The dielectric constant values of 20, 40, 60, 80% DMF (v/v) in 1, 3-butane diol were estimated by taking the intermediate values on the straight line of % composition – dielectric constant graph. These estimated values of dielectric constants, ϵ, with % composition of 1, 3-butane diol – DMF mixtures are shown in Table 1. The graph is shown in Fig. 1.

The density, d_0 of these solvent mixtures was determined by Magnetic float densitometer [19] at 298.15 K following the method, using equation,

$$d_0 = (W + w + f \times I) / (V + w / d_{pt}) \qquad (1)$$

The terms involved in this equation have their usual meanings. The weights, w, current, I, passing in the circuit and the corresponding values of d_0 as calculated by eq. 1 are given in Tables 4-7.

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

	Composition of mixtures (V/V)	Dielectric constant (ϵ)
1	20% DMF in 1,3-Butane diol	30.20
2	40% DMF in 1,3-Butane diol	31.80
3	60% DMF in 1,3-Butane diol	33.40
4	80%DMF in 1,3-Butane diol	35.00

The solution of Et_4NI, Pr_4NI, Bu_4NI and Pen_4NI salts of 0.02, 0.04, 0.06, 0.08, 0.10, 0.12 and 0.14 concentrations were prepared, one by one, in four 1, 3-butane diol – DMF mixtures eg. 20, 40, 60 and 80% DMF (v/v), taking one composition of solvent mixture at a time, Me_4NI was excluded from our study due to its solubility restrictions in these solvent mixtures. The density, d, of various solutions, was determined as usual.

Using the density, d_0 of solvent mixture and the density, d, of solution, the apparent molar volumes, ϕ_v were calculated by the following equation,

$$\phi v = [1000(d_0-d) / Cd_0] + [M / d_0] \qquad (2)$$

The ϕ_v – data have been shown along with the concentration of solutions in Table 2. The ϕ_v vs $\sqrt{C}$ curves were drawn for each electrolyte for each % composition of solvent mixture. These curves have been shown in Figs. 2-5. Then the slope S_v of ϕ_v vs $\sqrt{C}$ curves was calculated for each straight line. This slope is familiar as the Masson's slope and can be expressed by the equation,

$$\phi_v = \phi_v^0 + S_v \sqrt{C} \qquad (3)$$

Here, ϕ_v^0 is known as the apparent molar volume of electrolyte at infinite dilution.

The S_v data have been summarized in Table 3. ϕ_v^0 values can be obtained by extrapolating the ϕ_v vs $\sqrt{C}$ curve to the zero concentration axes. Thus ϕ_v^0 values were calculated for each electrolyte in each solvent mixture composition. Treating the ϕ_v^0 value to be as ϕ_v^0 (MS), thatis ϕ_v^0, values for each salt are also calculated from Figs. 2-5 by extrapolating the ϕ_v vs $\sqrt{C}$ curves to C=0 axis (y-axis). The intercepts on y-axis will give the values of transfer $\Delta\phi_v^0$. These values assume as ϕ_v^0 (MS) values (i.e. the apparent molar volume of salts at infinite dilution in mixed solvent system). The apparent molar volumes of transfer $\Delta \phi_v^0$ (tr) can also be calculated using the relation,

$$\Delta\phi_v^0 (tr) = \Delta\phi_v^0 (MS) - \Delta\phi_v^0(S) \qquad (4)$$

Here ϕ_v^0 (S) is the apparent molar volume of salts at infinite in pure solvent [20] (in this case DMF), at infinite dilution. The $\Delta\phi_v^0$ (tr) and ϕ_v^0 (MS) data have been given in Table 8. These data have been used for interpreting the ion-ion and ion-solvent interaction at the end of discussion.

3. RESULTS AND DISCUSSION

The estimated values of dielectric constants of 20, 40, 60 and 80% 1, 3-butane diol – DMF mixtures as calculated from graph (Fig. 1) are given in Table 1. The density values, d_0 of solvent mixtures of above compositions determined by Magnetic float densitometer are given in Tables 4 - 7. The ϕ_v – data for various R_4NI salt solutions of 0.02 to 0.14 M concentrations have been summarized in Table 2. ϕ_v vs. $\sqrt{C}$ curves for various salt solutions in different 1, 3-butane diol – DMF solvent mixtures have been given in Figs. 2-5. The S_v data of these curves are given in Table 3. The ϕ_v^0 (MS) values for R_4NI salts (R = Et, Pr, Bu, Pen) and $\Delta\phi_v^0$ (tr) data for various cases have also been summarized in Table 8.

It is clear by ϕ_v – data from Table 2 that, the apparent molar volume increases with the increase in concentration of the salt. This trend gives the positive S_v values for all electrolytes in various solvent mixture compositions in the entire range of salt concentration studied. The Figs. 2 – 5 indicate that, though the S_v values are positive, the magnitude of S_v goes on decreasing from Et_4NI to Pen_4NI salt in a given solvent mixture

composition. The curves indicate that magnitude of the slope too, goes decreasing for a given salt if the solvent mixture is varied by increasing the DMF content in 1,3 – butane diol – DMF mixture (i.e. if we go from 20 to 80% DMF solvent mixture). This trend is clear in Table 3.
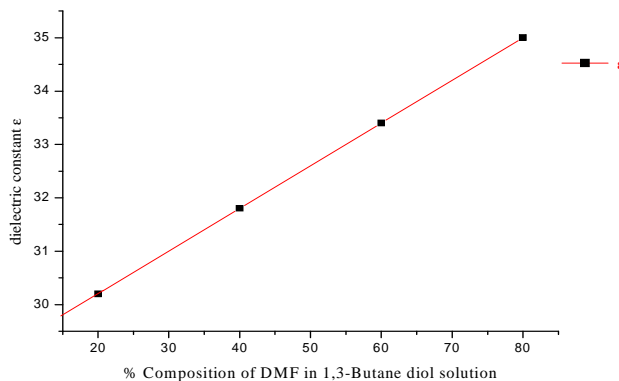

Fig. 1. Graph plotted between dielectric constant (ε) and % compositions of 1, 3 – butane diol in DMF solvent mixtures

Table 2. Apparent molar volume (ϕ_v) and $\sqrt{C}$ values for different electrolytes in different % compositions of DMF-1, 3-Butane Diol mixtures at 298.15 K

S. no.	% Composition of DMF in 1, 3-Butane diol	$\sqrt{C}$ $mol^{1/2}.dm^{-3/2}$	Apparent molar volume (ϕ_v) dm^3mole^{-1}			
			Et_4NI	Pr_4NI	Bu_4NI	Pen_4NI
1.	20%	0.141	88.37	141.80	178.06	209.37
2.	20%	0.200	101.07	149.42	183.21	213.96
3.	20%	0.245	109.98	155.66	188.27	217.55
4.	20%	0.283	117.97	161.55	192.32	220.59
5.	20%	0.316	125.37	165.69	195.36	223.65
6.	20%	0.346	131.31	169.62	198.40	226.20
7.	20%	0.374	136.85	173.15	201.29	228.14
8.	40%	0.141	95.22	149.48	184.43	216.31
9.	40%	0.200	105.67	154.84	188.26	218.61
10.	40%	0.245	112.89	159.01	190.90	221.06
11.	40%	0.283	119.05	162.89	193.49	222.57
12.	40%	0.316	124.98	166.02	195.05	224.09
13.	40%	0.346	129.96	168.45	196.95	224.94
14.	40%	0.374	133.95	171.00	199.03	226.44
15.	60%	0.141	129.97	180.74	220.24	255.56
16.	60%	0.200	138.11	184.77	222.18	257.52
17.	60%	0.245	140.13	187.84	223.86	258.18
18.	60%	0.283	148.89	191.44	225.49	259.02
19.	60%	0.316	153.93	194.01	227.09	259.94
20.	60%	0.346	157.97	196.41	227.97	260.22
21.	60%	0.374	161.02	201.52	229.06	261.01
22.	80%	0.141	136.88	188.28	229.25	266.05
23.	80%	0.200	142.54	191.34	230.22	266.33
24.	80%	0.245	146.88	192.85	230.84	266.69
25.	80%	0.283	150.88	194.96	231.22	266.92
26.	80%	0.316	155.09	196.46	231.78	267.20
27.	80%	0.346	158.08	197.81	231.97	267.35
28.	80%	0.374	160.95	199.07	232.03	267.56
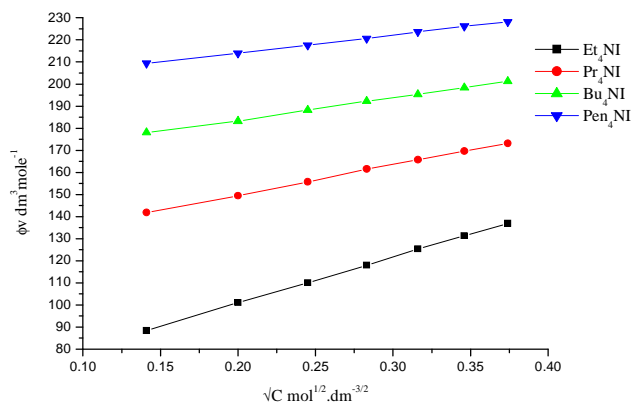
Fig. 2. Graph plotted between apparent molar volume (ϕ_v) and root of concentration ($\sqrt{C}$) for different electrolyte solutions in 20%DMF in 1, 3 – butane diol mixture,(v/v) at 298.15 K
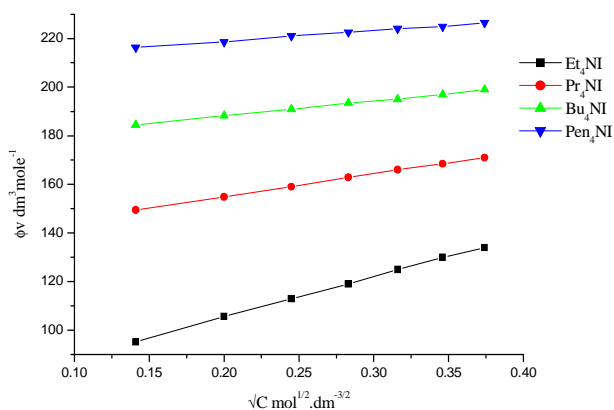


Fig. 3. Graph plotted between apparent molar volume (ϕ_v) and root of concentration ($\sqrt{C}$) for different electrolyte solutions in 40%DMF in 1, 3 – butane diol mixture,(v/v) at 298.15 K

It is evident from Table 3 that S_v values go on decreasing as the size of the salt molecule is successively increased that is the length of alkyl chain is increased. Since the size of alkyl chain cation increases from Et_4N^+ ion to Pen_4N^+ ion and the charge density on the ion will therefore decreases in the order,

$Et_4NI > Pr_4NI > Bu_4NI > Pen_4NI$
Decreasing order of the charge density $\longrightarrow$
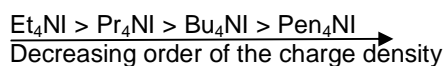
Ion – ion interaction depends on the charge density of the cation. High charge density of the ions gives rise to strong electrostatic ion – solvent dipole interactions or salvation and electrostriction (i.e. contraction of the solvent medium) which would be, per mole of the ions,

maximum at infinite dilution. As concentration increases, ion – ion interactions also increases; on the other hand, ion – solvent interaction or salvation, per mole of the ions decreases because of releasing the solvent molecules from the salvation sheath. This would give rise to increase in volume of solution and so the apparent molar volume of electrolyte would increase with in concentration. This implies a positive slope in ϕ_v vs $\sqrt{C}$ curves.

Greater is the charge density on the ion, stronger will be the ionic interactions and vice – versa. The charge density on the ions go on decreasing from Et_4N^+ to Pen_4N^+ cation, ionic interactions will become weaker and weaker as we move from Et_4NI to Pen_4NI salt. So the slope will go on

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diminishing. Since there is no negative slope found in the investigation for any salt in any solvent mixture composition, this indicates that there are no lyophobic ion – solvent interactions present in the solution. No enforcement of any solvent structure either 1, 3 – butane diol or DMF seems to be observed. There had been such lyophobic salt cation – solvent interactions present in the solution, as was discovered by Frank in the aqueous solution, a negative slope should have been observed due to the filling of void spaces of enforced solvent molecule structure (i.e. enlargement of structure of solvent molecule) by salt molecules. Some cavities are found in the larger tetra alkyl ammonium ions which are occupied by the solvent molecule and they are soon filled up. Thus, though the slope decreases solely due to penetration of solvent ions into cavities of R_4NI salts, it is never negative.
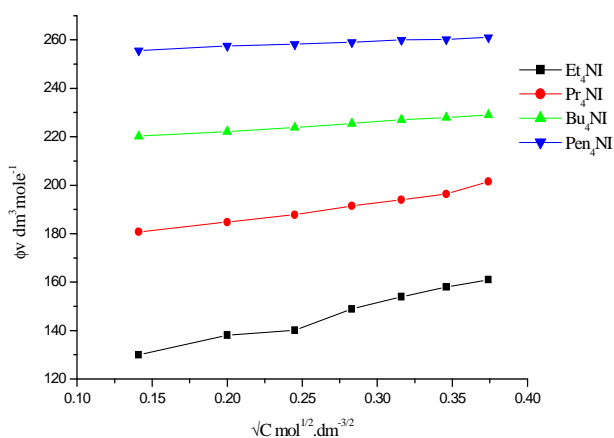
Fig. 4. Graph plotted between apparent molar volume (ϕ_v) and root of concentration ($\sqrt{C}$) for different electrolyte solutions in 60%DMF in 1, 3 – butane diol mixture,(v/v) at 298.15 K
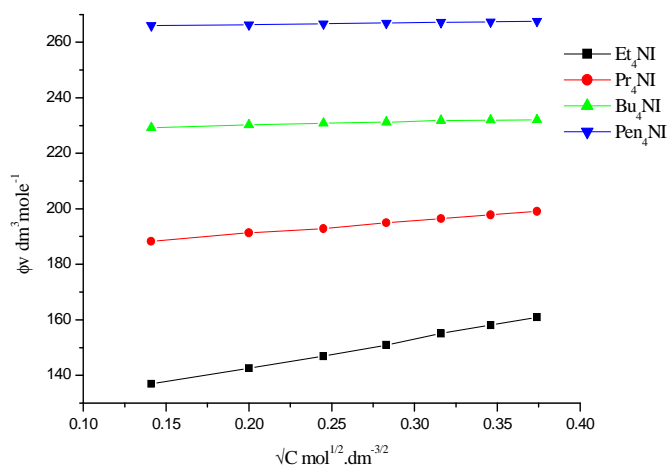
Fig. 5. Graph plotted between apparent molar volume (ϕ_v) and root of concentration ($\sqrt{C}$) for different electrolyte solutions in 80%DMF in 1, 3 – butane diol mixture,(v/v) at 298.15 K

Table 3. S_V values of some tetra alkyl ammonium iodides salt solutions in different compositions of 1, 3-butane diol – DMF mixtures

S. no.	Composition of solvent mixtures (v/v)	S_V – values ($dm^{9/2}mole^{-3/2} \times 10^{-3}$)			
		Et_4NI	Pr_4NI	Bu_4NI	Pen_4NI
1.	20% DMF in 1, 3-Butane diol (ϵ = 30.20)	208.50	136.16	100.79	81.68
2.	40% DMF in 1, 3-Butane diol (ϵ = 31.80)	166.81	93.29	61.54	43.49
3.	60% DMF in 1, 3-Butane diol (ϵ = 33.40)	137.13	85.07	38.73	22.35
4.	80% DMF in 1, 3-Butane diol (ϵ = 35.00)	104.57	46.07	12.27	6.64

Table 4. Estimated values of weight (w), used, current (I), passing in the circuit and the corresponding values of ϕ_v for 60%DMF in 1, 3-butane diol Et_4NI salt solution at 298.15 K

S. no.	Molarity (m) Mole.dm^{-3}	Weight (w) $Kg.10^{-3}$	Current (I) $Amp.10^{-3}$	Density (ρ_0) $Kg.m^{-3}$	$Conc.^{1/2} \sqrt{C}$ $mol^{1/2}.dm^{-3/2}$	Apparent molar volume ϕ_v dm^3mole^{-1}
1	0.02	2.10	277	969.885	0.141	129.97
2	0.04	2.20	335	972.199	0.200	138.11
3	0.06	2.30	395	974.553	0.245	140.13
4	0.08	2.40	425	976.308	0.283	148.89
5	0.10	2.50	456	978.083	0.316	153.93
6	0.12	2.60	483	979.779	0.346	157.97
7	0.14	2.70	509	981.454	0.374	161.02

Table 5. Estimated values of weight (w), used, current (I), passing in the circuit and the corresponding values of ϕ_v for 60%DMF in 1, 3-butane diol Pr_4NI salt solution at 298.15 K

S. no.	Molarity (c) Mole.dm^{-3}	Weight (w) $Kg.10^{-3}$	Current (I) $Amp.10^{-3}$	Density (ρ_0) $Kg.m^{-3}$	$Conc.^{1/2} \sqrt{C}$ $mol^{1/2}.dm^{-3/2}$	Apparent molar volume ϕ_v dm^3mole^{-1}
1	0.02	2.10	284	970.025	0.141	180.74
2	0.04	2.20	357	972.638	0.200	184.77
3	0.06	2.30	425	975.151	0.245	187.84
4	0.08	2.40	485	977.504	0.283	191.44
5	0.10	2.50	543	979.817	0.316	194.01
6	0.12	2.60	597	982.051	0.346	196.41
7	0.14	2.70	628	983.825	0.374	201.52

Table 6. Estimated values of weight (w), used, current (I), passing in the circuit and the corresponding values of ϕ_v for 60%DMF in 1, 3-butane diol Bu_4NI salt solution at 298.15 K

S. no.	Molarity (c) Mole.dm^{-3}	Weight (w) $Kg.10^{-3}$	Current (I) $Amp.10^{-3}$	Density (ρ_0) $Kg.m^{-3}$	$Conc.^{1/2} \sqrt{C}$ $mol^{1/2}.dm^{-3/2}$	Apparent molar volume ϕ_v dm^3mole^{-1}
1	0.02	2.10	302	970.383	0.141	220.24
2	0.04	2.20	397	973.435	0.200	222.18
3	0.06	2.30	489	976.427	0.245	223.86
4	0.08	2.40	578	979.358	0.283	225.49
5	0.10	2.50	664	982.229	0.316	227.09
6	0.12	2.60	751	985.120	0.346	227.97
7	0.14	2.80	777	987.951	0.374	229.06

Table 7. Estimated values of weight (w), used, current (I), passing in the circuit and the corresponding values of ϕ_v for 60%DMF in 1, 3-butane diol Pen_4NI salt solution at 298.15 K

S. no.	Molarity (c) Mole.dm^{-3}	Weight (w) Kg.10^{-3}	Current (I) Amp.10^{-3}	Density (ρ_0) Kg.m^{-3}	Conc.$^{1/2}$ $\sqrt{C}$ mol$^{1/2}$.dm$^{-3/2}$	Apparent molar volume ϕ_v dm^{3}mole^{-1}
1	0.02	2.10	324	970.822	0.141	255.56
2	0.04	2.20	441	974.312	0.200	257.52
3	0.06	2.30	558	977.802	0.245	258.18
4	0.08	2.40	673	981.252	0.283	259.02
5	0.10	2.60	728	984.662	0.316	259.94
6	0.12	2.85	756	988.111	0.346	260.22
7	0.14	3.10	780	991.480	0.374	261.01

Table 8. ϕv^0 (MS) and $\Delta\Phi v^0$ (tr) values for different electrolytes in 1,3-Butane diol – DMF at 298.15 K

S. no.	DMF in 1,3-Butane diol (v/v)	Et_4NI		Pr_4NI		Bu_4NI		Pen_4NI	
		Φv^0	$\Delta\Phi v^0$ (tr)	Φv^0	$\Delta\Phi v^0$ (tr)	Φv^0	$\Delta\Phi v^0$ (tr)	Φv^0	$\Delta\Phi v^0$ (tr)
1.	20%	59.10	-107.0	122.50	-116.30	167.56	-144.04	197.69	-180.23
2.	40%	71.99	-94.11	136.29	-102.51	175.84	-131.76	201.17	-167.73
3.	60%	109.83	-56.27	167.81	-70.99	214.59	-93.01	252.70	-125.20
4.	80%	121.73	-44.37	181.86	-56.94	227.70	-79.90	265.07	-112.83

Therefore Frank's hypothesis [18] of enforcement of water structure does not seen to be applicable in this case where water is replaced by DMF in the 1,3 – butane diol – water system. It is also evident from Table 3, that if we go down the columns for a salt, a slope goes on diminishing as the DMF content is increased in the 1,3 – butane diol – DMF mixture. The dielectric constant of solvent mixture increases as we move from 20% DMF (ε =30.20) to 80% DMF (ε = 35.00) in 1, 3 – butane diol. The dielectric constant of the medium has thus a significant influence on the magnitude of slope values. As the dielectric constant of the solvent mixture is increased the ion – ion interactions become weaker and weakerand so the S_v values show a decreasing trend down the columns. If we examine the downward trend in the S_v values down the columns, then, it is quite clear that though the S_v values are all positive, they were never found to be negative in this investigation. This once again proves that the enforcement of any of the structure of the solvents in the 1,3 – butane diol – DMF mixtures do not seem to occur by the influence of R_4NI salts. It is the dielectric constant of the solvent mixture which seems to be responsible for giving a decreasing trend of slopes column – wise. Ion – solvent interactions can also be interpreted in terms of $\Delta\phi_v^0$ (tr) and ϕ_v^0 (MS) values. These values are summarized

in Table 8. The data of this table indicate that $\Delta\phi_v^0$ (tr) and ϕ_v^0 (MS) values increases as we increase the concentration of DMF in 1,3 – butane diol – DMF mixture (i.e. As the concentration of 1,3 – butane diol is decreased in the mixture). The increase in $\Delta\phi_v^0$ (tr) and ϕ_v^0 (MS) values by increase in DMF content in the mixture may be attributed to decrease in electrostriction in presence of DMF. Thus the electrostriction effect, which brings about the shrinkage in the volume of solvent, is decreased in the mixed solvents as compared with that in either of the pure solvent component.

4. CONCLUSION

The following conclusions can be drawn from the outcome of investigation:

1. Frank's hypothesis of enforcement of water structure by large tetraalkyl ammonium salts not only is applicable in pure water solutions but seems to be applicable in non-aqueous - water mixture systems also. But if the water component of aqueous – non aqueous solvent mixture system is replaced by a solvent of an organic nature, say DMF, the Frank's hypothesis does not seem to be applicable for such non – aqueous – non – aqueous solvent mixture

systems. This is possibly because, though slope decreases slowly due to lesser ionic penetration effect, the cavities of non – aqueous solvents are soon filled up (due to non enforcement of solvent molecules that is no effect of R_4NI salts on the structure of non – aqueous solvent molecules.)

2. The dielectric constant of solvent medium has a marked effect in controlling the nature of Masson's slope, S_v.
3. The ions have different charge densities, depending on their relative sizes. The smaller ions have high charge density and therefore have strong ion – ion interactions and larger size of ions have low charge density on them showing weak ion – ion interaction.
4. From $\Delta\phi_v^0$ (tr) studies, it is understood, that ion – solvent interactions are weak in pure solvents in comparison to those in mixed solvents as electrostriction effect decreases in mixed solvent mixture.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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