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DETERMINATION OF DENSITIES OF SOME R_4NI- SOLUTION IN NMF-DMF SOLVENT MIXTURES AT 25^0 C BY MAGNETIC FLOAT DENSITOMETER AND STUDY MASSON'S EQUATION FROM Φ_V-DATA

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Abstract— A new technique of measuring the densities of solvents and solutions by using magnetic float densitometer has been given .The densitometer works on the electrostatic attraction of force developed by the passage of current through a solenoid. Using this technique, the densities (ρ_o's) of NMF-DMF mixtures at 0, 25, 50, 75, and 100% NMF in DMF (v/v) and those of solution (ρ_s's) of some tetra alkyl ammonium iodide salts namely Et_4NI, Pr_4NI, Bu_4NI and Pen_4NI have been determined experimentally by magnetic float densitometer at 25 ^{0}C. The apparent molar volumes (ϕ_v) have been calculated from density data and a graph is plotted against $\sqrt{C}$. The slopes, (S_v) of these curves show that in low dielectric constant (ϵ) medium all the four tetra alkyl ammonium salts have positive slope. But as the dielectric constant (ϵ) of the solvent medium is increased by adding NMF in DMF, each of the four electrolytes has negative slope. Such type of changes occurs due to the presence of specific molecular interactions between electrolyte ions and solvent molecules which are responsible for the stability of molecular structure and causes change in the thermo-dynamical properties. It has been explained on the basis of dielectric constant of the mixture, size and charge density of the electrolyte ion.

Keywords— Magnetic Float Densitometer, Apparent molar volume (ϕ_v), Dielectric constant (ϵ), N-methyl Formamide, Dimethyl Formamide, Tetra alkyl ammonium iodide salts, molecular interactions.

INTRODUCTION

The study of apparent molar volumes (ϕ_v) [1, 9, 14, & 19] of tetra alkyl ammonium salts R_4NX in water and in non-aqueous solvent mixtures, eg. Formamide, N-methyl Acetamide (NMA),N-methyl Propionamide (NMP), Dimethyl Sulphoxide (DMSO) and Propylene Carbonate (PC) shows that the slope $\mathbf{S_v}$ of apparent molal volume, (ϕ_v) Vs $\sqrt{\mathbf{C}}$ varies with solvent to solvent and also show positive as well as negative slope S_v – values for having low and high dielectric constant (ϵ) of the medium respectively. There are various non- aqueous solvents with water as one of the constituent were also used by the scientists to prepare solutions of R_4NX salts as Aqueous-Non-aqueous mixtures and then verifying the Masson's equation by using apparent molar volume (ϕ_v) data. The dielectric Constant of the medium was changed by adding, water to the non-aqueous solvent gradually.[13, 14] The results of these workers indicate that there seems to be an effect of dielectric of the combinations of two non- aqueous liquids giving the solvent mixtures of varying dielectric constants using R_4NI salts as solutes. But no one has carried out a systematic study covering entire range (lower to higher) of dielectric constant (ϵ) of the medium. It seemed interesting for us to examine the problem of change of slope $\mathbf{S_v}$, with dielectric constant of the medium by selecting such combination of liquid which can cover the lowest to highest value dielectric constant [11] and also whose density values fit in according to our magnetic float densitometer [10] requirement. This may perhaps throw a light on the effect of dielectric constant (ϵ) on the variation of the slope, $\mathbf{S_v}$ – values. Such combination of liquid mixtures (DMSO-Dioxane system) giving the lower to medium dielectric range [ϵ = 10.75 to 46.5] and the other combination, NMF- t-butanol Mixtures,

covering medium to high dielectric constant range [ϵ = 46.00 to 182.4] have already been studied. This Paper includes a system of two liquids namely NMF-DMF mixtures, which suits us according to needs and requirement of our Magnetic Float Densitometer. This system also covers medium to high dielectric constant range [ϵ = 36.7 to 182.40] of the liquid mixtures for our study. The Magnetic Float Densitometer can be operated with those liquids or liquid mixtures whose density is greater than the density of the magnetic float (that is it should be greater than 0.940010 g/ml).The density coverage of the selected system (NMF-DMF system) from 0% DMF to 100% DMF is from 0.944000 to 1.011006 g/ml. In this paper R_4NI salts (R= Et, Pr, Bu, Pen) are studied in NMF-DMF mixtures at varying compositions from the point of view of apparent molar (Φ_v) using Magnetic Float Densitometer.

MATERIAL AND METHODS

Dimethyl Formamide (DMF), after drying on freshly ignited quicklime, was purified by repeated vacuum distillation. The specific conductance of this sample was of the order of 10^{-7} mhos cm^{-1}. N-methyl Formamide [commercial grade, glaxo] was purified by azeotropic distillation with benzene. There are four tetra alkyl ammonium iodide salts, Et_4NI, Pr_4NI, Bu_4NI and Pen_4NI, which were used in the present investigation were purified by the method of Conway et al. Due to solubility restrictions Me_4NI salt was excluded from our present investigation. N-methy1 Formamide was gradually mixed with Di-methyl Formamide to get 0, 25, 50, 75 and 100% NMF in DMF (v/v). The dielectric constants (ϵ) of these solvent mixtures were not found to be reported in the literature. Therefore these were determined graphically by assuming the linear relationship between the dielectric constant (ϵ) and the composition. A graph was plotted between dielectric constant and composition of solvent mixture .The values of dielectric constants of 0, 25, 50, 75, and 100% NMF in DMF (v/v) mixtures, are computed from the graph. The values of dielectric constant (ϵ) are 36.7, 73.0, 109.5, 146.0 and 182.4 respectively.

Table 1: Estimated values of dielectric constants (ϵ) of the NMF+DMF Mixtures obtained from graph at 25^0C

Sr. No.	Composition of NMF in DMF (v/v)	Dielectric constant, (ϵ)
1	0% NMF	36.7
2	25% NMF	73.0
3	50% NMF	109.5
4	75% NMF	146.0
5	100% NMF	182.4

These solvent mixtures were used for making solutions of tetra alkyl ammonium salts. First of all the densities of 0, 25, 50, 75, and 100% NMF in DMF (v/v) mixtures were determined by Magnetic Float Densitometer at 25^0C. For this, the solvent mixture was taken in the solution container. The weights were added to the float so that it just touched the solution container. Then the current was passed in the pull down solenoid and then in the main solenoid by operating the circuit in proper sequential steps, ie by selecting push button no. 3 in top section; push button no. 2 in the battery section and then sequentially push button 1, 2 and 3 turn by turn in middle section of circuit. The observations were taken for weight 'w' and corresponding hold down current 'I', when the float touch the button of the solution container .For getting this equilibrium condition, the resistance bridge was also adjusted accordingly. Thus different observations were taken for 'w' and corresponding value 'I' for each solvent mixture was recorded in a table 2. Then ρ value

was calculated at 25^0C for each solvent mixture by using formula, $\rho_0 = (W + w + f \times I) / (V + w/\rho_{pt})$ [10]. Thus calculated ρ_0's were given in table 2.

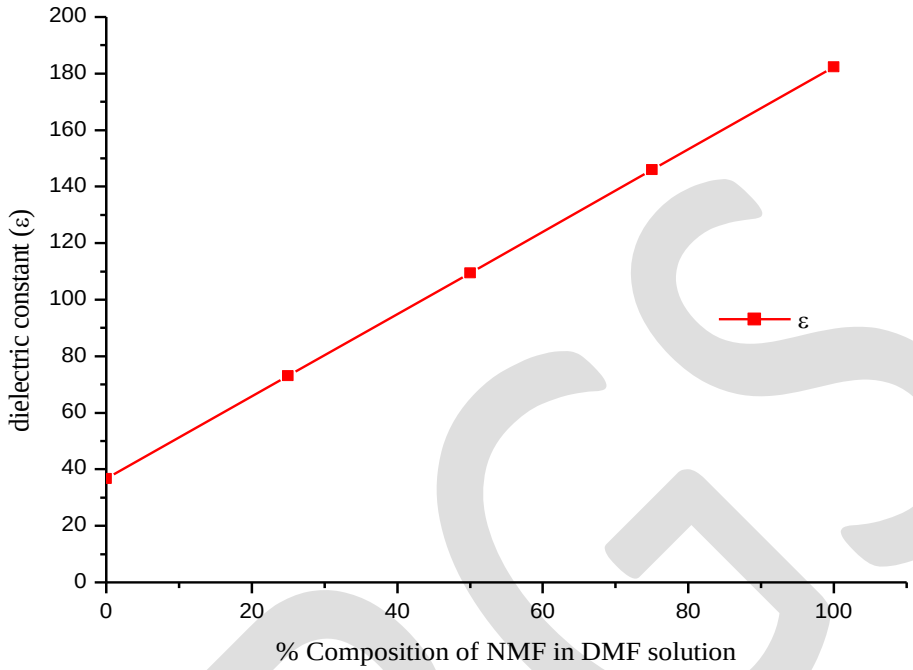

Figure1: Graph plotted between dielectric constant (ϵ) and % compositions of NMF in DMF solvent.

Table 2: Estimated values of densities (ρ_0's) of pure solvent mixtures at 25^0C

Sr. No.	% Composition (v/v) of NMF in DMF	W (g)	I (mA)	ρ_0 (g/ml)
1.	0% NMF	0.200	83.5	0.944000
2.	25% NMF	1.600	106.8	0.960700
3.	50% NMF	2.800	255	0.977549
4.	75% NMF	4.600	36.3	0.994000
5.	100% NMF	6.000	79.0	1.011006

RESULT AND DISCUSSION

The curves from Figure.2 of apparent molar volume ϕ_v v/s $\sqrt{C}$ for Et_4NI, Pr_4NI, Bu_4NI and Pen_4NI electrolytes are straight lines for the entire concentration range (0.002M – 0.026M) studied. Therefore Masson's equation $\phi_v = \phi_v^\circ + Sv\sqrt{C}$ [2, 3 12] is valid for these electrolytes in DMF - NMF solvent mixtures also. Fig. 2 shows that ϕ_v v/s $\sqrt{C}$ curves have positive slope in 0% NMF in DMF (i.e. in pure DMF) for all the above four electrolytes. The apparent molar volume (ϕ_v) increases with increase in electrolytes concentration and the density of Solutions also increases in each case as is evident from tables 3 to 6. Though the slope of each curve is positive yet it gradually decreases from Et_4NI to Pen_4NI. The value of apparent molar volume (ϕ_v) is greater for a molecule of larger size than the

preceding one at a definite concentration. [4, 5, 6, 7, 8] The slope Sv becomes negative as we mix 25 % NMF in DMF (ρ_0 = 0.960700, ϵ = 73.0), that is, if dielectric constant (ϵ) of the medium is increased from ϵ = 36.7 to ϵ =73.0 by adding N-Methyl Formamide.

Table 3: Estimated values of weight (w), used, current (I), passing in the circuit and the corresponding values of ϕ_V

For 75% NMF in DMF Et_4NI salt solution at 25^0C

Sr. No.	M (molarity)	w (g)	I (mA)	ρ (g ml^{-1})	√C $mole^{1/2}$ $dm^{-3/2}$	ϕ_V $dm^3.mole^{-1}\times10^3$
1.	0.002	4.610	40.5	0.994199	0.045	158.61
2.	0.006	4.620	57.0	0.994643	0.08	150.90
3.	0.010	4.630	74.0	0.995097	0.10	148.35
4.	0.014	4.640	92.0	0.995571	0.12	145.82
5.	0.018	4.650	110.0	0.996045	0.13	144.42
6.	0.022	4.660	130.0	0.996559	0.15	141.69
7.	0.026	4.670	147.5	0.997022	0.16	141.78

Table 4: Estimated values of weight (w), used, current (I), passing in the circuit and the corresponding values of ϕ_V

For 75% NMF in DMF Pr_4NI salt solution at 25^0C

Sr. No.	M (molarity)	w (g)	I (mA)	ρ (g ml^{-1})	√C $mole^{1/2}$ $dm^{-3/2}$	ϕ_V $dm^3.mole^{-1}\times10^3$
1.	0.002	4.610	39.5	0.994179	0.045	225.12
2.	0.006	4.620	54.0	0.994584	0.08	217.24
3.	0.010	4.630	70.0	0.995018	0.10	212.75
4.	0.014	4.640	87.0	0.995472	0.12	209.38
5.	0.018	4.650	102.5	0.995896	0.13	209.19
6.	0.022	4.660	122.5	0.996409	0.15	205.00
7.	0.026	4.670	140.0	0.996873	0.16	203.99

Table 5: Estimated values of weight (w), used, current (I), passing in the circuit and the corresponding values of ϕ_V

For 75% NMF in DMF Bu_4NI salt solution at 25^0C

Sr. No.	M (molarity)	w (g)	I (mA)	ρ (g ml^{-1})	√C $mole^{1/2}$ $dm^{-3/2}$	ϕ_V $dm^3.mole^{-1}\times10^3$
1.	0.002	4.610	39.0	0.994169	0.045	286.60
2.	0.006	4.620	53.0	0.994564	0.08	277.04

3.	0.010	4.630	68.5	0.994988	0.10	272.21
4.	0.014	4.640	85.5	0.995442	0.12	267.99
5.	0.018	4.650	102.5	0.995896	0.13	265.64
6.	0.022	4.660	122.5	0.996409	0.15	261.45
7.	0.026	4.670	140.0	0.996873	0.16	260.44

Table 6: Estimated values of weight (w), used, current (I), passing in the circuit and the corresponding values of ϕ_V

For 75% NMF in DMF Pen_4NI salt solution at 25^0C

Sr. No.	**M (molarity)**	**w (g)**	**I (mA)**	**ρ ($g\ ml^{-1}$)**	**√C $mole^{1/2}\ dm^{-3/2}$**	**ϕ_V $dm^3.mole^{-1}\times10^3$**
1.	0.002	4.610	39.5	0.994179	0.045	338.02
2.	0.006	4.620	54.0	0.994584	0.08	330.14
3.	0.010	4.630	70.0	0.995018	0.10	325.64
4.	0.014	4.640	88.5	0.995501	0.12	320.20
5.	0.018	4.650	105.5	0.995945	0.13	319.35
6.	0.022	4.660	127.5	0.996509	0.15	313.32
7.	0.026	4.670	150.0	0.997072	0.16	309.19

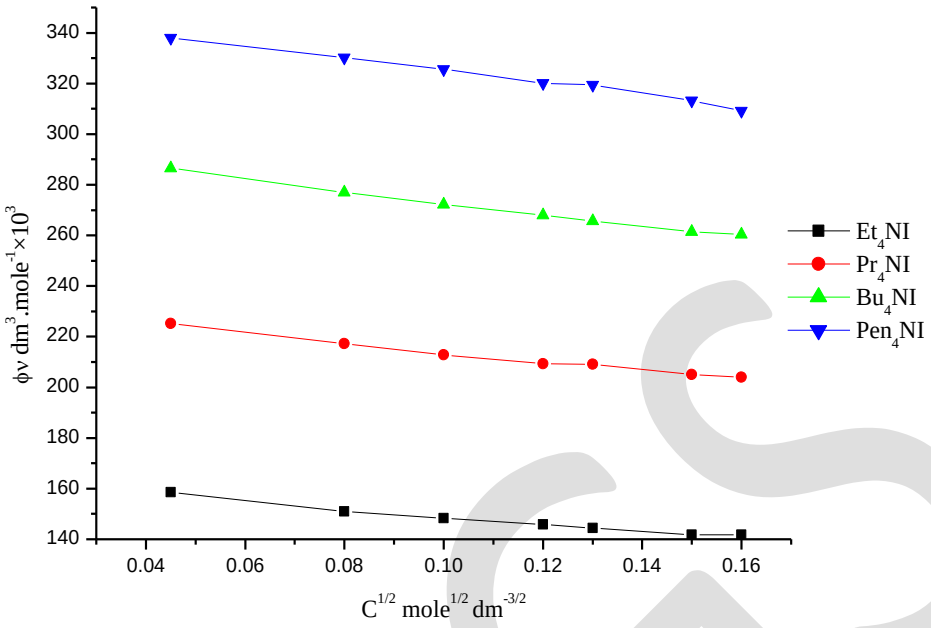

Figure 2: Graph plotted between apparent molar volume (ϕ_v) and root of concentration ($C^{1/2}$) of binary salt solutions (NMF + DMF + Salt).

The slope of all the electrolytes remains negatives in next other three compositions of NMF and DMF i.e. in 50, 75 and 100 % NMF. The electrolytes have positive slope in fig. 20 but these electrolytes have negative slope in fig. 21. As we proceed from fig. 21 to 24, the negative value of slope goes on increasing ie, the lines become more and more steep. Each figure shows that the steepness is higher for Pen_4NI than for Bu_4NI and, in turn, it is higher for Bu_4NI than Pr_4NI and so on. Thus it increases Et_4NI to Pen_4NI in the order $Et_4NI < Pr_4NI < Bu_4NI < Pen_4NI$ in a given solvent mixture having compositions 25% and more. In other wards if we look at the fig. 20 to 24 and see the nature of variation of slope from Et_4 NI to Pen_4NI in each solvent mixture (0, 25, 50, 75, and 100%, NMF in DMF). It decreases from smaller tetra alkyl ammonium ion to larger tetra alkyl ammonium ion, (ie. The negative slope becomes more negative). Table LXXII clearly show that for each electrolyte, the slope goes on decreasing as the dielectric constant is increased, by adding NMF gradually to DMF. It also decreases from Et4NI TO Pen4NI for a definite composition of solvent mixture. The observations of fig. 20 and 21 reveal that the changeover of the slope from positive to negative takes place at somewhere between 0% and 25% NMF, that is, between the dielectric constant ϵ = 36.7 and 73.0.

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CONCLUSION

The apparent molar volumes (ϕv) are positive and large for all the tetraalkyl ammonium salts in all the % compositions of NMF in DMF solvent due to the presence of weak ionic interactions of the solvent molecule. Thus we conclude that the variation of slope S_v– value from Et_4NI (smaller in size) to Pen_4NI (larger in size) shown in table no. 7. Table.7 clearly indicates that the S_v– value goes on decreasing as the dielectric constant (ϵ) is increased for each electrolyte, by adding NMF to DMF gradually to a definite % composition of solvent mixture. This observation confermed that the changeover of the slope from positive to negative takes place at somewhere between 0 % and 25 % NMF (ϵ =36.7 to 73.0)

REFERENCES:

[1] Pathak R N, Saxena I, Archana and Mishra A K, (2009) "Study of the Influence of Alkyl Chain Cation Solvent Interactions on the Slope of ΦV vs. √C Curves in 1,5-Pentane Diol - DMF Solvent Mixtures by Apparent Molar Volume Measurements"Indian Council Chem., 26(2), 170.

[2] Parmar M L and Guleria M K, (2009) "Partial molar volumes of oxalic acid and its salts in water-rich binary aqueous mixtures of methanol"Indian J. Chem., 48 (A), 806.

[3] Bhattarai A and Das B, The Effects of Concentration "Temperature and Solvent Composition on Partial Molar Volumes of Cetytrimethylammonium Bromide in Methanol– Water mixed Solvent Media" J Nepal Chem Soc., 2008 / 2009, **23**, 82

[4] Palani R, Geetha A and Saravanan S, Rasayan "Intermolecular interactions of some amino acids in aqueous 1, 4-dioxane solutions at 298.15k" J Chem., 2008, **1(3)**, 495-502.

[5] Romero Carmen M and Paez Manuel S "Volumetric Properties of Aqueous Binary Mixtures of 1-Butanol, Butanediols, 1, 2, 4 -Butanetriol and Butanetetrol at 298.15 K"J Solution Chem., 2007, **36,** 237-245.

[6] Kandpal K, Joshi B K, Joshi S K and Kandpal N D, "Interaction Studies of Dilute Aqueous Oxalic Acid" E- J Chem., 2007, **4(4)**, 574-580

[7] M. Deetlefs, K. Seddon, M. Shara, (2006), "Predicting physical properties of ionic liquids" Phys. Chem. Chem. Phys.8, 642–649.

[8] Ali A., Hyder S. And Yasmin A, "Viscometric studies of α-amino acid in aqueous NaCl and $MgCl_2$ at 303K" Indian J. Phys., 2005, 79,157.

[9] Deshmukh M M, Sastri N V and Gardre S R, J Chem Phys., 2004, **121(24),** 12402; DOI:10.1063/1.1819892.

[10] Pathak R N and Saxena I, "Magnetic float densitometer - A modified version" Indian J Eng Mat Sci., 1998, **5**, 278-284.

[11] Millero F J, "Structure and Transport Process in Water and Aqueous Solutions" Sharma R A, Ed., Wiley- Inter Science, New York W.Y. 1971, Chapter 15,

[12] Millero F J, Chem Rev, "Molal volumes of electrolytes"1971, **71**, 147-176; DOI: 10.1021/cr60270a001.

[13] Gopal R and Siddiqi M A, "Variation of partial molar volume of some tetra-alkylammonium iodides with temperature in aqueous solutions" J Phys Chem., 1968, **72**, 1814.

[14] Saxena I, Devi R, Kumar V, "Determination of densities of some R_4NI- solution in DMSO-Dioxane solvent mixtures at 25^0C by magnetic float densitometer and then study Masson's equation from ϕ_v data." Indian journal of Applied Research, vol: 5| Issue: 3| march 2015|ISSN-2249-555X, 518-519.

[15] Sonar AN, Pawar NS, "Acoustic and viscometric properties of Digoxin and Thiabendazole in 1, 4- Dioxane at 303K." E-Journal of chemistry, 2010, 7(3), 789-794.

[16] Pathak RN, Saxena I, Archana, Kumar R, Singh N, "Study of the influence of alkyl chain cation- solvent interactions on the slope of ϕ_v vs √C curves in 1, 5- Pentane Diol- DMF solvent." Chemical Science Transactions, 2014, 2(1), 87-92.