Study of Ionic Interactions in Solution of Some Tetraalkylammonium Iodides in N-Methylformamide-T-Butanol Mixtures by Magnetic Float Densitometer.

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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□'s) of N-methyiformamide (NMF)-t-butanol mixtures at 22,40, 60, 80,& 100% N-methylformamide in t-butanol (v/v) and those of solution (ρ□'s) of some tetraalkylammonium iodide, namely Et_4NI, Pe_4NI, Bu_4NI &Pen_4NI in these solvent mixtures have been determined experimentally by magnetic float densitometer at 25□c. The apparent volumes have been calculated from density data and plotted against √conc. The slopes of these curves show that in low dielectric constant medium (22%NMF, Є=46), all the four tetraalkylammonium salts have positive slope. But as the dielectric constant of the solvent medium is increased by adding N-methylformamide in t-butanol, each of the four electrolytes has negative slope. The data have been explained on the basis of dielectric constant of the solvent mixtures and size of the electrolyte ion.

Keywords- Densitometer, Apparent molar volume, Dielectric constant.

Introducation

Ion- ion and solvent interactions in different electrolyte solution using aqueous and non aqueous mixtures as the solvent. Their basic approach was, first to find out the density, from the density data the apparent molar volumes ($□_v$' s)were calculated to explain ion-ion and ion- solvent interactions and slope (S□) of Masson's equation.

$$□□ = □□□ + S□ \sqrt{C} \qquad (1)$$

Where □□□ is the limiting apparent molal volume and C, be the molar concentration The accuracy of the measurements of □□ of electrolytes depends on the accuracy with which the densities of the electrolyte solution are measured, as □□ is also related with the density of the solution in the manner.

$$□□ = 1000\ (ρ□□\ ρ)/ρ□C+M/ρ□ \qquad (2)$$

Where ρ = density of solution

ρ□ = density of solvent mixture

M = molecular weight and

C = concentration. (In moles dm□^{3}of an electrolyte)

That is why; we have used a new technique of density measurements of solvent /solvent mixtures/solution using Magnetic Float Densitometer. Our apparatus design was such it could measure the density of those solution /solvent mixtures whose value was not less than 0.940010 g/ml. the density of the float. To study the apparent molal volume of R□NI salts (R=Et, Pr. Bu & Pen) in NMF-t- butanol mixture at 25°c, five compositions of the mixture 22, 40, 60,80 & 100% NMF (v/v) have been selected. The dielectric constants of these mixtures have been estimated by plotting a graph, assuming a linear relationship between composition and dielectric constant.

Experimental

The method of measurement of densities (ρ□'s) of solvent mixtures and the densities (ρ□'s) of solutions by magnetic float densitometer have been given in detail elsewhere.[5]t-butanol was dried overnight over freshly ignited quicklime and fractionally distilled (b.p.82°c), collecting the fraction. Commercial grade methylformamide was purified by azeotropic distillation with benzene.

Tetraalkylammonium iodide were purified in the usual manner, dried and kept in vacuum desiccators. N-methylforamide was mixed with t-butanol in certain definite proportions, e.g., 22,40,60,80 & 100% NMF (v/v) to get the solvent mixtures of varying dielectric constant. Since the dielectric constants of these mixtures were not available in the literature, the same were computed by assuming a linear relationship between compositions and dielectric constant and plotting a graph in them, the mid-values of dielectric constant computed from the graph (Fig.1) were shown in the Table.1 along with the two extreme values. Five compositions (22, 40, 60, 80 and 100% NMF) of solvent mixtures were prepared. The solution of Et□NI, Pr□NI, Bu□NI and Pen□NI were prepared on molal basis using these solvent mixtures. The densities of the solvent mixtures (Ref.Table 2) and the solution (Ref. Table 3-6) were determined by the Magnetic Float Densitometer. In the same manner described earlier in our previous communication[5]. The observations have been summarised in twenty two tables after converting data of molality into molarity. But here only one set of such tables are included in this paper for the sake of convenience. From the density data apparent molal volume (Φ□'s) were calculated as usual. The graphs were plotted in Φ□ vs √C for each electrolyte using the data, only one such plot is shown here (Ref.Fig.2, Table 3-6).

Result and Discussion

□□ vs √c curves were found to be straight lines in each case, therefore, Masson' equation holes good for all the four R□NI(R=Et, Pr, Bu & Pen) salts in various NMF–t-butanol mixtures in the entire concentration range selected. If the dielectric constant is varied by increasing the NMF content in t-butanol solvent, the slope of φ□ vs √C curves also changes. In low dielectric constant medium (22%NMF, Є=46) all the four tetraalkylammonium iodide salts, Et□NI, Pr□NI, Bu□NI, and Pen□NI, have positive slope through the value of the slope decreases from Et□NI to Pen□NI. But as the dielectric constant is increased by adding NMF in t-butanol slowly up to 40% NMF,(Є□□ =78), each the four electrolytes has negative S□ value. The experimental slopes, (S□'s) are found to be negative in higher dielectric constant- mixtures, e.g., 60, 80 and 100% NMF content in t-butanol.

TABLE 1 Dielectric constant, Є, obtained from graph

Composition of NMF in t butanol (v/v)	Dielectric constant (ϵ)
0% NMF	9.66
22% ”	46.00
40% ”	78.000
60% ”	113.00
80% ”	147.00
100% ”	182.00

TABLE 2 Densities (ρ□'s) of solvent Mixtures at 25□c

Sl. No.	%Composition (v/v) of NMF in t-butanol	W (g)	I (mA)	ρ□ (g/ml)
1	22% NMF	0.200	58	0.943490
2	40% ”	1.200	44	0.954811
3	60% ”	2.000	30	0.963802
4	80% ”	4.000	53	0.987401
5	100% ”	6.000	79	1.011006

The whole picture is quite clear from the data Table7.It is also evident from this Table that as the size of the electrolyte molecule is increased in a solvent mixture, the S□ values goes on decreasing. This happens to be the case in every solvent mixture. This means that not only the dielectric constant that affects the slope but it the size of the electrolyte molecules also which has to be taken into consideration in the variation of the slope in Φ□ vs. √C curves. Thus the investigation of the apparent molal volumes of the R□NI salts in NMF-t-butanol solvent mixtures reveals that the dielectric constant of the medium and the size of the electrolyte molecules both are the deciding factors in controlling the slope of Φ□ vs. √C curves.

TABLE 3 22%NMF in t-butanol Et□NI = 257.16, ρ□=0.943490, Є=46.00

Sl.N0.	M (molarity)	W (g)	I (mA)	P ($g\ ml^{-1}$)	√c ($mol^{1/2}$) dm^{-3}/□	□□ ($dm^3 mole^{-1}$)
1.	0.002	0.200	76	0.943849	0.045	81.58
2.	0.006	0.250	82	0.944549	0.080	86.98
3.	0.010	0.300	86	0.945210	0.100	90.24
4.	0.014	0.350	90	0.945870	0.120	92.98
5.	0.018	0.400	93	0.946510	0.130	94.48
6.	0.022	0.450	94	0947110	0.150	98.06
7.	0.026	0.500	96	0.947730	0.160	99.52

TABLE 4 22%NMF in t-butanol Pr□NI=313.27, ρ□=0.943490, Є□=46.00

Sl.No.	M (molarity)	W (g)	I (mA)	ρ (gml^{-1})	√c ($mole^{1/2} dm^{-3}$/□	□□ $dm^3 mole^{-1}$
1.	0.002	0.200	79	0.943909	0.045	107.48
2.	0.006	0.250	92	0.944749	0.080	111.26
3.	0.010	0.300	104	0.945569	0.100	113.34
4.	0.014	0.350	114	0.946349	0.120	115.46
5.	0.018	0.400	125	0.957148	0.130	11 6.56
6.	0.022	0.450	134	0.947908	0.150	118.88
7.	0.026	0.500	144	0.948688	0.160	119.68

TABLE 5 22%NMF in t-butanol Bu□NI =369.38, ρ□= 0.943490 Є = 46.00

Sl.N0	M (molarity)	W (g)	I (mA)	ρ ($g\ ml^{-1}$)	√c $mole^{1/2}\ dm^3$/□	□□ $dm^3 mole^{-1}$
1.	0.002	0.200	81	0.943949	0.045	149.94
2.	0.006	0.250	96	0.944829	0.080	153.31
3.	0.010	0.300	112	0.945729	0.100	155.14
4.	0.014	0.350	126	0.946588	0.120	156.86
5.	0.018	0.400	140	0.947448	0.130	157.82
6.	0.022	0.450	154	09483307	0.150	159.43
7.	0.026	0.500	168	0.949167	0.160	160.28

TABLE 6 22%NMF in t-butanol Pen□NI =425.49, ρ□= 0.943490 Є =46.00

Sl.N0	M (molarity)	W (g)	I (mA)	ρ (g ml⁻¹)	√c mole½ dm³/□	□□ dm³mole⁻¹
1.	0.002	0.200	83	1.047270	0.045	188.52
2.	0.006	0.250	102	1.047700	0.080	191.00
3.	0.010	0.300	122	1.048130	0.100	192.26
4.	0.014	0.350	141	1.048520	0.120	193.52
5.	0.018	0.400	160	1.048706	0.130	194.26
6.	0.022	0.450	179	1.049090	0.150	195.46
7.	0.026	0.500	198	1.049280	0.160	196.18

TABLE 7 Φv and √c value for different electrolytes in NMF-t-butanol mixture

SI.no.	NMF-t-Butanol % Composition	√c	Φv			
			Et_4NI,	Pr_4NI,	But_4NI,	$Pent_4NI$
1	22%	0.045	81.58	107.48	149.94	188.52
2	22%	0.08	86.98	111.26	153.31	191.00
3	22%	0.10	90.24	113.34	155.14	192.26
4	22%	0.12	92.98	115.46	156.86	193.52
5	22%	0.13	94.48	116.56	157.82	194.26
6	22%	0.15	98.06	118.88	159.43	195.46
7	22%	0.16	99.52	119.68	160.28	196.18
8	40%	0.045	142.04	170.62	198.86	228.04
9	40%	0.08	139.78	168.28	195.58	224.04
10	40%	0.10	138.58	166.92	194.00	221.81
11	40%	0.12	137.34	165.48	191.69	220.08
12	40%	0.13	136.77	164.88	190.76	219.05
13	40%	0.15	135.58	163.62	189.11	216.55
14	40%	0.16	134.88	162.83	188.15	214.89
15	60%	0.045	150.94	190.38	239.2	277.64
16	60%	0.08	147.56	186.42	233.51	271.05
17	60%	0.10	145.46	184.14	229.9	267.14
18	60%	0.12	143.46	181.58	226.46	262.69
19	60%	0.13	142.48	180.48	225.1	260.82

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20	60%	0.15	140.32	178.13	221.8	256.93
21	60%	0.16	139.06	176.82	219.92	255.07
22	80%	0.045	160.42	197.24	263.00	320.02
23	80%	0.08	155.74	192.28	256.07	311.09
24	80%	0.10	153.09	189.37	252.79	305.64
25	80%	0.12	150.47	186.38	248.94	299.77
26	80%	0.13	149.13	184.99	247.35	297.52
27	80%	0.15	146.32	182.23	243.46	292.45
28	80%	0.16	144.79	180.92	242.09	289.68

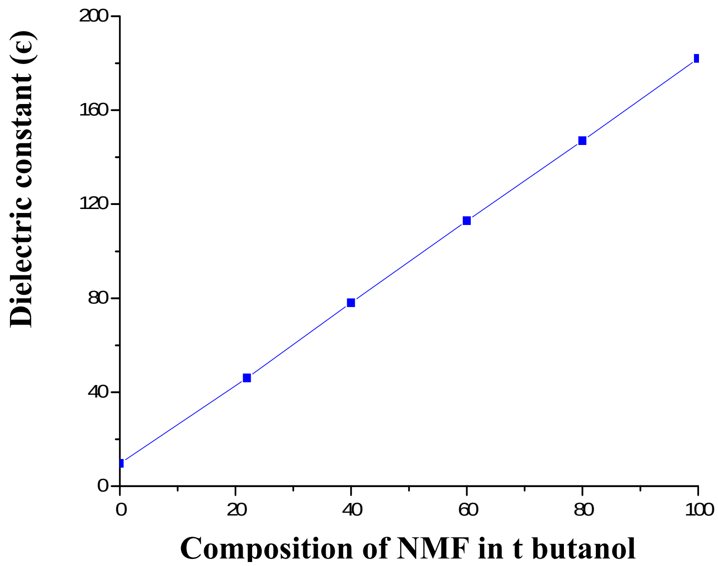

Fig. 1 Graph for the estimation of dielectric constant of various NMF-t-butanol mixtures at 25□c.

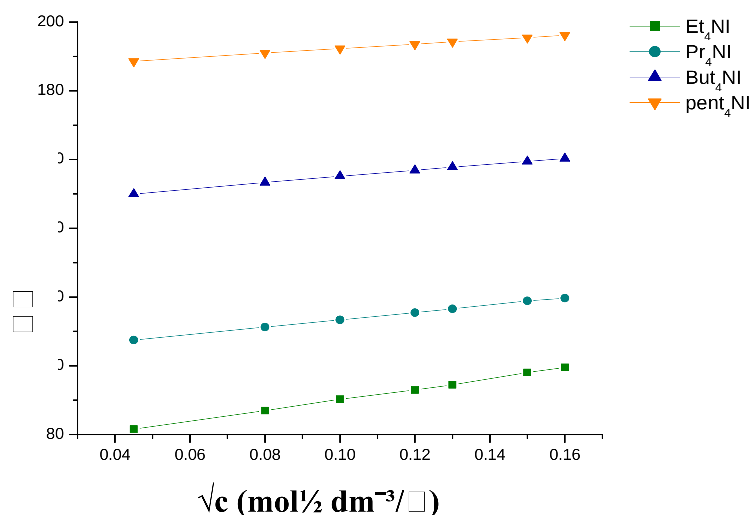

Fig.2 Graph between □v and √c for different electrolyte solution in 22% NMF in t-Butanol mixtures

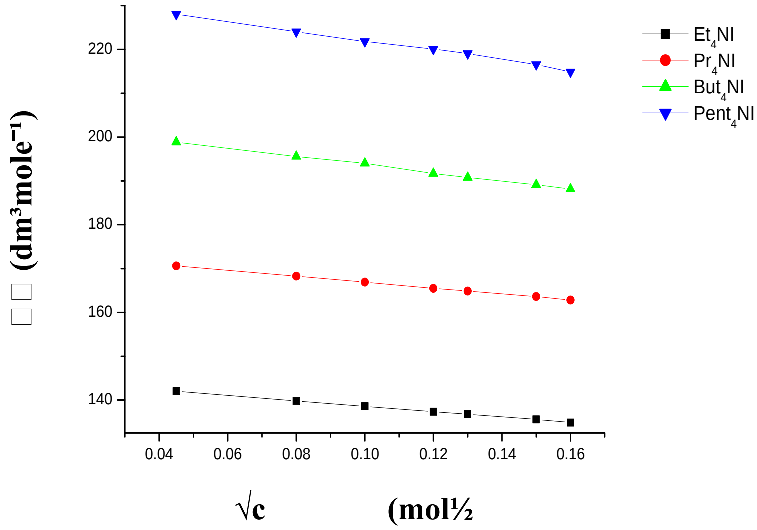

Fig.3. Graph between □v and √c for different electrolyte solution in 40% NMF in t-Butanol mixtures

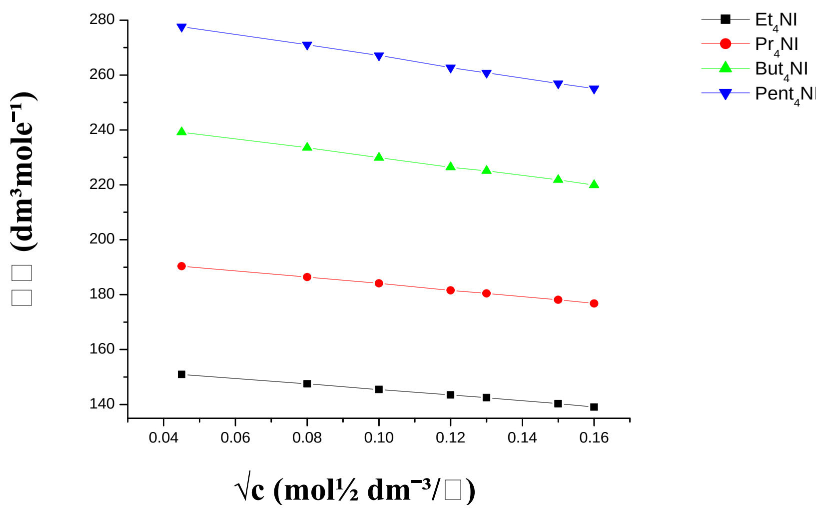

Fig.4. Graph between □v and √c for different electrolyte solution in 60% NMF in t-Butanol mixtures

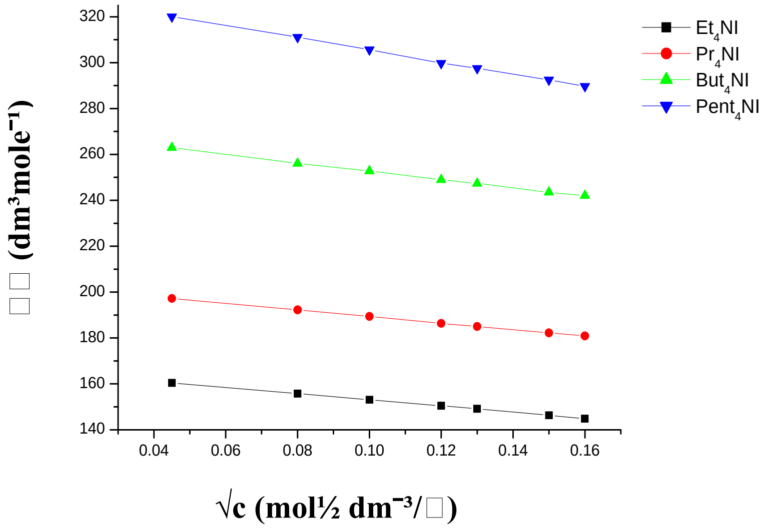

Fig.5. Graph between □v and √c for different electrolyte solution in 80% NMF in t-Butanol mixtures

Conclusion

Ion- ion and solvent interactions in different electrolyte solution using aqueous and non aqueous mixtures as the solvent. Their basic approach was, first to find out the density data, thus obtained, the apparent molar volumes (□v's) have been calculated and plotted against √conc. The slopes of these curves show that in low dielectric constant medium (22%NMF, Є=46), all the four tetraalkylammonium salts have positive slope. But as the dielectric constant of the solvent medium is increased by adding N-methylformamide in t-butanol, each of the four electrolytes gives negative slope.

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