Study of the Influence of Alkyl Chain Cation - Solvent Interactions on the Slope of $\Phi_V$ vs. $\sqrt{C}$ Curves in 1,5-Pentane Diol - DMF Solvent Mixtures by Apparent Molar Volume Measurements

R. N. PATHAK*, INDU SAXENA, ARCHNA, RAHUL KUMAR and NARENDRA SINGH

Department of Chemistry, Lucknow University, Lucknow -226007, India
rnpk@sify.com

Received 15 April 2013 / Accepted 8 May 2013

Abstract: The concept of Frank’s hypothesis (that is the effect of large tetra alkyl ammonium ions on the solvent structure, especially water, in the ion-ion and ion-solvent interactions) was found to be not applicable when water was replaced by one of the organic solvents e.g. Dimethyl formamide (DMF), in the solvent mixture, that is, if the study involves ion-ion and ion-solvent interactions in 1,5-pentane diol - DMF solvent mixture containing large cations of tetraalkyl ammonium iodides. The densities of binary solvent mixtures and salt solutions have been measured at 298.15 K by magnetic float densitometer. The apparent molar volumes at infinite dilution, $\Phi_V^0$, determined by $\Phi_V$ – values in the solvent mixtures, have been utilized to estimate the partial molar volumes of transfer, $\Delta\Phi_V^0(\text{tr})$, for various tetraalkyl ammonium iodide salts from DMF to 1,5-Pentane diol.

Keywords: Ion - solvent Interactions, 1, 5-Pentane diol- DMF mixtures

Introduction

Devanathan and Fernando\textsuperscript{1} reported abnormally high activity coefficients of aqueous solutions of tetraalkyl ammonium salts while carrying out emf measurements. Their observations were confirmed by Bower and Robinson\textsuperscript{2}. The abnormally high activity coefficients were also observed by Frank\textsuperscript{3} in his emf measurement work of such solutions. He explained the high activity coefficients on the basis of his hypothesis according to which the structure of water is enforced around the $R_4N^+$ ions on account of the water-hating influence of the large alkyl chains. This results in the formation of cavities inside the enhanced water structure and $R_4N^+$ ions are accommodated in the cavities so formed. So the fugacity of the solvent and the $R_4N^+$ ion is lowered, on the other hand the fugacity of $I^-$ ions is increased. Because of this, even the larger $R_4N^+$ ions seem to be solvated on account of hydrophobic enforcement of water structure and hence large values of activity coefficients of solutions are obtained. In our earlier communication\textsuperscript{4} 1, 5-pentane diol- water combination was used to see the validity of Franks hypothesis in the solutions of $R_4NI$ salts in the binary solvent mixtures, the water being one of the components. The idea was to
replace water by another non-aqueous solvent in 1, 5-Pentane diol- water combination i.e.
1,5-pentane diol- DMF were taken to see whether such solute-solvent hating effect is still
there and the structure of any of the binary solvents is affected by the ion-solvent interactions.

In order to make sure that the behavior of enhancement of solvent structure is confined
only either to pure aqueous solutions or the solutions in binary solvent mixtures in which
one of the components should necessarily be water, the extension of the work to other
similar solvent media of varying dielectric constant is very much desirable. 1, 5-Pentane
diol- DMF mixtures provide such media in which water component is replaced by a non
aqueous solvent, namely, DMF. These mixtures have been used as solvent media in which
the dependence of the slope of the $\Phi$ curve on $\sqrt{C}$ curves on the structural changes, if any, in
the solvent molecules with the addition of $R_4NX$ salts has been examined in this work.

Since the apparent molar volumes and partial molar volumes of electrolytes have
proved to be very useful tool in elucidating the structural interactions (i.e. ion-ion, ion-
solvent and solvent-solvent) occurring in solution, the help of these physical parameters, has
therefore, been taken in this work to study the problem.

The apparent molar volume at infinite dilution, $\Phi_v^0$ and the apparent molar volume of
transfer $\Delta\Phi_v^0(tr)$ parameters have also been taken into consideration to discuss the ionic
interactions in these solutions.

**Experimental**

The tetraalkyl ammonium iodide salts, Et$_4$NI, Pr$_4$NI, Bu$_4$NI and Pen$_4$NI which were used in
present investigation were purified by the method of Conway et al. Dimethyl formamide (DMF)
of Qualigen’s Glaxo grade, after drying on freshly ignited quicklime, was purified by distilling
under reduced pressure. The middle fractions of the successive distillate were redistilled under
reduced pressure till the electrical conductance of the final product was of the order of
$10^{-7}$ ohm$^{-1}$ cm$^{-1}$. The purified samples were stored in dark coloured bottles. This DMF was used to
prepare 20, 40, 60 and 80% (v/v) solvent mixtures with 1, 5-pentane diol of Fluka purum grade.

The dielectric constants of these compositions have not been reported in the literature so
far. Therefore the values of dielectric constants of these solvent mixtures were determined
by plotting a graph assuming a linear relationship between dielectric constants and
composition with the help of dielectric constant of pure 1,5-pentanediol ($\varepsilon$=26.3) & of pure
DMF ($\varepsilon$=36.7) which are available in literature, the dielectric constants of intermediate
compositions 20, 40, 60 and 80% DMF in 1,5-pentane diol were estimated by this graph and
are given in Table 1.

**Table 1.** Estimated values of dielectric constant of 1, 5-pentane diol-DMF mixtures used as
a solvent at 298.15 K

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Composition of mixtures (v/v)</th>
<th>Dielectric constant ($\varepsilon$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20% DMF in 1,5-pentanediol</td>
<td>28.4</td>
</tr>
<tr>
<td>2</td>
<td>40% DMF in 1,5-pentanediol</td>
<td>30.4</td>
</tr>
<tr>
<td>3</td>
<td>60% DMF in 1,5-pentanediol</td>
<td>32.5</td>
</tr>
<tr>
<td>4</td>
<td>80% DMF in 1,5-pentanediol</td>
<td>34.6</td>
</tr>
</tbody>
</table>

The density, $d_0$, of these solvent mixtures were determined by Magnetic Float
Densitometer at 298.15 K, using Eq. 1

$$d_0 = \frac{(W+w+f.I)}{(V+w/d_P)}$$  (1)
The terms involved in this equation have their usual meanings. The data of solvent mixtures, \( i.e., \) weight, \( w \) used, current, \( I \), passing in the circuit and the corresponding values of \( d_0 \) calculated by Eq.1 are recorded in Table 2.

### Table 2. Density data of 1, 5-pentane diol -DMF mixtures used as solvent at 298.15 K

<table>
<thead>
<tr>
<th>Solvent mixture</th>
<th>Weight ( w ) kg.10(^{-3})</th>
<th>Current ( I ) Amp.10(^{-3})</th>
<th>Density ( d_0 ) kg.m(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% DMF in 1,5-pentanediol</td>
<td>2.30</td>
<td>785</td>
<td>982.327</td>
</tr>
<tr>
<td>40% DMF in 1,5-pentanediol</td>
<td>1.80</td>
<td>660</td>
<td>974.048</td>
</tr>
<tr>
<td>60% DMF in 1,5-pentanediol</td>
<td>1.00</td>
<td>608</td>
<td>963.743</td>
</tr>
<tr>
<td>80% DMF in 1,5-pentanediol</td>
<td>0.200</td>
<td>590</td>
<td>954.108</td>
</tr>
</tbody>
</table>

The solutions of 0.02, 0.04, 0.06, 0.08, 0.10, 0.12 and 0.14 \( M \) concentrations of the tetraalkyl ammonium iodides, namely, \( \text{Et}_4\text{NI}, \text{Pr}_4\text{NI}, \text{Bu}_4\text{NI} \) and \( \text{Pen}_4\text{NI} \) were prepared in above selected four compositions of 1,5-pentane diol – DMF mixture, one by one taking one composition at a time. The densities, \( d \), of these solutions were measured by Magnetic Float Densitometer at 298.15 K using Eq.1 replacing \( d_0 \) by \( d \ i.e. \)

\[
d = \frac{(W+w+f.I)}{(V+w/dPt)}
\]  

(2)

\( \text{Me}_4\text{NI} \) salt could not be studied due to its solubility restrictions. Using the density, \( d_0 \), of solvent mixtures and the densities, \( d \), of solutions, the apparent molar volumes, \( \Phi_V \), were calculated for each solution using following equation;

\[
\Phi_V = \frac{[1000(d_0-d)]}{C d_0} + \frac{[M]}{d_0}
\]  

(3)

The terms used in this equation have their usual meanings. \( \Phi_V \) vs. \( \sqrt{c} \) curves were drawn for each salts in each composition of 1, 5-pentane diol - DMF mixture and are shown in Figure 1-4. Then slopes \( S_v \) of these curves were calculated for each salt and are shown in Table 3 along with solvent mixture composition.

**Figure 1.** Graph between \( \Phi_V \) and \( \sqrt{c} \) for different electrolyte solutions in 20% DMF in 1,5-pentane diol mixture, 298.15 K

**Figure 2.** Graph between \( \Phi_V \) and \( \sqrt{c} \) for different electrolyte solutions in 40% DMF in 1,5-pentane diol(v/v) (v/v) at mixture at 298.15 K
Figure 3. Graph between \( \Phi_v \) and \( \sqrt{c} \) for different electrolyte solutions in 60% DMF in 1,5-pentane diol (v/v) at mixture 298.15 K.

Figure 4. Graph between \( \Phi_v \) and \( \sqrt{c} \) for different electrolyte solutions in 80% DMF in 1,5-pentane diol, (v/v) at mixture 298.15 K.

\( \Phi_v^0 \) values for each salt are also calculated from Figure 1-4 by extrapolating the \( \Phi_v \) vs. \( \sqrt{c} \) curve to \( C = 0 \) axis (y-axis). The intercepts on y-axis will give the values of \( \Phi_v^0 \). These values are assumed as \( \Phi_v^0 \) (MS) values (i.e apparent molar volume of salts at infinite dilution in mixed solvent system). The apparent molar volumes of transfer, \( \Delta \Phi_v^0 \) (tr), are calculated using the relation

\[
\Delta \Phi_v^0 \text{(tr)} = \Phi_v^0 \text{(MS)} - \Phi_v^0 \text{(S)}
\]  

(4)

Here \( \Phi_v^0 \) (S) is the apparent molar volume of salts at infinite dilution in pure solvent \( (\text{in this case DMF}) \). Subscripts MS and (tr) for \( \Phi_v^0 \) and \( \Delta \Phi_v^0 \) data are shown in Table 4.

**Results and Discussion**

The dielectric constant of pure 1, 5-pentane diol (\( \varepsilon = 26.3 \)) can be gradually increased by adding DMF (\( \varepsilon = 36.7 \)) to it. Thus four types of 1,5-pentane diol- DMF mixtures of varying dielectric constants, were prepared, namely, 20% DMF (\( \varepsilon = 28.4 \)), 40% DMF (\( \varepsilon = 30.4 \)), 60% DMF (\( \varepsilon = 32.5 \)) and 80% DMF (\( \varepsilon = 34.6 \)) in 1,5-pentane diol (v/v). Density measurements of some R\( _4 \)NI salt solutions in these solvent mixtures were done experimentally and \( \Phi_v \) values then calculated with molar conc. C for each salt. Then \( \Phi_v \) vs. \( \sqrt{C} \) curves were drawn for each salt in various composition and \( S_v \) values were calculated.

After, the study of curves in Figure 1-4, it is seen that the apparent molar volume \( \Phi_v \) increases with increasing concentration of salt for all the cases, hence slopes were found positive for each salt and in each solvent mixture. This is also evident from Figure 1-4 in which the straight lines show the increasing trend of \( \Phi_v \) values with increasing concentration. As the \( \Phi_v \) vs. \( \sqrt{C} \) curves are found to be straight lines it is clear that the Masson’s equation is valid for all the salts in the entire range of concentration selected.

\[
\Phi_v = \Phi_v^0 + S_v \sqrt{C}
\]  

(5)

If we examine the \( S_v \) data of Table 3, it is quite clear that \( S_v \) values are all positive whether the composition of solvent mixture is changed or the salt species is changed. Since no negative value of \( S_v \) is found, the hydrophobic alkyl chain-solvent interactions are found to be absent here. No enforcement of solvent structure (either of 1,5-pentane diol or dimethyl formamide) is seen in this system. Thus the Frank’s hypothesis of ‘enforcement of
water structure does not seem to be applicable when the water component of 1,5- pentane diol- water system is replaced by organic solvent, DMF.

**Table 3.** Sv- values of Tetra alkyl ammonium iodide salt solutions in different compositions of 1,5-Pentanediol - DMF mixtures

<table>
<thead>
<tr>
<th>Composition of solvent mixtures (v/v)</th>
<th>20%DMF in 1,5-pentanediol ($\varepsilon$=28.40)</th>
<th>40% DMF in 1,5-pentanediol ($\varepsilon$=30.40)</th>
<th>60% DMF in 1,5-pentanediol ($\varepsilon$=32.50)</th>
<th>80% DMF in 1,5-pentanediol ($\varepsilon$=34.60)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_4$NI</td>
<td>450.93</td>
<td>333.99</td>
<td>231.94</td>
<td>158.29</td>
</tr>
<tr>
<td>Pr$_4$NI</td>
<td>434.08</td>
<td>315.32</td>
<td>210.29</td>
<td>121.40</td>
</tr>
<tr>
<td>Bu$_4$NI</td>
<td>392.93</td>
<td>240.07</td>
<td>153.21</td>
<td>75.11</td>
</tr>
<tr>
<td>Pen$_4$NI</td>
<td>324.58</td>
<td>183.05</td>
<td>76.87</td>
<td>25.12</td>
</tr>
</tbody>
</table>

The decreasing trend of Sv, in moving row wise from Et$_4$NI to Pen$_4$NI in the Table 3, for a fixed solvent composition, shows that there is a marked effect of the size of electrolyte molecule on the magnitude of slope. The slope goes on decreasing as the smaller molecule is replaced by a bigger molecule successively. This happens in each binary solvent- mixture composition. This trend can easily be interpreted by the two influencing factors. Firstly, increase of ionic size decreases the charge density on the ion which results in the weak ion- ion interaction with decreasing value of charge density. Successive weak ion- ion interactions give the decreasing values of slope, hence the magnitude of the slope is smaller for Pen$_4$NI than Bu$_4$NI and likewise the magnitude of slope is smaller for Bu$_4$NI than Pr$_4$NI and so on. Secondly, bigger size alkyl chains provide large number of cavities inside the alkyl chains than those available in smaller size alkyl chains. The molecules of solvent mixtures are accommodated inside these void spaces of alkyl chain of R$_4$NI. Such void spaces may be available in the long alkyl chain of 1,5- pentane diol. Thus interpenetration of ions of solute into solvent molecule and vice versa can take place which causes the reduced values of slope Sv. There will be little contribution of addition of solute to 1,5- Pentane diol – DMF mixture and so the small values of Sv. Sv values also decreases as we go down the columns from 20 to 40% DMF for a particular salt. This decreasing trend of Sv values down the columns can be explained on the basis of the effect of dielectric constant of the solvent media on the slope. It is know that electrostatic forces of attraction, F, between the ions, is inversely proportional to dielectric constant of solvent medium (i.e. $F \alpha \frac{1}{\varepsilon}$), The increase in the value of dielectric constant of the solvent medium results in weak electrostatic forces of attraction between the ions and hence ion- ion interactions become weaker and weaker as there is a gradual increase of dielectric constant of the medium. In the present study, the gradual increase of dielectric constant of medium is done by increasing the DMF content in the 1,5-pentane diol – DMF mixture i.e. as we move from 20 to 80% DMF in the 1,5-pentane diol down the columns of Table 3. Hence the decreasing values of slopes are obtained.

**Table 4.** $\Phi_v^0$ (MS) and $\Delta\Phi_v^0$ (tr) values for different electrolytes in 1,5-pentane diol – DMF mixture at 298.15 K

<table>
<thead>
<tr>
<th>DMF in 1,5-Pentane diol, (v/v)</th>
<th>Et$_4$NI</th>
<th>Pr$_4$NI</th>
<th>Bu$_4$NI</th>
<th>Pen$_4$NI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_v^0$</td>
<td>$-109.51$</td>
<td>$-130.86$</td>
<td>$-169.84$</td>
<td>$-203.25$</td>
</tr>
<tr>
<td>$\Delta\Phi_v^0$ (tr)</td>
<td>$-109.51$</td>
<td>$107.94$</td>
<td>$137.76$</td>
<td>$149.65$</td>
</tr>
<tr>
<td>$\Phi_v^0$</td>
<td>$107.94$</td>
<td>$137.76$</td>
<td>$174.65$</td>
<td>$203.25$</td>
</tr>
<tr>
<td>$\Delta\Phi_v^0$ (tr)</td>
<td>$107.94$</td>
<td>$137.76$</td>
<td>$174.65$</td>
<td>$203.25$</td>
</tr>
<tr>
<td>$\Phi_v^0$</td>
<td>$-130.86$</td>
<td>$137.76$</td>
<td>$174.65$</td>
<td>$203.25$</td>
</tr>
<tr>
<td>$\Delta\Phi_v^0$ (tr)</td>
<td>$-130.86$</td>
<td>$137.76$</td>
<td>$174.65$</td>
<td>$203.25$</td>
</tr>
<tr>
<td>$\Phi_v^0$</td>
<td>$137.76$</td>
<td>$174.65$</td>
<td>$203.25$</td>
<td>$203.25$</td>
</tr>
<tr>
<td>$\Delta\Phi_v^0$ (tr)</td>
<td>$137.76$</td>
<td>$174.65$</td>
<td>$203.25$</td>
<td>$203.25$</td>
</tr>
<tr>
<td>$\Phi_v^0$</td>
<td>$-169.84$</td>
<td>$174.65$</td>
<td>$203.25$</td>
<td>$203.25$</td>
</tr>
<tr>
<td>$\Delta\Phi_v^0$ (tr)</td>
<td>$-169.84$</td>
<td>$174.65$</td>
<td>$203.25$</td>
<td>$203.25$</td>
</tr>
<tr>
<td>$\Phi_v^0$</td>
<td>$203.25$</td>
<td>$203.25$</td>
<td>$203.25$</td>
<td>$203.25$</td>
</tr>
<tr>
<td>$\Delta\Phi_v^0$ (tr)</td>
<td>$203.25$</td>
<td>$203.25$</td>
<td>$203.25$</td>
<td>$203.25$</td>
</tr>
</tbody>
</table>
Conclusion

The $\Phi_{V}^{0}$ values (Table 4) are positive and large for the tetraalkyl ammonium salts in all the composition of 1, 5-pentane diol – DMF mixtures, showing, thereby, the presence of weak ion- solvent interactions. Increase in $\Phi_{V}^{0}$ and $\Delta \Phi_{V}^{0}(tr)$ values with increasing concentration of DMF in 1,5-pentane diol may be attributed to increase in electrostriction in presence of DMF in the solvent mixture. Thus the electrostriction effect, which brings about the shrinkage in the solvent is increased in pure DMF as compared with that in the mixed solvent. Since electrostriction primarily reflects electrolyte- solvent interaction, it can be inferred that electrolyte - solvent interaction increases (while ion-ion interaction decreases) with increase in DMF content in this solvent mixture.

References