Paper Published
Conductivity of N-ethylpyridinium iodide in water-dioxan mixtures

B R Pujari, G Dixit & B Behera
Department of Chemistry, Sambalpur University, Jyoti Vihar, Sambalpur 768 019
Received 12 January 1995; revised 20 March 1995; accepted 17 April 1995

The conductivity data of N-ethylpyridinium iodide in water-dioxan mixture are analysed by Onsager's limiting law to get both $\Lambda_0$ and association constant $K_a$. Activity coefficient data obey Guntelberg's equation. $\Lambda_0$ decreases and $K_a$ increases with increase in viscosity of the solvent system. The results are discussed in terms of ion-ion and ion-solvent interactions.

Conductivity studies on N-methylpyridinium iodide and its methyl substituted derivatives in 90 and 100% acetone and ethanol solvent mixtures, water-methanol, water-ethanol and water-dioxan mixtures in the entire solvent composition range indicate ionic association and hydrophobic hydration of the pyridinium ion.

In this note we report the conductance studies of N-ethylpyridinium iodide (NEPI) in water-dioxan mixture at 25°C.

Experimental
Preparation of the salt, its purification, gravimetric estimation of iodide as silver iodide, purification and preparation of water-dioxan mixtures and conductivity measurements of the salt solutions in its concentration range of $10^{-2}$ to $10^{-3}$ M at 25°C were carried out as described earlier. Maximum concentration of dioxan in the mixture was limited to 50% because of solubility of the salt.

Results and discussion
The values of the physical constants of water-dioxan solvent systems at 25°C are reported earlier. N-ethylpyridinium iodide ionizes in solution as

$$C_2H_5PyI \rightarrow C_2H_5Py^+ + I^- \quad \ldots \ldots (1)$$

and the ionization constant $K_a$ is given by

$$K_a = \frac{\alpha^2 C}{1-\alpha} \cdot f_1^2 = K' f_2^2 \quad \ldots \ldots (2)$$

or $pK_a = pK_a - 2 \log f_2 \quad \ldots \ldots (3)$

The conductance data were analysed by Onsager's limiting law

$$\Lambda = \Lambda_0 - (B_1 \Lambda_0 + B_2) \sqrt{\alpha C} \quad \ldots \ldots (4)$$

where the degree of ionization $\alpha$ and the constants $B_1$ and $B_2$ are taken as

$$\alpha = \frac{\Lambda}{\Lambda_0}, \quad B_1 = \frac{8.20 \times 10^5}{(\epsilon T)^{3/2}}, \quad B_2 = \frac{82.4}{(\epsilon T)^{1/2}} \quad \ldots \ldots (5)$$
The activity coefficient $f_\pm$ was calculated using Guntelberg's equation,

$$-\log f_\pm = \frac{\Lambda_0 \sqrt{c}}{1 + \sqrt{c}}$$  \hspace{1cm} (6)

The symbols used in the equations have their usual meaning. Equations (3) and (4) were solved by the method of least squares since the plots of $\Lambda_0$ versus $\sqrt{c}$ are linear in the concentration ranges studied for the salt. The values of the derived parameters are included in Table 1.

The $\Lambda_0$, $K_A = 1/K_a$, the association constant, and the viscosity of the solvent system $\eta_\nu$, are plotted against the mole fraction, $x_2$, of dioxan in Fig. 1. Examination of the Table and the Fig. 1 reveals that the $\Lambda_0$ values decrease and $K_A$ values increase with increase in $x_2$ and $\eta_\nu$ of the solvent system. This shows that the viscosity of the medium plays an important role on the mobility of the ions NEP$^+$ and I$^-$ in solution.

The activity coefficients calculated using Eq. (6) are plotted in Fig. 2 which reveals that $-\log f_\pm$ bears a linear relationship with $I^{1/2}$. The values of $A$ both calculated and experimentally obtained from Fig. 2 for the solvent systems are in good agreement (Table 1). This shows that the use of Guntelberg's equation for the calculation of $f_\pm$ in the determination of $K_A$ is suitable for the present system.

Interactions of the type ion-ion (NEP$^+$ – I$^-$) and ion-solvent (NEP$^+$-solvent; I$^-$-solvent) occur both in water-rich and dioxan-rich regions in the solvent system. This has been conclusively proved in the case of NMPI from the studies of viscosity and apparent molar volumes in aqueous solutions. It may be presumed that NEP$^+$ ion gets solvated in water-rich region and I$^-$ ion interacts with dioxan in the form of charge transfer complex in the dioxan-rich region of the solvent system.

Acknowledgement

Financial assistance from the CSIR, New Delhi, is gratefully acknowledged.

References

DIELECTRIC CONSTANTS OF SOME MISCIBLE AQUEOUS-ORGANIC SOLVENT MIXTURES

B. R. PUJARI, B. BARIK and B. BEHERA

Department of Chemistry, Sambalpur University, Jyoti Vihar, Sambalpur – 768 019, India

(Received 8 April 1997)

The dielectric constants of some aqueous-organic solvent mixtures have been analysed by an equation analogous to Grunberg and Nissan equation. The hydration numbers are found out at the maxima and minima of the plots of $\Delta \varepsilon$ versus $x_2$. The extent of hydration of organic solvents is discussed in the light of structure of the solvents. It is shown that the equations can be very well applied to aqueous-organic solvent mixtures. An interaction parameter $d$ is defined to fit the dielectric constant data of the mixtures which bears a linear relationship with $e_2$.

Keywords: Dielectric constants; aqueous-organic solvent mixtures; hydration number; water structure

INTRODUCTION

The dielectric constants of mixtures of polar–polar liquids is of great importance in physical and pharmaceutical chemistry. These liquids are associated to some extent. The probabilities of the occurrence of A-A, B-B and A-B interactions are expected when two polar liquids A and B are mixed together. The extent of hydration of water-miscible organic liquids can be determined from density, viscosity and dielectric constants of these mixtures.

Hasted [1] has reviewed the dielectric properties of aqueous-organic solvent mixtures and aqueous solutions of non-electrolytes. Certain more modern mixture formulas for polar spheres in non-polar media [2–6] almost give rise to identical results for the volume fraction.
Schott [7] has found out the deviations of experimental dielectric constants using

\[ \log e_{12} = x_1 \log e_1 + x_2 \log e_2 \]  \hspace{1cm} (1)

analogous to Kendall equation [8] for viscosity, where \( x \) and \( e \) stand for mole fraction and dielectric constants and the subscripts 1, 2 and 12 stand for water, organic liquid and their mixtures respectively. This equation is analogous to that of Arrhenius [9] equation for viscosity and therefore it has a theoretical basis. Grunberg and Nissan [10] modified equation (1) with an interaction parameter \( d \) for viscosity as

\[ \log n_{12} = x_1 \log n_1 + x_2 \log n_2 + x_1 x_2 d. \]  \hspace{1cm} (2)

The parameter \( d \) can be both positive and negative and is a measure of the strength of interaction between two liquids in the solution [11].

The interactions as shown above is not taken care of in equation (1). Survey of literature reveals that the dielectric constant data is not analysed according to Grunberg and Nissan equation. Therefore in this paper an attempt is made to analyze the dielectric constant data of some aqueous-organic solvent mixtures by a method analogous to that of Grunberg and Nissan at 25°C.

MATERIALS AND METHODS

The dielectric constant data at 25°C are taken from literature [12]. The data are shown graphically in Figures 1 and 2 as a function of mole fraction of the organic components.

The plots indicate that the dielectric constant of water gradually decreases with addition of the organic liquid. The decrease is not linear but exponential. The nature of the curves indicates the existence of interaction between the two liquids. Hence an interaction parameter should explain the non-linearity of the plots. Basing on this analogy the Grunberg-Nissan equation (eqn. (2)) for viscosity [10] can be extended to dielectric constants of solvent mixtures as

\[ \log e_{12} = x_1 \log e_1 + x_2 \log e_2 + d x_1 x_2 \]  \hspace{1cm} (3)
FIGURE 1 $e_{\text{exp}}$ as a function of $x_2$.

FIGURE 2 $e_{\text{exp}}$ as a function of $x_2$. 
Eqn. (2) is used to calculate the dielectric constants of the mixtures at various compositions. Deviations in dielectric constants are defined as

$$\Delta \varepsilon = \varepsilon_{12}^{\text{calc}} - \varepsilon_{12}^{\text{exp}}$$  \hspace{1cm} (4)$$

while percent relative deviations in dielectric constants are calculated as

$$\text{Relative deviation in } \varepsilon_{12} = 100 \times \frac{\Delta \varepsilon}{\varepsilon_{12}^{\text{exp}}}$$  \hspace{1cm} (5)$$

RESULTS AND DISCUSSION

The mean of the deviations calculated by eqn. (4) and (5) is given in Table I. The low values of the percent relative deviation clearly show that eqn. (3) can be universally applied to aqueous-organic solvent mixtures which are thoroughly miscible.

The interaction parameter $d$ for different organic solvents is given in Table I. The empirical parameter $d$ is calculated for each composition by the equation.

$$d = \frac{\log(\varepsilon_{\text{cal}}/\varepsilon_{\text{exp}})}{x_1x_2}$$  \hspace{1cm} (6)$$

<table>
<thead>
<tr>
<th>Organic Solvent</th>
<th>$\varepsilon$</th>
<th>$d$</th>
<th>$x_2$</th>
<th>$n_0$</th>
<th>% mean</th>
<th>R.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>31.5</td>
<td>-0.044</td>
<td>0.19, 0.69</td>
<td>4.26, 0.45</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
<td>-0.230</td>
<td>0.28, 0.48</td>
<td>2.57, 1.08</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td>1-Propanol</td>
<td>20.1</td>
<td>-0.525</td>
<td>0.31</td>
<td>2.23</td>
<td>4.58</td>
<td></td>
</tr>
<tr>
<td>2-Propanol</td>
<td>18.0</td>
<td>-0.540</td>
<td>0.42</td>
<td>1.38</td>
<td>4.85</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-butanol</td>
<td>9.9</td>
<td>-0.816</td>
<td>0.20</td>
<td>4.00</td>
<td>6.22</td>
<td></td>
</tr>
<tr>
<td>Glycerol</td>
<td>40.1</td>
<td>+0.150</td>
<td>0.11, 0.23</td>
<td>8.10, 3.30</td>
<td>6.29</td>
<td></td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>37.7</td>
<td>+0.060</td>
<td>0.40</td>
<td>1.50</td>
<td>3.63</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>19.1</td>
<td>-0.450</td>
<td>0.42</td>
<td>1.38</td>
<td>12.33</td>
<td></td>
</tr>
<tr>
<td>Dioxan</td>
<td>2.1</td>
<td>-1.050</td>
<td>0.20</td>
<td>4.00</td>
<td>3.70</td>
<td></td>
</tr>
</tbody>
</table>
The mean of the $d$-values was taken for further calculation. It provides a useful measure of the interactions between pairs of miscible liquids reaching a maximum or minimum at the composition of strongest interaction. It is negative for alcohols, acetone and dioxan containing one or no hydroxy groups (groups-I) and positive for glycerol and ethylene glycol (group-II) containing polyhydroxy groups. This confirms the views of Fort and Moore [11]. The plot of $d$ versus $\varepsilon_2$ is shown in Figure 3.

Which shows that $d$ bears a linear relationship with $\varepsilon_2$ empirically as

$$d = 0.03\varepsilon_2 - 1.07 \quad (7)$$

FIGURE 3 $d$ as a function of $\varepsilon_2$. 
The empirical parameter $d$ takes into account the interactions A-A, B-B and A-B. The negative values of $d$ for group-I solvents indicate that the interaction A-B dominates over A-A and B-B and for group II compounds the reverse is true. Because of the greater interactions between A and B, the water structure gets disrupted by the addition of organic solvents which results in the negative value of $d$.

The deviations of the experimental dielectric constants are plotted in Figures 4 and 5 as function of $x_2$.

The figures reveal that there exists maxima in cases of methanol, ethanol, 1-propanol, 2-propanol, $t$-butanol, ethylene glycol, glycerol and minima in case of acetone and dioxan in the solvent mixtures. In case of methanol, ethanol and glycerol there exists two maxima in the aqueous solvent mixtures. Compositions corresponding to these

![Diagram](image-url)
maxima and minima determine the extent of hydration and thus the hydration number $n_h$ can be calculated from

$$n_h = \frac{x_1}{x_2}$$  \hspace{1cm} (8)

The values of $n_h$ are set out in Table I. In case of methanol, ethanol and glycerol, there are two hydration numbers: one for the water-rich region and the other for the organic solvent-rich region. It is well known that association of alcohols is governed by the association equilibria:

$$(\text{ROH})_n + \text{ROH} \rightleftharpoons (\text{ROH})_{n+1}$$  \hspace{1cm} (9)
Organic liquids interact with water through hydrogen bonds as OH...O. Because of the association equilibrium (Eqn.-9) there exists two maxima in case of methanol, ethanol and glycerol due to two values of \( n \). The water-alcohol mixtures are treated as heterogeneous mixtures. The pure alcohol is conceived as containing very long molecular chains which can penetrate into the three dimensional network structure of water and the water structure gets disrupted at higher concentrations of organic solvents.

Thus one can get the value of \( d \) from eqn. (7) using the known value of the dielectric constant \( \varepsilon_2 \) of the organic component and utilise this value in eqn.(3) to calculate the dielectric constants of water-organic solvent mixtures at various compositions.

References

AN EMPIRICAL RELATION FOR THE EVALUATION OF THE DIELECTRIC CONSTANTS OF SOME MISCIBLE AQUEOUS-ORGANIC SOLVENT MIXTURES AT 298.15 K

R. MOHAPATRA, B. R. PUJARI, B. BARIK and B. BEHERA*

Department of Chemistry, Sambalpur University, Jyoti Vihar, Sambalpur—768 019, Orissa, India

(Received 12 November 1999)

Dielectric constants of some miscible aqueous-organic solvent mixtures at 25°C have been analyzed by an equation analogous to Tamura and Kurata equation for viscosity. The hydration numbers \( n_h \) found out from the plots of \( \Delta \varepsilon \) vs. \( x_2 \) are explained in terms of H-bonding both in water-rich and alcohol-rich medium.

Keywords: Dielectric constants; Aqueous-organic solvent mixtures; Hydration number

INTRODUCTION

The dielectric constants of some thoroughly miscible aqueous-organic liquid mixtures are of considerable importance in physical and pharmaceutical chemistry. These liquids are associated. The extent of hydration of water-miscible organic liquid mixtures can be determined from density, viscosity [1] and dielectric constants [2] of these mixtures. The dielectric properties of aqueous-organic solvent mixtures and aqueous solutions of nonelectrolytes have been studied by using mixture formulas of viscosity for polar spheres in non-polar media [3–13].

*Corresponding author.
Tamura and co-workers [14,15] have analyzed the viscosity data of binary mixtures of liquids and solutions of nonelectrolytes by the following equations

\[ \eta = x_1^2 \eta_1 + 2x_1x_2 \eta_{12} + x_2^2 \eta_2 \]  
(1)

\[ \eta = x_1 \eta_1 + 2(x_1x_2 \eta_2) ^{1/2} \eta_{12} + x_2 \eta_2 \]  
(2)

where \( x_i \) and \( \eta \) stand for mole fraction and viscosity and subscripts 1, 2 and 12 stand for water, organic liquid and their mixtures respectively. The volume fraction \( v_2 \) was calculated by taking the density and weight fraction of the solution and solid respectively.

Equations (1) and (2) fit well the viscosity data at 25°C. Therefore in this paper an attempt is made to analyze the dielectric constant data of some aqueous-organic solvent mixtures at 25°C by the above two equations.

MATERIALS AND METHODS

The dielectric constant data at 25°C are taken from literature [16]. They are represented graphically in Figures 1 and 2 as a function of \( x_2 \), the mole fraction of the organic components.

Examination of the figures shows that the dielectric constant of water decreases in an exponential manner which indicates the existence of interaction between the two liquids in the mixtures. The data were analyzed [17] by

\[ \log \varepsilon_{12} = x_1 \log \varepsilon_1 + x_2 \log \varepsilon_2 + dx_1x_2 \]  
(3)

which is analogous to the viscosity equation of Grunberg and Nissan [18].

The work of Tamura and coworkers [14,15] has prompted us to use the viscosity equations for analysis of dielectric constant data of aqueous-organic solvent mixtures by using Eqs. (1) and (2) as

\[ \varepsilon = x_1^2 \varepsilon_1 + 2x_1x_2 \varepsilon_{12} + x_2^2 \varepsilon_2 \]  
(4)
FIGURE 1 $\varepsilon_{\text{exp}}$ as a function of $x_2$.

FIGURE 2 $\varepsilon_{\text{exp}}$ as a function of $x_2$. 

- Methanol
- Ethanol
- 1-Propanol
- 2-Propanol
- t-BuOH
- EG
- Glycerol
- Acetone
- Dioxane
\[ \varepsilon = x_1 v_1 \varepsilon_1 + 2(x_1x_2v_1v_2)^{1/2} \varepsilon_{12} + x_2v_2 \varepsilon_2 \]  

(5)

The volume fraction \( v_2 \) of the organic component in the mixture was calculated by Looyenga’s [6, 7] method as

\[ v_2 = \left( \varepsilon_1^{1/3} - \varepsilon_2^{1/3} \right) / \left( \varepsilon_2^{1/3} - \varepsilon_1^{1/3} \right) \]  

(6)

\[ v_1 = 1 - v_2 \]  

(7)

The deviations and the percent relative deviations in dielectric constants are calculated as

\[ \Delta \varepsilon = \varepsilon_{12, \text{calc}} - \varepsilon_{12, \text{exp}} \]  

(8)

Relative deviation in \( \varepsilon_{12} \) = \( 100 \times \frac{\Delta \varepsilon}{\varepsilon_{12, \text{exp}}} \)  

(9)

RESULTS AND DISCUSSION

The physical parameters from dielectric constants of some water miscible organic solvents at 25°C are set out in Tables I and II.

The percentage mean relative deviation values clearly show that Eqs. (4) and (5) can be applied to these aqueous-organic solvent mixtures which are thoroughly miscible and associated.

Schott [9] has pointed out while analyzing the viscosity and dielectric constant data by using Kendall equation [13] that deviations in \( \Delta \eta \) and \( \Delta \varepsilon \) vs. \( x_2 \) give a useful measure of the extent of hydration

<table>
<thead>
<tr>
<th>Organic solvent</th>
<th>( \varepsilon_2 )</th>
<th>( x_2 )</th>
<th>( n_0 )</th>
<th>% Mean R.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>31.5</td>
<td>0.22, 0.82</td>
<td>3.55</td>
<td>0.22</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
<td>0.24, 0.90</td>
<td>3.17</td>
<td>0.11</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>20.1</td>
<td>0.23</td>
<td>3.55</td>
<td>31.17</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>18.0</td>
<td>0.23</td>
<td>3.35</td>
<td>33.8</td>
</tr>
<tr>
<td>( t )-Butanol</td>
<td>9.9</td>
<td>0.21</td>
<td>3.76</td>
<td>58.7</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>37.7</td>
<td>0.22, 0.85</td>
<td>3.35</td>
<td>0.18</td>
</tr>
<tr>
<td>Glycerol</td>
<td>40.1</td>
<td>0.22</td>
<td>3.55</td>
<td>10.90</td>
</tr>
<tr>
<td>Acetone</td>
<td>19.1</td>
<td>0.23</td>
<td>3.35</td>
<td>21.79</td>
</tr>
<tr>
<td>Dioxan</td>
<td>2.1</td>
<td>0.20</td>
<td>4.0</td>
<td>88.57</td>
</tr>
</tbody>
</table>
TABLE II Physical parameters of some water-miscible organic solvents at 25°C from Eq. (5)

<table>
<thead>
<tr>
<th>Organic solvent</th>
<th>$x_2$</th>
<th>$n_h$</th>
<th>% Mean R.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.19, 0.80</td>
<td>4.26, 0.25</td>
<td>4.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.14, 0.76</td>
<td>6.14, 0.32</td>
<td>7.06</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>0.11, 0.73</td>
<td>8.09, 0.37</td>
<td>8.23</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.11, 0.73</td>
<td>8.09, 0.37</td>
<td>9.6</td>
</tr>
<tr>
<td>t-Butanol</td>
<td>0.14, 0.72</td>
<td>6.14, 0.39</td>
<td>20.4</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>0.17, 0.73</td>
<td>4.8, 0.37</td>
<td>4.2</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.14, 0.70</td>
<td>6.14, 0.43</td>
<td>2.9</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.17, 0.75</td>
<td>4.8, 0.33</td>
<td>10.03</td>
</tr>
<tr>
<td>Dioxan</td>
<td>0.16</td>
<td>5.25</td>
<td>48.86</td>
</tr>
</tbody>
</table>

of the organic components in the miscible mixtures. The deviations of the experimental dielectric constants of both the Eqs. (4) and (5) as a function of $x_2$ are shown in Figures 3—6.

Examination of Figures 3 and 4 indicate that methanol, ethanol and ethylene glycol show both maxima and minima in the mixtures and rest of the organic components show only maxima. Examination of Figures 5 and 6 indicate that all the organic components show both maxima and minima excepting dioxan, which shows only a maxima. The mole fractions $x_2$ of all the organic components corresponding to maxima and minima are shown in Tables I and II. Compositions of these mole fractions indicate the extent of hydration represented by the hydration number $n_h$ as

$$n_h = \frac{x_1}{x_2}$$

The hydration numbers of the organic components in the mixture are set out in Tables I and II.

The percentage relative deviations of Eq. (4) are much higher than that of Eq. (5). The hydration numbers obtained by Eq. (4) (Tab. I) are almost same for all the organic components whereas the hydration numbers obtained by Eq. (5) are different from solvent to solvent.

In alcohol-water mixtures the existence of maxima and minima is observed in water-rich regions and alcohol-rich regions respectively [19] which is reflected in the measurement of Walden product and measurement of relaxation times [20]. In aqueous-alcohol solutions, the structure of solutions increases with increasing amount of alcohols.
FIGURE 3  $\Delta \varepsilon$ as a function of $x_2$ for Eq. (4).

FIGURE 4  $\Delta \varepsilon$ as a function of $x_2$ for Eq. (4).
FIGURE 5  $\Delta e$ as a function of $x_2$ for Eq. (5).

FIGURE 6  $\Delta e$ as a function of $x_2$ for Eq. (5).
and decreases at high alcohol content. It is well known that association of alcohols is governed by the association equilibria:

\[(\text{ROH})_n + \text{ROH} \rightleftharpoons (\text{ROH})_{n+1}\]  

(11)

It has been shown qualitatively that water re-establishes a three-dimensional H-bonded arrangement in aqueous-alcoholic mixtures which enforces hydrophobic association of the cosolvent molecules represented by

\[(\text{ROH})_{\text{aq}} + (\text{ROH})_{\text{aq}} \rightleftharpoons (\text{HOR}. \text{ROH})_{\text{aq}}\]  

(12)

Presumably the equilibria (11) and (12) take place in alcohol-rich and water-rich medium resulting in low and high hydration numbers \(n_h\) respectively.

On the basis of the above analogy we conclude that Eq. (5) fits the dielectric constant data of aqueous-organic solvent mixtures well because of low percentage relative deviation and existence of maxima and minima with two hydration numbers which explains the equilibria represented by Eqs. (11) and (12).

References

DIELECTRIC CONSTANTS OF MIXTURES