



A Study of Masson's Slope in Dioxane-Formamide Mixture by Magnetic Float Densitometer Using Tetra Alkyl Ammonium Iodides at 25 °C

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Apparent molar volume of Et₄NI, Pr₄NI, Bu₄NI and Pen₄NI salt solutions have been determined in different compositions of dioxane-formamide mixture of (0, 15, 25, 35, 45 and 59 % formamide in dioxane) by density measurement at 25 °C from apparent molar volume. The slope of Masson's equation have been analyzed for these salts. The obtained parameters have been interpreted in terms of polar and non-polar behaviour and hydrogen bonding of organic solvents used in the solutions. The slopes are found to be positive for all the electrolytes in different compositions of solvent mixtures except for 59 % formamide mixture in which all the R₄NI salts gave negative slope.

Key Words: Ion-ion solvent interaction, Apparent molar volume, Dielectric constant.

INTRODUCTION

The literature survey shows that many scientists^{1,2} have been working on ion-ion and ion-solvent interactions in different electrolyte solutions using aqueous and non-aqueous mixtures as the solvents. Their basic approach was first to find out the densities of solvent-mixtures and solutions and then from density data, they have calculated the apparent molar volumes (ϕ_v^S) to explain ion-ion and ion-solvent interactions³⁻⁶ and slope (S_v) of Masson's equation. $\phi_v = \phi_v^0 + S_v\sqrt{c}$, where ϕ_v^0 is the limiting apparent molar volume and c be the molar concentration.

The studies on apparent molar volumes in solvents of low and medium dielectric constants⁵⁻⁹ reported that there is a positive slope, on their ϕ_v versus \sqrt{c} curves for tetraalkyl ammonium salts. The apparent molar volume work in water and other solvents of high dielectric constants, showed a negative slope in ϕ_v versus \sqrt{c} curves for these salts.

Many workers tried to solve this peculiar behaviour of the slope (sometimes positive and sometimes negative) of tetraalkyl ammonium salts. In an attempt to get clear picture of Masson's slope, it is worthwhile to investigate how the slope (S_v) observed for some tetraalkyl ammonium salts on formamide would change on increasing the dielectric constants of the solvent by adding suitable quantities of dioxane.

We have determined the densities (ρ_o 's) of formamide-dioxane mixtures and the densities (ρ_o 's) of some tetraalkyl ammonium iodide solutions in these solvents mixtures by entirely new technique magnetic float densitometer.

EXPERIMENTAL

The dielectric constants of six compositions of 0, 15, 25, 35, 45, 59 % formamide in dioxane have been determined by assuming a linear relationship between them. A graph was plotted between them taking first and last points and then joining them. The dielectric constants of other compositions were also calculated.

The densities (ρ_o 's) of solvent mixtures and the densities (ρ 's) of tetraalkyl ammonium iodide solutions prepared in these solvent mixture were determined by magnetic float densitometer¹⁰. ρ_o data have been shown in Table-1 and ρ data have been summarized in Table-2.

TABLE-1
ESTIMATED VALUES OF DIELECTRIC CONSTANTS FOR DIOXANE-FORMAMIDE MIXTURES USING GRAPH (NOT GIVEN HERE) DENSITIES (ρ_o 's) OF THESE SOLVENT MIXTURES AT 25 °C

Composition of formamide in dioxane (%)	Dielectric constant (ϵ)	Density (ρ_o) (g/mL)
0	2.1	1.034000
15	17.5	1.045175
25	28.5	1.058053
35	39.5	1.070521
45	49.5	1.081883
59	65.0	1.094125

The apparent molar volumes (ϕ_v 's) of these solutions in the concentration range $C = 0.002-0.014$ m were calculated from the density data of Tables 1 and 2 using the equation:

TABLE-2
DENSITY (ρ) AND APPARENT MOLAR VOLUME (ϕ_v) DATA OF SOME TETRA-ALKYL
AMMONIUM IODIDE SOLUTIONS IN DIOXANE-FORMAMIDE MIXTURES AT 25 °C

\sqrt{c} (mol ^{1/2} L ^{-1/2})	(a) 0 % Formamide in dioxane							
	Et ₄ NI		Pr ₄ NI		Bu ₄ NI		Pen ₄ NI	
	ρ (g mL ⁻¹)	ϕ_v (cm ³ mol ⁻¹)	ρ (g mL ⁻¹)	ϕ_v (cm ³ mol ⁻¹)	ρ (g mL ⁻¹)	ϕ_v (cm ³ mol ⁻¹)	ρ (g mL ⁻¹)	ϕ_v (cm ³ mol ⁻¹)
0.045	1.034254	125.9	1.034250	182.1	1.034268	227.6	1.034325	254.3
0.063	1.034440	142.3	1.034460	191.8	1.034509	234.2	1.034591	268.6
0.077	1.034606	151.0	1.034631	201.8	1.034689	246.2	1.034857	273.4
0.089	1.034726	160.9	1.034781	208.6	1.034879	251.0	1.035083	280.6
0.100	1.034840	167.5	1.034912	214.8	1.035069	253.9	1.035289	286.8
0.110	1.034927	174.0	1.035003	222.0	1.035180	262.1	1.035475	292.6
0.118	1.034994	180.1	1.035074	228.8	1.035311	266.7	1.035661	296.8
(b) 15 % Formamide in dioxane								
0.045	1.045413	132.2	1.045408	188.3	1.045431	230.9	1.045445	277.9
0.063	1.045587	147.5	1.045590	200.5	1.045628	246.1	1.045682	285.8
0.077	1.045747	154.8	1.045747	208.5	1.045825	250.8	1.045884	294.0
0.089	1.045865	163.5	1.045894	213.7	1.045983	257.8	1.046085	298.3
0.100	1.045994	167.7	1.046007	220.1	1.046140	262.1	1.046275	301.9
0.110	1.046064	175.2	1.046118	224.5	1.046277	266.5	1.046441	306.2
0.118	1.046135	180.5	1.046189	230.4	1.046393	271.2	1.046592	310.3
(c) 45 % Formamide in dioxane								
0.045	1.082032	168.8	1.081990	240.1	1.082023	276.7	1.081959	358.2
0.063	1.082173	170.7	1.082111	236.9	1.082139	282.3	1.082060	352.7
0.077	1.082314	171.3	1.082212	238.9	1.082276	280.9	1.082141	353.5
0.089	1.082459	171.1	1.082283	243.3	1.082393	282.5	1.082247	351.2
0.100	1.082604	171.1	1.082380	243.6	1.082509	283.6	1.082348	350.3
0.110	1.082735	172.1	1.082457	245.3	1.082626	284.2	1.082449	349.7
0.118	1.082856	173.5	1.082534	246.6	1.082742	284.7	1.082544	349.6
(d) 59 % Formamide in dioxane								
0.045	1.094253	176.5	1.094197	253.4	1.094211	298.3	1.094135	384.3
0.063	1.094408	170.4	1.094313	243.4	1.094322	291.4	1.094196	372.7
0.077	1.094525	174.1	1.094409	243.1	1.094453	287.6	1.094281	365.1
0.089	1.094682	171.4	1.094526	240.5	1.094593	284.2	1.094398	357.7
0.100	1.094816	171.9	1.094662	237.2	1.094738	281.6	1.094499	354.7
0.110	1.094972	170.5	1.094778	236.6	1.094907	278.0	1.094650	348.9
0.118	1.05128	169.6	1.094914	234.8	1.095092	274.5	1.094806	344.4

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

M = Molecular weight of solution, C = concentration and ρ_o = density of solvent, ρ = density of solution.

RESULTS AND DISCUSSION

The apparent molar volumes (ϕ_v 's) were calculated in 0, 15, 25, 35, 45 and 59 % formamide in dioxane from density data obtained by magnetic float densitometer for Et₄NI, Pr₄NI, Bu₄NI and Pen₄NI salts in each solvent mixtures and then ϕ_v versus \sqrt{c} curves were drawn for each solvent composition. The first salt tetraalkyl ammonium iodide could not be examined in these mixtures due to solubility restriction.

The ϕ_v versus \sqrt{c} curves for all the electrolytes are found to be straight lines hence Masson's equation would be applicable in all the cases in the concentration range 0.002-0.014 M.

It is clear from Table-2 that the apparent molar volume (ϕ_v) increases with increase in concentration for each electrolyte from 0 % to 45 % formamide for all cases except for Pen₄NI for which ϕ_v 's show a decreasing trend in 45 % formamide. As shown in Table-2 in case of 59 % formamide the data, however, indicate a reverse trend that is ϕ_v decreases with increasing electrolyte concentration irrespective of the electrolyte selected.

Table 2(a-d) show that the apparent molar volume, Φ_v , increases with electrolyte concentration from 0 to 45 % formamide for all cases except for Pen₄NI for which Φ_v 's show a decreasing trend in 45 % formamide. As we can show from Table-2, for 59 % formamide, the data, however, indicate a reverse trend, that is, Φ_v decreases with increasing electrolyte concentration irrespective of the electrolyte selected. These trends can be, more clearly, understood by Φ_v versus \sqrt{C} curves in 0, 15, 25, 35, 45 and 59 % formamide in dioxane for R₄NI salts (R = Et, Pr, Bu and Pen) as clear by graph.

The magnitude of the slope, S^*_v , seems to have different in different cases as can be seen by the relative steepness of each curve or by obtaining the slopes, S^*_v , by using Φ_v versus \sqrt{C} curves in each case (Figs. 1-4). A clear picture regarding the variation in Masson's experimental slope in different cases can be had by examining the Table-3, wherein, all the S^*_v values are summarized.

In Table-3, the column-wise changes indicate the effect of dielectric constant of the medium on Masson's experimental slope while the row-wise changes depict the effect of size of solute molecules on this slope. Let us first examine the column-wise trends. If we increase the dielectric constant of the dioxane by mixing into it another solvent, formamide, of high dielectric constant in definite proportion say 0, 15, 25, 35, 45 and 59 %

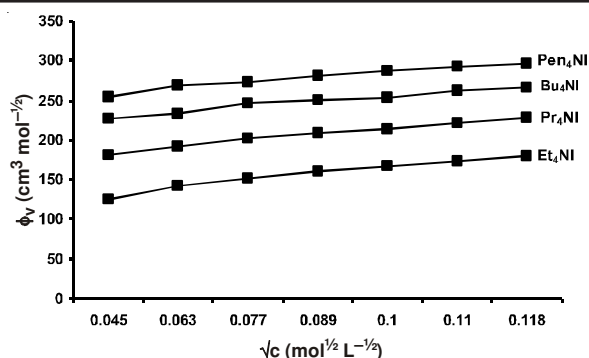


Fig. 1. ϕ_v versus \sqrt{c} curves for Et_4NI , Pr_4NI , Bu_4NI and Pen_4NI salts in 0 % formamide in dioxane (v/v) in the concentration range 0.002-0.014 m at 25 °C

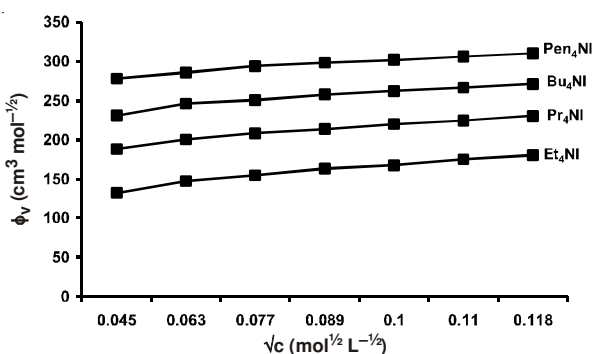


Fig. 2. ϕ_v versus \sqrt{c} curves for Et_4NI , Pr_4NI , Bu_4NI and Pen_4NI salts in 15 % formamide in dioxane (v/v) in the concentration range 0.002-0.014 m at 25 °C

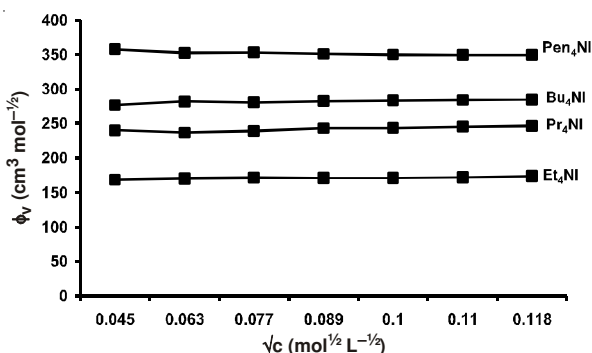


Fig. 3. ϕ_v versus \sqrt{c} curves for Et_4NI , Pr_4NI , Bu_4NI and Pen_4NI salts in 45 % formamide in dioxane (v/v) in the concentration range 0.002-0.014 m at 25 °C

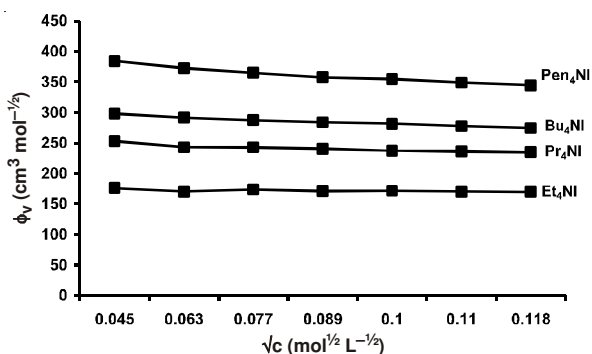


Fig. 4. ϕ_v versus \sqrt{c} curves for Et_4NI , Pr_4NI , Bu_4NI and Pen_4NI salts in 59 % formamide in dioxane (v/v) in the concentration range 0.002-0.014 m at 25 °C

TABLE- 3

 S^*_v -VALUES ($\text{cm}^3 \text{mol}^{-3/2} \text{L}^{1/2}$)

Composition (%) of formamide and dioxane with their estimated values of dielectric constants (ϵ)	Et_4NI	Pr_4NI	Bu_4NI	Pen_4NI
0 Formamide ($\epsilon = 2.1$)	877.19	606.74	526.32	575.37
15 Formamide ($\epsilon = 17.5$)	615.38	574.47	454.35	434.36
25 Formamide ($\epsilon = 28.5$)	422.22	444.44	266.67	329.41
35 Formamide ($\epsilon = 39.5$)	290.91	336.28	218.18	121.21
45 Formamide ($\epsilon = 49.5$)	61.86	186.05	84.03	-133.33
59 Formamide ($\epsilon = 65.0$)	-96.39	-290.91	-111.10	-491.23

formamide (v/v) the slope S^*_v of each electrolyte goes on diminishing down the column. This clearly shows that on increasing the dielectric constant of the solvent medium, the Masson's slope goes on decreasing.

The row-wise trend indicate some other trend for the variation in slope. The slope of Pr_4NI is smaller than that of Et_4NI and the slope of Bu_4NI is smaller than that of Pr_4NI , etc. That is the magnitude of the slope varies in the order $\text{Et}_4\text{NI} > \text{Pr}_4\text{NI} > \text{Bu}_4\text{NI} > \text{Pen}_4\text{NI}$ in each solvent mixture. This clearly indicates that the size of the solute molecule has also an influence on the slope. As the size of the solute molecule increases from Et_4NI to Pen_4NI down the row in each solvent mixture, the experimental slope goes on decreasing.

The explanation for increase in Φ_v with electrolyte concentration which yields positive value of Masson's experimental slope, S^*_v , is that the interionic attraction of ion-ion increases due to two reasons. Firstly, the dielectric constant of the solvent mixture is low ($\epsilon = 2.1-65.0$). The lower dielectric constant of the solvent medium favours the strong ion-ion interaction. Secondly, by increasing the electrolyte concentration slowly, the ions come closer to each other causing a strong ion-ion interaction.

The negative value of S^*_v in some cases in this system of solvent mixture may be attributed to be due to following two reasons:

(i) Here in formamide-dioxane system, dioxane is non-polar and non-hydrogen bonded solvent. In presence of formamide in the solvent mixture, the higher tetraalkyl ammonium ions act as structure promoter for formamide. The structure promoting nature of ions will lead to decrease in Φ_v with increase in concentration of electrolyte which yields negative slope. When there is a lesser amount of formamide present in the solvent mixture, say, upto 35 % formamide, the structure promotion is not effective. But as the formamide content, is increased to 45 % or above, this effect of structure promotion of solvent molecules sets in, giving rise to negative S^*_v . The structure promoting power of R_4N^+ ions are in the order, $\text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+$. Pen_4NI , being the largest molecule of the four salts studied, it starts its dominance of structure promotion at 45 % formamide content. But as soon as the content increases to 59 % formamide, all of the four electrolytes Et_4NI , Pr_4NI , Bu_4NI and Pen_4NI seem to participate in structure promotion, yielding negative slope in each case. The slope is more negative for Pen_4NI than for Bu_4NI and, in turn, the slope for Bu_4NI is more negative than Pr_4NI and so on in 59 % formamide because of relative molecular size of solute molecules.

(ii) Bigger molecules of solute when come closer to each other starts interpenetrating into one another due to void spaces present in them. Therefore addition of solute does not contribute towards volume. This causes the decrease in apparent molar volume by increasing the concentration yielding negative slope in Φ_v versus \sqrt{C} curves. This interpenetration tendency is also in the order: $\text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+$ because of relative molecular size of solute molecules. This interpenetration effect is seemed to be absent when the solvent molecules are non-polar and non-hydrogen bonded none of the solvent constituent of such nature was present in the solvent mixture. But this effect goes on increasing if one non-polar and non-hydrogen bonded solvent is replaced by a polar and hydrogen bonded solvent. The dominance of interpenetration effect increases if the second non-polar and non-hydrogen bonded solvent constituent is further replaced by another polar and hydrogen bonded solvent, thus constituting both the solvents of the same nature in the solvent mixture.

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