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Determination of Densities of some R4NI - Solutions in DMSO – Dioxane Solvent Mixtures at 250cby Magnetic float Densitometer and then study Masson's Equation from ϕvData.

KEYWORDS: Densitometer, Dielectric constant. Masson's equation.

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ABSTRACT *Magnetic Float Densitometer (MFD) measures the densities of very dilute as well as very concentrated solutions accurately. It has been seen experimentally that for the same solution, if the weight on the float is increased, corresponding current will decrease and vice versa. Using this technique, the densities (ρ_o's) of DMSO-Dioxane solvent mixtures at different % compositions and those of solution (ρ_o's) of some tetraalkylammonium iodide, namely Et4NI, Pr4NI, Bu4NI & Pen4NI have been determined experimentally by MFD at 25°c. ϕv vs √c curves were plotted for all the four electrolytes, are straight lines which indicates that the Masson's equation applies in all the cases. the slope, Sv, is positive for each electrolyte in all the five solvent Mixtures (ranges from ϵ 10.75 to 46.60).However as the dielectric constant is slowly increased, the Sv values goes on decreasing for the electrolytes.*

INTRODUCTION-

The apparent molar volume ϕv, of electrolytes in solution is, in general given by Masson's equation

$$\Phi = \phi v^0 + Sv \sqrt{C}$$

Where ϕv^0 is the limiting apparent molar volume, C, the concentration in g mole.$dm^{-3,}$ and Sv the experimental slope of the ϕ_v vs √c curve. In aqueous, the slope Sv is positive for common electrolytes as well as for the tetraalkylammonium iodides (R_4NI), containing the smaller of the R_4N^+ ions at ordinary concentrations. In 1968 Miller observed a negative slope (Sv) for$NaNO_3$ and NaBr in N-methyl Propionamide (NMP) and ascribed it to be due to the high dielectric constant of the solvent. since Sv values, in the same solvent, may be positive or negative, depending on the electrolyte dissolved and for an electrolyte in the same solvent, the sign of Sv may vary with the concentration, the explanation given on the basis of dependence of only dielectric constant of the medium is not convincing .In order to explain the behaviour of the larger R_4NI salts in aqueous and non aqueous solutions. It has been suggested that the negative slope would occur if the volume of the solute ions is relatively larger as compared to that of the solvent molecules and if the interpenetration of the ion take place. This is also not fully convincing as higher R_4NI- salt also give positive slope in low dielectric constant medium , namely methanol, DMSO, DMF and propylene carbonate. We have selected Dioxane –DMSO mixtures to cover lower range (from € =10.75to 46.60) keeping the salts same i.e. R_4NI in each case. The accuracy of measurements of apparent molar volume of electrolyte solutions depends upon how accurately we determine the densities of these solutions. We have used the Magnetic Float Densitometer, modified by us, in our own laboratory for determining the densities of solution at 25^0cthe densitometer referred here have already been discussed in detail. The float used in the densitometer has density equal to 0.940010g/ml.Therefore selection of the non aqueous- non aqueous mixture has been made in such a way that in no case the densities of pure solvent mixture are less than the density of the float i.e. 0.940010g/ml. Dioxane- DMSO is one such a system which suits our requirements.

EXPERIMENTAL

Dimethyl sulphoxide (DMSO) (fluka, purum) was purified by first refluxing it for several hours with freshly ignited quicklime and then distilling under reduced pressure. The middle fractions of the successive distillate were redistilled till the electrical conductance of the final product was≤ 10^{-7} ohm^{-1}. The purified samples were stored in dark coloured bottles. Doubly distilled AR Dioxane was used with above DMSO to prepare solvent mixture. Due to decrease in solubility of the R_4NI iodides with increase in Dioxane content only dilute concentration range (0.02-0.026M) could be used for preparing solution. Me_4NI has also solubility restriction in few organic solvent; hence tetra alkyl iodides from Et_4NI, onwards, were taken for our investigations. Tetra alkyl ammonium iodides were purified in the usual manner. Five solvent mixtures, namely, 20, 40, 60, 80, & 100% DMSO in Dioxane (v/v) were prepared. The dielectric constants were computed by graph, for each composition assuming linear relationship between composition and dielectric constant. The computed values of € indifferent composition of DMSO in Dioxane is (0% =2.10,20% =10.75,40% =19.75,60%=28.75, 80%=37.75, 100%=46.60),and their corresponding densities are (ρ0's) at 25^0c, of five solvent mixtures were determined by Magnetic Float Densitometer. Then taking one solvent mixture at time and seven concentrations (0.02-0.026) for each Tetra alkyl salts e.g. Et_4NI, Pr_4NI, Bu_4NI &Pen_4NI, solution of different molarities were prepared. The densities of these solutions were determined at 25^0c by magnetic float densitometer as following manner. Magnetic float densitometer was first kept in a toshniwal constant temperature bath maintained at 25±...01°C.The solution container was filled with solvent mixture (say 20% DMSO in Dioxane (v/v) to measure $\rho_{0,}$or solution to measure ρ. The weights were added to the float so that it was about to sink in the solution. The key k_1 and K_2 were kept closed. The number of turns in the main solenoid was selected as 700 by the top section of the circuit by button no.3 down both the batteries were switched on by operating battery section (pushing button) no.2 down). Then the middle section of the circuit was operated .This section control the operation of both the coils. By pressing button no. 1, pull down solenoid "ON'. Push button no. 2 makes both the coils 'ON'.

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Push button no. 3 breaks the circuit of pull down solenoid and only main solenoid remains 'ON'. The observations were taken at push button no. 3. The resistance bridge was adjusted by selecting proper values of the components so that the float just touched the bottom of the solution container. This was viewed by telescope and light focussing arrangement. The observations were recorded for five solvent mixtures and for different solution of R_4NI salts.

RESULTS AND DISCUSSION

It has been experimentally shown that for the solution, if the weight on the float is increased, corresponding current will decreases and vice versa. But for different solution there may not be regularity in weight and corresponding values of current. For 20,40,60,80 and 100%DMSO in Dioxane v/v, the ρ_0 values are 1.047000, 1.068000, 1.075000, 1.088000 and 1.0101000 g/ml respectively. Me_4NI could not be examined in these mixtures due to solubility restrictions. ϕv vs √c curves, for all the four electrolytes, viz. Et_4NI, Pr_4NI, Bu_4NI & Pen_4NI in the concentration range (0.002-0.026M) and in all the five solvent mixtures, are straight lines indicating that Masson's equation applies in all cases. The observations clearly indicates that, the apparent molar volume ϕv increases with increase in concentration for all the four R_4NI electrolytesstudied.If individual electrolyte is examined then it is found that for a particular concentration in each case the apparent molar volume, ϕv, increases with increasing the content of DMSO in Dioxane slowly. This shows that dielectric constant of the medium has an influence on ϕv values and hence on Sv of ϕv vs √C curves. Examining the Masson's equation critically it is found that the slope, Sv is positive for each electrolyte in all the five solvent mixtures. However as the DMSO content is raised (on the dielectric constant is slowly increased) the Sv value goes on decreasing for each of the electrolyte. The slope seem to increase as the site of the molecule increases in a row which raises doubt in the fact that if the solute particle is large as compared to the solvent molecule or molecules, the slope should decrease instead of increasing. From this discussion the conclusion is drawn that the dielectric constant of the medium, appears to effect the Sv values strongly or in other words it plays an important role in determining the nature of the slope in ϕv vs √C curves.

Table 1

Φv and √c value for different electrolytes in DMSO-Dioxane mixture at 25°C

Sl.No.	DMSO-Dioxane % Composition	√c	Φv			
			Et_4NI,	Pr_4NI,	Bu_4NI,	Pen_4NI
1	20%	0.045	153.88	202.4	247.74	278.18
2	20%	0.08	166.02	214.34	260.22	290.98
3	20%	0.10	172.98	220.5	267.02	298.46
4	20%	0.12	179.44	227.52	274.37	306.52
5	20%	0.13	182.86	230.94	277.38	309.92
6	20%	0.15	190.24	237.14	284.34	317.65
7	20%	0.16	193.96	240.43	288.12	321.43
8	40%	0.045	170.72	211.87	255.05	278.55
9	40%	0.08	181.15	223.25	265.07	292.41
10	40%	0.10	187.34	229.48	270.55	299.98
11	40%	0.12	193.48	236.04	276.21	307.77
12	40%	0.13	196.29	239.23	279.15	312.29
13	40%	0.15	202.63	245.61	284.93	320.03
14	40%	0.16	205.25	249.04	288.05	324.59
15	60%	0.045	179.1	223.03	255.44	278.07
16	60%	0.08	190.46	230.35	266.04	292.13
17	60%	0.10	197.45	235.06	271.97	300.92
18	60%	0.12	203.94	239.59	278.16	308.76
19	60%	0.13	207.38	242.17	281.23	312.53
20	60%	0.15	213.73	246.46	286.81	320.88
21	60%	0.16	217.22	248.85	289.63	324.75
22	80%	0.045	206.85	235.68	258.78	285.48
23	80%	0.08	210.28	242.28	270.10	297.34
24	80%	0.10	212.34	246.37	275.98	304.43
25	80%	0.12	214.38	250.20	281.94	310.98
26	80%	0.13	215.42	252.43	285.89	314.29
27	80%	0.15	217.56	255.97	291.79	320.79
28	80%	0.16	218.48	257.68	295.02	323.85
29	100%	0.045	215.24	247.22	268.78	291.04
30	100%	0.08	218.52	251.02	277.04	300.88
31	100%	0.10	220.46	253.13	281.52	307.08
32	100%	0.12	222.34	255.38	286.19	313.00
33	100%	0.13	223.29	256.48	288.37	315.62
34	100%	0.15	225.31	258.62	292.91	321.42

Fig.1.Graph between ϕv and √c for different electrolyte solution in 100%

DMSO-Dioxane mixtures

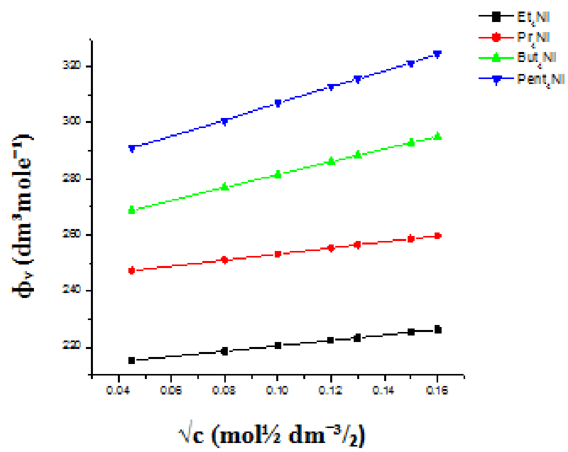

TABLE 2

Sl.No.	Composition Of DMSO in Dioxane (v/v)	Dielectric constant (€)as computed from graph	S_v values ($dm^{9/2}$ $mole^{-3/2}$ 10^{-3})			
			Et_4NI	Pr_4NI	Bu_4NI	Pen_4NI
1.	20% DMSO	10.75	326.0	333.3	341.5	400.0
2.	40% DMSO	19.75	313.4	332.5	339.6	391.3
3.	60% DMSO	28.75	270.0	322.6	304.3	348.0
4.	80% DMSO	37.75	139.2	230.8	338.0	339.0
5.	100% DMSO	46.6	100.0	102.6	250.0	288.5

Sv values for some tetra alkyl ammonium iodides in different DMSO -Dioxane mixtures at25°c.

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