INTRODUCTION

The literature survey shows that many scientists 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 (φv) to explain ion-ion and ion-solvent interactions and slope (Sv) of Masson’s equation.

φv = φv0 + Sv√c, where φv0 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 constants reported that there is a positive slope, on their φv versus √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 φv versus √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 (Sv) 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 (ρo’s) of formamide-dioxane mixtures and the densities (ρ’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’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. ρo data have been shown in Table-1 and ρ data have been summarized in Table-2.

### Table-1

| Composition of formamide in dioxane (%) | Dielectric constant (ε) | Density (ρ) (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 (φv’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:
The apparent molar volumes ($\phi_v$) were calculated in 0, 15, 25, 35, 45 and 59 % formamide in dioxane from density data obtained by magnetic float densimeter for Et$_4$NI, Pr$_4$NI, Bu$_4$NI and Pen$_4$NI salts in each solvent mixture and the $\phi_v$ 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 $\phi_v$ 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 ($\phi_v$) increases with increase in concentration for each electrolyte from 0 % to 45 % formamide for all cases except for Pen$_4$NI for which $\phi_v$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, $\phi_v$ decreases with increasing electrolyte concentration irrespective of the electrolyte selected.

Table 2(a-d) show that the apparent molar volume, $\phi_v$, increases with electrolyte concentration from 0 to 45 % formamide for all cases except for Pen$_4$NI for which $\phi_v$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, $\phi_v$ decreases with increasing electrolyte concentration irrespective of the electrolyte selected. These trends can be, more clearly, understood by $\phi_v$ versus $\sqrt{c}$ curves in 0, 15, 25, 35, 45 and 59 % formamide in dioxane for R$_4$NI salts (R = Et, Pr, Bu and Pen) as clear by graph.

The magnitude of the slope, $S^*$, seems to have different in different cases as can be seen by the relative steepness of each curve or by obtaining the slopes, $S^*$, by using $\phi_v$ 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 $S^*$, 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 %
formamide (v/v) the slope $S^*$, 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$_{NI}$ is smaller than that of Et$_{NI}$ and the slope of Bu$_{NI}$ is smaller than that of Pr$_{NI}$, etc. That is the magnitude of the slope varies in the order Et$_{NI} >$ Pr$_{NI} >$ Bu$_{NI} >$ Pen$_{NI}$ 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$_{NI}$ to Pen$_{NI}$ down the row in each solvent mixture, the experimental slope goes on decreasing.

The explanation for increase in $\Phi$, with electrolyte concentration which yields positive value of Masson’s experimental slope, $S^*$, is that the interionic attraction of ion-ion increases due to two reasons. Firstly, the dielectric constant of the solvent mixture is low ($\varepsilon = 2.1$-$65.0$). 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 $S^*$, 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 $\Phi$, with increase in concentration of electrolyte which yields negative slope. When there is a lesser amount of formamide present in the solvent mixture, say, up to 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 $S^*$. The structure promoting power of R$_{NI}^+$ ions are in the order, Pen$_{NI}^+ >$ Bu$_{NI}^+ >$ Pr$_{NI}^+ >$ Et$_{NI}^+$. Pen$_{NI}$, 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$_{NI}$, Pr$_{NI}$, Bu$_{NI}$ and Pen$_{NI}$ seem to participate in structure promotion, yielding negative slope in each case. The slope is more negative for Pen$_{NI}$ than for Bu$_{NI}$ and, in turn, the slope for Bu$_{NI}$ is more negative than Pr$_{NI}$ and so on in 59 % formamide because of relative molecular size of solute molecules.

### Table 3

| Composition (%) of formamide and dioxane with their estimated values of dielectric constants ($\varepsilon$) | Et$_{NI}$ | Pr$_{NI}$ | Bu$_{NI}$ | Pen$_{NI}$ |
|---------------------------------------------------------------|----------|----------|----------|-----------|
| 0 Formamide ($\varepsilon = 2.1$)                             | 877.19   | 606.74   | 526.32   | 575.37    |
| 15 Formamide ($\varepsilon = 17.5$)                           | 615.38   | 574.47   | 454.35   | 434.36    |
| 25 Formamide ($\varepsilon = 28.5$)                           | 422.22   | 444.44   | 266.67   | 329.41    |
| 35 Formamide ($\varepsilon = 39.5$)                           | 290.91   | 336.28   | 218.18   | 121.21    |
| 45 Formamide ($\varepsilon = 49.5$)                           | 61.86    | 186.05   | 84.03    | -133.33   |
| 59 Formamide ($\varepsilon = 65.0$)                           | -96.39   | -290.91  | -111.10  | -491.23   |
(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 $\Phi$ versus $\sqrt{C}$ curves. This interpenetration tendency is also in the order: Pen$_4$N$^+$ > Bu$_4$N$^+$ > Pr$_4$N$^+$ > Et$_4$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.

ACKNOWLEDGEMENTS

The authors are thankful to Head, Department of Chemistry Lucknow University, Lucknow for providing the laboratory facilities.

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