EFFECT OF SOLVENT ON THE CONDUCTANCE OF TETRAMETHYL AMMONIUM BROMIDE IN AQUEOUS N, N-DIMETHYL FORMAMIDE

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ABSTRACT
The conductance of Tetramethyl ammonium bromide has been studied in water -N, N-dimethyl formamide mixtures of different compositions in the temperature range 303-318K. The molar conductance data collected at different concentrations of the electrolyte is analyzed using Shedlovsky and Krauss - Bray models. The limiting molar conductance is found to be dependent on the temperature and dielectric constant of the medium. Increase in temperature and decrease in dielectric constant of the aquo-organic mixture increase the limiting molar conductance values. From these effects, the activation energy of the conducting process and distance of separation between the ions are calculated. From the effect of temperature on the ion pair association constant $K_A$, the enthalpy change accompanied by the ion pair formation is calculated. The solvation number computed in each solvent suggests that, the solvent solute interactions are dependent on the dielectric constant of the medium.

Keywords: Ion - Pair Association Constant, Ion-Pair Dissociation Constant, Solvation Number, Tetra Methyl Ammonium Bromide.

1. INTRODUCTION

Conductance studies in single and mixed solvent systems have continued to be of great interest to chemists. The literature is replete with conductance data of many electrolytes in aqueous, organic and in binary organic solvent systems. The conductance behavior of many ions in mixed solvent systems is reported to be influenced by a number of factors including solvent solute interactions, solvent - solvent interactions, densities and viscosities of the mixed solvent systems and the extent of solvation of the ionic species.

Literature survey Manikyamba et al\textsuperscript{1-15} indicates that, the conductance data and viscosity data of different electrolytes is useful in analyzing the ion solvent interactions and solvation behavior of the ions.

The present work deals with the conductance behavior of Tetramethyl ammonium bromide in aqueous N, N-dimethyl formamide at different temperatures between 303 and 318 K. In the present communication the results of these studies are presented.

2. EXPERIMENTAL SECTION

Deionized water was distilled and used. N, N-dimethyl formamide (DMF) (Sd-fine) was used as such. Tetramethyl ammonium bromide (Spectrochem) sample is also used without further purification. A conductivity bridge (ELICO. Model - 180) equipped with a glass conductivity cell of cell constant 0.9845cm\textsuperscript{-1} was used to measure the conductance of the solution. The cell is calibrated using standard (0.1M) KCl solution. The precision of the conductivity bridge is ±10µS. A stock solution of 0.05M Tetramethyl ammonium bromide was prepared in water / aqueous organic solvent mixtures of different compositions (v/v) in the range 0 to 80% organic component. The solute was found to be insoluble above this composition. i.e. 90% and 100% organic solvent . The solution was diluted to different concentrations using different volumes of solvent/ solvent mixture and the conductance values were measured in the temperature range 303-318 K. The solvent / Solvent in the mixture used in these studies have conductance values in the range 20-40 µS. The conductance of the solvent was subtracted to get the conductance of the solute at each concentration. The molar conductance values calculated from the observed conductance are analyzed using Kraus-Bray equation\textsuperscript{16} and Shedlovsky equation\textsuperscript{17} (eq\textsuperscript{2})

\[
\frac{1}{\Lambda} = \frac{\Lambda}{K_c \Lambda_0} + \frac{1}{\Lambda_0} \\
\frac{1}{S\Lambda} = \frac{S_f^2K_c\Lambda}{\Lambda_0} + \frac{1}{\Lambda_0}
\]  

(eq\textsuperscript{2})

\(\Lambda\) is molar conductance at concentration C, \(\Lambda_0\) is the limiting molar conductance. \(K_\Lambda\) is the association constant of the ion pair, \(K_c\) is the dissociation constant, \(f_\pm\) is the mean ionic activity coefficient, \(S\) is a factor given by

\[
S = \left[ \frac{Z}{2} + \sqrt{1 + \left( \frac{Z}{2} \right)^2} \right]
\]

(3)

\[
Z = \left[ \frac{\alpha\Lambda + \beta}{\Lambda_0} \right] (C\Lambda)^{1/2}
\]

Where

(4)

\[
\beta = 82.50 \left( \frac{1}{\eta} \right) (\epsilon T)^{1/2}
\]

(5)
Effect of Solvent On The Conductance of Tetramethyl Ammonium Bromide In Aqueous N, N-Dimethyl Formamide

\( \varepsilon \) is the dielectric constant \( \eta \) is the viscosity of the medium. \( \approx 8.204 \times 10^4 (\varepsilon T)^{1/2} \) S is calculated using \( \Lambda_0 \) obtain from the Onsagar model using the plot of \( \Lambda \) against \( \sqrt{C} \). The least square analysis of the using the above two equations (1,2) is satisfactory with linear correlation coefficients in the range 0.93-0.96.

3. RESULTS AND DISCUSSION

The molar conductance (\( \Lambda \)) was determined from the solvent corrected specific conductance for tetramethyl ammonium bromide in water, DMF, in various compositions (v/v) of water - DMF mixtures at 303, 308, 313 and 318 K. The values were analyzed using Debye- Huckel - Onsagar, Kraus - Bray and Shedlovsky models of conductivity to evaluate molar conductance at infinite dilution \( \Lambda_0 \). The values thus obtained are shown in Table-1.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>0% DMF (1)</th>
<th>20% DMF (1)</th>
<th>40% DMF (1)</th>
<th>60% DMF (1)</th>
<th>80% DMF (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>123.3</td>
<td>123.4</td>
<td>85.2</td>
<td>85.1</td>
<td>83.1</td>
</tr>
<tr>
<td>308</td>
<td>154.5</td>
<td>154.5</td>
<td>104.8</td>
<td>104.8</td>
<td>100.8</td>
</tr>
<tr>
<td>313</td>
<td>174.3</td>
<td>174.2</td>
<td>113.9</td>
<td>114.0</td>
<td>133.9</td>
</tr>
<tr>
<td>318</td>
<td>189.2</td>
<td>189.1</td>
<td>125.0</td>
<td>124.9</td>
<td>134.4</td>
</tr>
</tbody>
</table>

1- Shedlovsky model  2- Kraus Bray model

Expected values increase with increase in temperature in all the cases due to increase in thermal energy and mobility of the ions. Limiting molar conductance values are observed to be dependent on composition of the solvent also. At each temperature these values are maximum in pure water. With the addition of DMF to water they gradually decrease. The composition of DMF could not be extended beyond 80% as TMAB was not soluble.

The decrease \( \Lambda_0 \) is due to increase in the proportion of DMF may be due to decrease in the dielectric constant of the medium. On adding co-solvent to water, solvent - solvent interaction increases. Since conductivity increases with increase in temperature, it is supposed that this variation has to follow Arrhenius relation

\[
\frac{1}{T} \approx \frac{E_a}{R} = \Lambda
\]

\( E_a \) is the energy of activation of rate process, \( R \) is gas constant and \( T \) is the temperature on absolute scale. From the slope of the linear plot of versus \( \frac{1}{T} \), \( E_a \) is evaluated. The \( E_a \) values are tabulated in Table-2.

Table 2 Computed thermodynamic parameters for tetramethyl ammonium bromide under varying compositions (v/v) water-DMF mixtures.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>0% DMF</th>
<th>20% DMF</th>
<th>40% DMF</th>
<th>60% DMF</th>
<th>80% DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a (KJ.mol^{-1}) )</td>
<td>19.2</td>
<td>16.81</td>
<td>23.2</td>
<td>17.16</td>
<td>17.06</td>
</tr>
</tbody>
</table>

4. ASSOCIATION AND DISSOCIATION CONSTANT:

From the slopes of the linear least square analysis using Kraus-Bray and Shedlovsky models, the association constant (\( K_A \)) and the dissociation constant (\( K_C \)) of the ion pair have been evaluated and presented in Table 3. \( K_A \) values decrease with the increase in temperature in
0%, 20%, 40% (v/v) DMF- water mixture, indicating the exothermic behavior of the system. At all other compositions $K_A$ values increase with increase in temperature, indicating the endothermic behaviors of the system. i.e. ion pair formation is accompanied by absorption of heat.

Table 3 $K_A$ and $K_C$ values of tetramethyl ammonium bromide in water - DMF mixtures.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>0% DMF</th>
<th>20% DMF</th>
<th>40% DMF</th>
<th>60% DMF</th>
<th>80% DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_A$</td>
<td>$K_C$</td>
<td>$K_A$</td>
<td>$K_C$</td>
<td>$K_A$</td>
</tr>
<tr>
<td>303</td>
<td>4.16</td>
<td>0.24</td>
<td>3.54</td>
<td>0.28</td>
<td>28.40</td>
</tr>
<tr>
<td>308</td>
<td>5.61</td>
<td>0.18</td>
<td>5.10</td>
<td>0.20</td>
<td>29.34</td>
</tr>
<tr>
<td>313</td>
<td>5.77</td>
<td>0.17</td>
<td>5.20</td>
<td>0.19</td>
<td>30.23</td>
</tr>
<tr>
<td>318</td>
<td>7.00</td>
<td>0.14</td>
<td>5.50</td>
<td>0.18</td>
<td>31.25</td>
</tr>
</tbody>
</table>

The data presented in Table-3 indicates that $K_A$ values vary due to change in the composition of the solvent mixture also. This shows that ion pair formation is influenced by the dielectric constant of the medium. Maximum $K_A$ value is observed in 40% (v/v) DMF-water mixture.

5. SLVATION NUMBER

The solvation number (Sn) which is the number of solvent molecules in the solvent around the species is calculated from the effect of dielectric constant $\varepsilon$ on $\Lambda_0$ based on the equation

$$\log\Lambda_0 = \log\Lambda_0^\infty - \frac{Z_A Z_B e^2}{d_{AB} k_B T}$$

(6)

$Z_A e$, $Z_B e$ are the ionic charges, $k_B$ is Boltzmann constant, $T$ is the temperature and $d_{AB}$ is the distance between the centers of the two ions $\Lambda_0$ is liming molar conductance in solvent of infinite dielectric constant. The plot of $\log\Lambda_0$ against $1/\varepsilon$ is linear and from the slope of this plot, is computed. $Sn$ is computed using the relation,

$$S_n = \frac{d_{AB} - r_i}{r_{solvent}}$$

(7)

Where $r_i$ is the Stokes radius of the ion calculated using the equation

$$r_i = \frac{0.8200}{\eta_0^{0.5}} + 0.0103 \varepsilon + r_y$$

(8)

Where $r_y = 0.85A^0$ for dipolar unassociated solvents and 1.13A$^0$ for protic and associated solvents.

Table 4 Solvation number for tetramethyl ammonium bromide in various compositions of water - DMF mixtures at 303K

<table>
<thead>
<tr>
<th></th>
<th>0% DMF</th>
<th>20% DMF</th>
<th>40% DMF</th>
<th>60% DMF</th>
<th>80% DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>1.00</td>
<td>0.71</td>
<td>0.65</td>
<td>0.38</td>
<td></td>
</tr>
</tbody>
</table>

The solvation number data of the ion thus determined at 303K in all the binary solvent systems studied is shown in Table-4. These values are nearly constant except in 80% (v/v) DMF water mixture. Suggesting that the ion- solvent interactions are nearly independent of the composition of the aquo organic solvent mixture. In 80% (v/v) DMF - water-mixture the solvation number is slightly less. This is attributed to a decrease in the interaction between the ion pair and the solvent.
6. CONCLUSION
The conclusion from these experimental observations that ion-ion interactions are strong in higher percentage of DMF while ion-solvent interactions are weaker in DMF compared to other solvent mixtures for all three electrolytes.

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Conflict of Interest- NIL

REFERENCES

