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Determination of densities, apparent molar volume and apparent molar volume of transfer of some R_4NI salt solutions in NMF-DMSO mixtures using magnetic float densitometer and then to study of ionic Interaction at 303.15 K

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Binary solvent mixtures of different (%) compositions have been prepared at 303.15 K using tetra alkyl ammonium iodides (R_4NI) of 0.02 M to 0.14 M to investigate inter ionic interaction, ion-ion and ion solvent interactions in NMF-DMSO solvent mixture containing large cations of tetra alkyl ammonium iodides (R_4NI). The densities (ρ_0) of binary solvent mixtures and salt solutions have been measured by magnetic float densitometer. The apparent molar volume at infinite dilution ϕ_v^0, in the solvent mixtures, have been utilized to estimate the apparent molar volumes of transfer $\Delta\phi_v^0$ (tr), for various tetra alkyl ammonium iodide salts (R_4NI) from NMF-DMSO mixtures. The observed trend and variations of dielectric constant and density with different (%) composition of NMF – DMSO provide useful information about the structural interactions.

Keywords: Binary mixtures, Dimethyl sulfoxide, Density, Ion-ion interaction, Magnetic float densitometer

The apparent molar and density work[1,2], reveals that the determination of apparent molar volume is directly related to the density of solvent and solution. Apparent molar volume ϕ_v is further related to the electrolyte concentration by following the equation

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

Where, ϕ_v^0 is the apparent molar at infinite dilution; ‘c’ is the molar concentration and S_v is Masson's slope. This slope is a very important factor and seems to be a deciding factor for strong and weak ionic interactions.

Many scientists, in the past, have been working on apparent molar volume and trying to find out the nature of this slope. It was found to be positive in water[4-7] for common salts as well as for tetra-alkyl ammonium iodide (R_4NI) salts containing the small of the R_4N^+ ions, e.g., Me_4N^+ and Et_4N^+ but it was negative for R_4NI salts, containing the large R_4N^+ ions. Knowledge of the thermo-physical properties of individual components and their solvent mixture is of great help in understanding the complex structure of the liquid, which is the reason for the selection of this binary solvent system. Adding R_4NI salt of increasing alkyl chain lengths (i.e., from Et_4NI to Pen_4NI salt) to determine the molecular interactions in the solvent mixture at temperature 303.15 K. In 1968, Millero[27] observed a negative slope, S_v for $NaNO_3$ and NaBr in N-methyl propanamide (NMP). He ascribed the cause of the negative slope to be due to the high dielectric constant of the solvent mixture.

The ϕ_v work done by earlier scientists[4,10] indicates that it may have a positive or negative value in the same solvent depending on the electrolyte dissolved and also the same electrolyte may give positive and negative slopes with the variation in concentration (i.e. very low to high concentration). It means that nature, as well as, the concentration of the electrolyte affects the Masson’s slope (S_v). Their observation confirmed that the solute-solvent hating effect exists and the structure of any of the binary solvents mixture is affected by the ion –solvent interactions. Some workers suggested the negative slope for the larger of the R_4NI salts in water to be due to the enhancement of its tetrahedral structure by the hydrophobic R_4N^+ water interactions[5,19]. From the studies, it appears that, in general, a negative slope occurs only in solvents of high dielectric constant for R_4NX salts. Common salts generally show positive slope in low and high dielectric constant media except for few exceptions in which NaBr, $NaNO_3$, and NH_4Br in NMP[16,27] and NaCl, NaBr, KBr and KNO_3 in NMA[15] indicated negative slope. Many studies have been made on the intermolecular interaction in the binary liquid mixture at temperature 303.15 K using a magnetic float densitometer. The solvent mixture of two different natures, one being an aqueous and other the non-aqueous, may not give a clear picture of the slope due to the presence of one solvent in the other due to dissimilar nature. The study of thermodynamic properties of binary liquid containing electrolyte mixtures provides good measures of solute-solvent interactions. The present investigation is related to thermodynamic properties like density, dielectric constant, for the binary solvent mixture of (NMF+DMSO) with ionic species tetra alky ammonium iodide (R_4NI) salts.

Materials and Methods

All the chemical viz., NMF-DMSO organic solvents, and R_4NI salts, namely, Et_4NI, Pr_4NI, Bu_4NI, and Pen_4NI, etc. were obtained from Fluka Chemical Ltd India. The R_4NI salts used in the present investigation were purified by the method of Conway et.al., DMSO-NMF (Fluka, Purum, India) after being dried on freshly ignited quicklime, were purified by distilling under reduced pressure. The middle fraction of the successive distillate was redistilled under reduced pressure till the electric conductance of the final product was of the order of 10^{-7} $ohm^{-1}cm^{-1}$ or less. The purified sample was stored in dark-colored bottles and kept in a dry box until used. Also, the purity of the pure solvent was checked by comparing the measured densities and dielectric constant values with those reported in the literature. Using the purified solvents, measured at 303.15 K along with literature values and the same temperatures are given in the Table 1. NMF was used to prepare binary solvent mixtures of 0, 20, 40, 60, 80 & 100% with 100, 80, 60, 40, 20% DMSO (v/v). The value of dielectric constants (ϵ) for different % compositions of NMF + DMSO was measured with the help of BI-870 dielectric constant meter (absolute accuracy of ±2%).

Table 1 — Estimated values of dielectric constant obtained ($\in$) from the graph (NMF in DMSO)

% Composition of NMF in DMSO (v/v)	Estimated values Dielectric constant ($\in$)
0% NMF in DMSO	46.60
20% NMF in DMSO	73.00
40%NMF in DMSO	101.00
60% NMF in DMSO	128.00
80% NMF in DMSO	155.00
100% NMF in DMSO	182.40

The densities and dielectric constant of these solutions (non-aqueous and aqueous) were determined at temperature 303.15 K. Then the density of the solution/solvent is calculated by using the formula of a magnetic float densitometer.

$$\rho \text{ or } \rho_0 = \frac{W + w + f \times I}{\left(V + w/\rho_{pt}\right)} \quad \dots (2)$$

The values of parameters f = weight equivalent of current and V = volume of the magnetic float are determined by first calibrating the magnetic float densitometer. The magnetic float densitometer is calibrated with distilled water at 303.15 K by measuring the hold down current (I) when various weights w, are added to the float using the following equation.

$$w = -\left[\frac{f}{1-\rho_{H_2O}/\rho_{Pt}}\right] \times I + \left[\frac{\rho_{H_2O}\, v - W}{1-\rho_{H_2O}/\rho_{Pt}}\right] \quad \dots (3)$$

This equation resembles with y = mx+c and will give a straight line if weights, w, are plotted against current, I, the observations of weight, w, used and the corresponding hold down current, I am recorded in the Table 2 and the curve between ‘w’ and ‘I’ is shown in Fig. 1. Thus by calibration, the value of the weight equivalent of current was found to be f = 1.644 g/A and volume of float, V = 82.365 ml. In Eqn (2), W = weight of float, w = weight put on the magnetic float, ρ_{pt} = density of platinum. The observations, the weight ‘w' (in grams) and corresponding values of currents, I (in ampere) for these above-mentioned solvent mixtures were recorded in Table 3 and the densities $\rho_{0'}{}^{s}$calculated by Eqn (2) were also given in the last column of Table 3.

When w and I are known for a solution/solvent the density ρ of the solution or the density ρ_0 of solvent can be easily calculated using Eqn (2).

Apparent molar volume ϕ_v can be calculated by using the following equation

$$\phi_v = \frac{1000\,(\rho_o - \rho)}{C\,\rho_o} + \frac{M}{\rho_o} \quad \dots (4)$$

Table 2 — Calibration of magnetic float densitometer at 303.15 K

S. No.	Weight (w) (Kg x 10^{-3})	Current (I) (Ampere x 10^{-3})
1	4.720	0.350
2	4.650	0.390
3	4.520	0.465
4	4.410	0.530
5	4.280	0.605
6	4.160	0.675
7	4.060	0.735

The values of densities, ρ's, of salt solution, and corresponding apparent molar volumes, ϕ_v's of different electrolyte concentrations have been recorded in the table. The experimental slope S_v, as defined by Eqn (1) can be calculated for each line ϕ_v vs $\sqrt{c}$ curves.

Results and Discussion

The experiment values of solvent density and dielectric constant for the binary solvent mixtures (NMF-DMSO) containing R_4NI salts of different concentration 0.02 M to 0.14 M have been calculated at 303.15 K. The behaviour of the R_4NI salts in the non-aqueous and aqueous solution have been measured over a range of temperature in the present investigation studies were made with different % compositions of NMF in a binary system (NMF-DMSO) v/v, while DMSO varies with different % compositions 0, 20, 40, 60, 80, and 100% with NMF for the entire range of selected compositions. Taking 0% NMF in DMSO and corresponding dielectric constants (46.60) i.e. (0% NMF, 46.60) as the first point and 100% NMF in DMF and corresponding dielectric constant (182.40) i.e. (100% NMF, 182.40) as the last point and joining the two extremeness (Fig. 1) data, the dielectric constant over all intermediate composition of solvents i.e. 20, 40, 60 and 80% NMF can thus be estimated by this curve as shown in Fig. 2. The estimated values of dielectric constants are shown in Table 1 by putting an asterisk (*) on the value. When the dielectric constant becomes high (taking higher NMF content in the solvent mixture, the same salts should give a negative slope in ϕv vs √c curves. This is quite clear from our studies, summarized in Table 4.

All the four Et_4NI, Pr_4NI, Bu_4NI, Pen_4NI salts give a positive slope. In 0 % (ϵ = 46.6) and 20% (ϵ =73.00) NMF solvent mixtures. As the dielectric constant is increased further i.e. 40% (ϵ =101.0) NMF solvent mixture, Et_4NI, and Pr_4NI, give the positive value of slope Sv while Bu_4NI and Pen_4NI start giving the negative value of slope Sv. The order of the ionic sizes of these four salts is $Et_4N^+ < Pr_4N^+ < Bu_4N^+ < Pen_4N^+$, Et_4N^+, and Pr_4N^+, being smaller ions, the

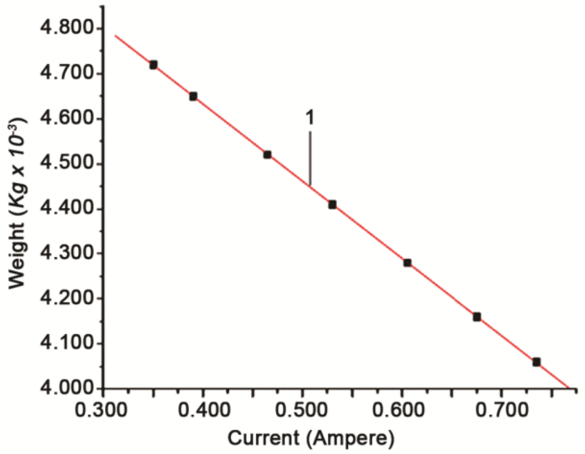

Fig. 1 — Graph between dielectric constant 'ϵ' and mixture composition

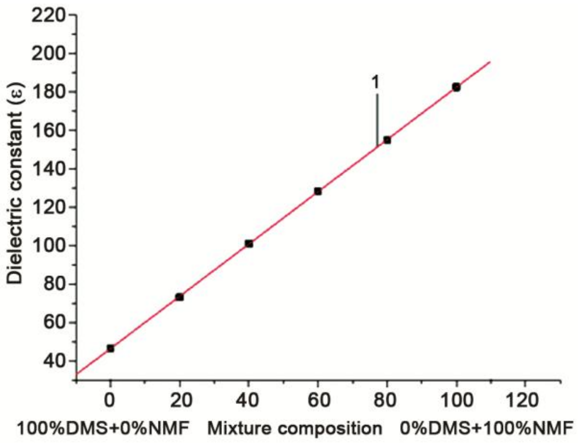

Fig. 2 — Calibration of magnetic float densitometer at 303.15 K

Table 3 — Density data of solvent mixtures NMF in DMSO) at 303.15 K

S. No.	%Composition (NMF in DMSO) with their Estimated values of dielectric constant	Weight (w) kg×10^{-3}	Current (I) (Ampere	Density(ρ_0) (kg dm^{-3})
1	0%NMF in (∈) = 46.6 (pureDMSO)	13.50	0.275	1.1010
2	20%NMF (∈) =73.0	11.00	0.810	1.0830
3	40%NMF (∈) =101.0	11.50	0.424	1.0650
4	60%NMF (∈) =128.0	8.00	0.731	1.0470
5	80%NMF (∈) =155.0	6.50	0.694	1.0290
6	100%(∈) = NMF Pure NMF(∈) = 182.0	5.00	0.658	1.0110

Table 4 — S_v-values tetra-alkyl ammonium iodide salt solutions in different compositions of NMF in DMSO

Composition of solvent mixture (v/v)	S_v ($dm^{9/2}mole^{-3/2}$) values			
	Et_4NI	Pr_4NI	Bu_4NI	Pen_4NI
0% NMF in (∈) = 46.6 (pure DMSO)	28.1	11.8	12.7	3.4
20% NMF (∈) =73.0	14.1	5.8	8.3	2.7
40% NMF (∈) =101.0	17.6	4.3	−15.7	−21.7
60% NMF (∈) =128.0	9.0	−15.3	−24.6	−34.1
80% NMF (∈) =155.0	−21.3	−48.9	−50.7	−69.9
100% (∈) =NMF Pure NMF(∈) = 182.0	-25.9	-55.5	-72.2	-58.2

ionic interactions are strong in presence of these ions as compared with Bu_4N+ and Pen_4N^+ ions hence the Et_4N^+ and Pr_4N^+ lead to the positive value of Sv while Bu_4N^+ and Pen_4N^+ give a negative value. In 60% (ϵ = 128.0) NMF in the DMSO mixture, Pr_4NI also gives the negative value of the slope Sv. If the NMF content is further increased in the solvent mixture i.e. in 80%(ϵ = 155.0) and 100% (ϵ =182.4) NMF in DMSO, all the four Et_4NI, Pr_4NI, Bu_4NI, Pen_4NI salts give the negative values of slope Sv because now the dielectric constant of the mixture is considerably raised to a higher value which weakens the ionic interactions. In that case, apparent molar volume ϕv decreases with an increase in electrolyte concentration. ϕv vs √c curve for all the R_4NI salts (R= Et_4, Pr_4, Bu_4,Pen_4) in various NMF -DMSO solvent mixtures within the concentration range 0.02M-0.14 M are straight lines. The Sv value, however, shows the decreasing trend from Et_4NI to Pen_4NI. The trend in slope variations with the size of electrolyte captions and with dielectric constant can be, very well seen in Table 4. The variation of slope Sv with dielectric constant can well be understood by plotting Sv values with dielectric constant and then to see the effect of dielectric constant on the Masson's slope Sv. These curves are shown in Fig. 3. The transitions in slope at a particular value of dielectric constant for each electrolyte, as calculated from the curves of Fig. 3, are shown in Table 5.

Table 5 — Transitions in slope at a particular value of dielectric constant for each electrolyte, as calculated from Fig. 3

Different salt Solutions	Transition points of dielectric constant of solvent mixtures
Et_4NI	136.00
Pr_4NI	110.94
Bu_4NI	82.98
Pen_4NI	76.89

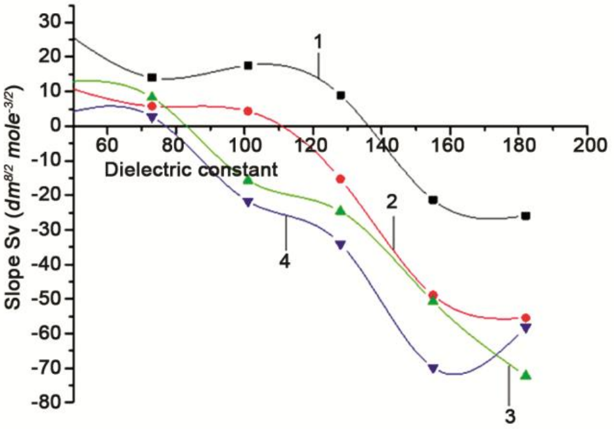

Fig. 3 — Curve between slope S_v and dielectric constant ‘ϵ’ for different R_4NI salt Solution of NMF in DMSO mixtures

The transition point (ϵ-values) for Et_4NI, Pr_4NI, Bu_4NI, and Pen_4NI are (ϵ = 136.00, ϵ = 110.94, ϵ = 82.98 and ϵ = 76.89), respectively. If ϕv vs √c curve is extrapolated to zero concentration (i.e. C=0), the ϕv value, at which the curve intersects the y-axis, is called $ϕv^0$, the apparent molar volume of electrolyte at infinite dilution. If the medium is pure solvent, it is shown as $ϕv^0$(S). The value of $ϕv^0$ in DMSO is taken as $ϕv^0$(S) and the value of $ϕv^0$ in NMF -DMSO mixture is taken as $ϕv^0$ (MS). The difference in these two values i.e. $ϕv^0$ (MS)– $ϕv^0$(S) is equal to $ϕv^0$(tr), the apparent molar volume of the transfer. The $ϕv^0$(S) and $ϕv^0$(MS), then $ϕv^0$(tr) values for R_4NI salts, in different (NMF+DMSO) composition, were determined from ϕv vs √c curves and are summarized Table 6. If we increase the dielectric constant of DMSO by mixing into it another solvent NMF of high dielectric constant in definite proportion, say, 0%(ϵ =46.6), 20%(ϵ =73.0), 40%(ϵ =101.0), 60%(ϵ = 128.0), 80%(ϵ =155.0) and 100%(ϵ = 182.4) NMF in DMSO, the slope Sv clearly shows that, on increasing the dielectric constant of the solvent medium, the Masson's slope goes on decreasing. NMF content in DMSO, the greater will be the dielectric constant of the medium. The high dielectric constant of the medium weakens the intrinsic forces. According to interpenetration theory of ionic interaction says that there is always a possibility of interpenetration of ion into ion or ion into solvent or solvent into ion in void spaces present in the larger of the species, leads to decrease in apparent molar volume ϕv with increase in concentration as the addition of electrolyte, in that case, does not contribute to volume of solution, instead the volume of solution decrease on increasing

Table 6 — Φ_v^0(S), Φ_v^0(MS) and $\Delta\Phi_v^0$(tr) values of tetra alkyl ammonium iodide salt solutions in compositions of NMF in DMSO

NMF in DMSO (v/v)	Et_4NI		Pr_4NI		Bu_4NI		Pen_4NI	
	Φ_v^0(S)/ Φ_v^0(MS)	$\Delta\Phi_v^0$(tr)	Φ_v^0(S)/ Φ_v^0(MS)	$\Delta\Phi v^0$(tr)	Φ_v^0(S)/ Φv^0(MS)	$\Delta\Phi_v^0$(tr)	Φ_v^0(S)/ Φ_v^0(MS)	$\Delta\Phi_v^0$(tr)
0%	159.36	-----	231.49	------	309.32	-----	380.63	------
20%	165.03	5.67	234.68	3.19	314.76	5.42	383.72	3.09
40%	166.38	7.02	235.61	4.12	320.57	11.25	389.56	8.93
60%	173.80	14.44	240.42	8.93	324.02	14.7	395.21	14.58
80%	181.10	21.74	248.44	16.95	337.70	28.38	406.07	25.44

salt concentration, the slopes are expected to be the row-wise trend reveals that the slope also decreases. The data clearly indicate that the size of the solute molecules also affects Sv values. Since the size of the molecule increases from Et_4NI to Pen_4NI, by increasing the size of the solute molecules, the slope Sv decreases. The row-wise fall in steepens of the curve may be attributed to being due to the following reason. The size of the electrolyte ions is increasing in the order Et_4N^+< Pr_4N^+, < Bu_4N^+< Pen_4N^+ as the larger the size of ion, the smaller will be its charge density. Therefore the charge density of ion will be in reverse order, i.e. it will be highest for Et_4N+ ion and lower for Pen_4N^+ ion. The ion-ion interaction in the case of Et_4N^+ ion will be greatest giving the large value of slope Sv in ϕv vs √c curves. This ion interaction will go on decreasing because of decrease seeing the amount of charge density of ions from Et_4N^+ ion to Pen_4N^+ ion. Thus the slope will also be in decreasing order and apparent molar volume of transfer $\Delta\phi^0$v(tr) referring to be the Table 6, it is evident that the value of ϕ^0v(MS), the apparent molar volume of electrolyte at infinite dilution in NMF-DMSO solvent mixture and $\Delta\phi^0$v(tr), the apparent molar volume transfer for the same electrolyte at infinite dilution, increase with decreasing concentration of DMSO in the solvent mixture. The increase in ϕ^0v(MS) and $\Delta\phi^0$v(tr) values with decreasing concentration of DMSO may be attributed to the decrease in electrostriction in presence of DMSO thus the electrostriction effect, which brings about the shrinking in the volume of solvent is decreased in the mixed solvent (NMF – DMSO solvent mixture) as compared with that in pure NMF. Since electrostriction primarily reflects electrolyte solvent infractions. The data of ϕ^0v(MS) in Table 6, also indicate the ϕ^0v(MS), values are positive and large for all the tetra alkyl ammonium iodide (R_4NI) salts in the all four % compositions 20, 40, 60 and 80% NMF mixtures in DMSO, showing the presence of strong ion-solvent interactions.

Conclusions

The apparent molar volume of electrolyte at infinite dilution in NMF-DMSO solvent mixture and $\Delta\phi^0$v(tr):, the apparent molar volume transfer for the same electrolyte at infinite dilution, increase with decreasing concentration of DMSO in the solvent mixture. The increase in ϕ^0v(MS) and $\Delta\phi^0$v(tr) values with decreasing concentration of DMSO may be attributed to the decrease in electrostriction in presence of DMSO thus the electrostriction effect, which brings about the shrinking in the volume of solvent is decreased in the mixed solvent Binary mixture (NMF – DMSO) as compared with that in pure NMF. All the four salts (Et_4NI, Pr_4NI, Bu_4NI, and Pen_4NI) give the negative/positive value of slope Sv because now the dielectric constant of the mixture is considerably raised to a higher value which weakens the ionic interactions. This is due to the accommodation of solvent molecules in a large cavity in case of higher alkyl chain length and breaking of hydrogen bonding as well as the formation of strong hydrogen bonding in case of lower alkyl chain length cation, that validated Frank's hypothesis.

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