Conductance Studies of Aqueous Ionic Liquids Solutions [emim][BF$_4$] and [bmim][BF$_4$] at Temperatures from (283.15 to 318.15) K

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We present for the first time the determination of molar conductances, $\Lambda$, of ionic liquids solutions (ILs) such as 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF$_4$] and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF$_4$] as a function of temperature. The data was analyzed with Barthel’s lcCM model to obtain ionic association constants, $K_A$, limiting molar conductances, $\Lambda_o$ of these electrolytes. The examined ionic liquids are practically fully dissociated in water over the whole temperature range (283.15 to 318.15 K). From the temperature dependence of the limiting molar conductivities the Eyring’s activation enthalpy of charge transport was determined. The Walden product values were also calculated.

Keywords: limiting molar conductance, 1-alkyl-3-methylimidazolium tetrafluoroborate, ion association, thermodynamic functions

1. INTRODUCTION

The data of physical and chemical properties on ionic liquids (ILs) are essential for both theoretical research and industrial application. A survey of literature indicates that physical properties of pure ionic liquids have been studied extensively, but the thermophysical and thermodynamic properties of ILs, and in particular their aqueous or organic mixtures, have not been studied in a systematic way so far. A literature review indicates that almost nothing is known about the temperature dependence of the transport properties of dilute ILs solutions, despite the importance of the infinite-dilution limit of such data in understanding the ion-ion and ion-solvent interactions and the possibility of prediction of ILs in specific applications.
The most intensively investigated ILs are those with imidazolium cation, but very little conductivity studies concerned the ionic association of ILs in molecular solvents [1-13]. From these papers results that the alkyl chain length of the cation, type of anion, and physical properties of the molecular solvents affect the ionic association constants. The ionic liquids are solvated to a different extent by the molecular solvents, and the ionic association is affected significantly by ionic solvation [11]. Studies on the ionic association and solvation behavior of ionic liquids in various solvents as a function of the temperature have been a subject of interest lately [14, 15]. The results of the conductance measurements of 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate solutions in N,N-dimethylformamide [14] confirm that in this dipolar aprotic solvent a slight ion association occurs for the ionic liquids over the whole investigated temperature range (like other ionic liquids in acetonitrile, methanol and ethanol). In turn, in protic solvent 1-PrOH a strong ionic association was observed for the ILs [15] (similarly in 2-propanol, 1-butanol and 1-pentanol). Water promotes significantly dissociation of the various ionic liquids [3, 4, 8, 10, 11, 16]. In fact similar to the classical electrolytes, the ln $K_A$ values of the ILs were found to increase linearly with the reverse of the dielectric constants of the solvents, which indicates that the electrostatic interaction between the ions are predominant for the ionic association of the ILs [1].

Conductometry is a reliable, affordable and convenient electrochemical technique, which provides valuable information on ion-solvent interactions, ion-ion association and solvent structure. Such studies are of considerable interest for the optimal use of ionic liquid solutions in high energy batteries and other electrochemical systems and for understanding the ion pair effect in such systems. Therefore, the studies allow the prediction of ILs in various specific applications.

To the best of our knowledge there are no conductometric data available in the literature about ILs tested in water at various temperatures. We present in this manuscript, precise conductivity measurements which have been carried out in dilute solutions of [emim][BF$_4$] and [bmim][BF$_4$] in water at temperatures range (283.15K - 308.15) K at atmospheric pressure. Imidazolium’s ionic liquids were chosen because of their thermal and chemical stability and the insignificant impact of air and moisture. The obtained data were used to calculate the values of the limiting molar conductances, $\Lambda_0$, and the association constants, $K_A$, on the basis of IcCM model. The Eyring activation enthalpy of charge transport, $\Delta H^\dagger_A$, as well as the Walden producers, $\Lambda_\omega \eta$, for the electrolytes have been evaluated.

2. EXPERIMENTAL

2.1. Reagents and chemicals

The specifications of used chemicals are summarized in Table 1.

<table>
<thead>
<tr>
<th>chemical name</th>
<th>source</th>
<th>initial mass fraction purity</th>
<th>purification method</th>
<th>final water mass fraction</th>
</tr>
</thead>
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<td>[emim][BF$_4$]</td>
<td>Fluka</td>
<td>0.990</td>
<td>none</td>
<td>&lt;0.0002$^a$</td>
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<td></td>
<td></td>
<td>&lt;0.00015$^b$</td>
</tr>
</tbody>
</table>
Double distilled, deionized and degassed water with a specific conductance better than $0.5 \cdot 10^{-6}$ S $\cdot$ cm$^{-1}$ was used for the preparation of the mixed solvents.

2.2. Apparatus

All the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with a precision of $\pm 1 \cdot 10^{-5}$ g.

The measurement procedure was based on the method described by Bešter-Rogač et al. [8, 17] and used by us in our previous works [14, 15, 18, 19]. Conductivity measurements were performed with a three-electrode cell with the use of a Precise Component Analyser type 6430B (Wayne-Kerr, UK) under argon atmosphere and at the different frequencies, $\nu$, (0.2, 0.5, 1, 2, 3, 5, 10, 20) kHz. The temperature was kept constant within 0.003 K (Calibration Thermostat Ultra UB 20F with Through-flow cooler DLK 25, Lauda, Germany). The details of the experimental procedure for conductometric measurements were described in our previous paper [14]. The uncertainty of the measured values of conductivity was 0.03%.

3. RESULTS AND DISCUSSION

Table 2. Molar conductances, $\Lambda$, corresponding molalities, $m$, and density gradients, $b$, for aqueous solutions of [emim][BF$_4$] and [bmim][BF$_4$] over the temperature range from (283.15 to 318.15) K

<table>
<thead>
<tr>
<th></th>
<th>$10^3 m$ mol kg$^{-1}$</th>
<th>$\Lambda$ S cm$^2$ mol$^{-1}$</th>
<th>$10^3 m$ mol kg$^{-1}$</th>
<th>$\Lambda$ S cm$^2$ mol$^{-1}$</th>
<th>$10^3 m$ mol kg$^{-1}$</th>
<th>$\Lambda$ S cm$^2$ mol$^{-1}$</th>
<th>$10^3 m$ mol kg$^{-1}$</th>
<th>$\Lambda$ S cm$^2$ mol$^{-1}$</th>
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<td>77.722</td>
<td>0.4864</td>
<td>88.836</td>
<td>0.5901</td>
<td>100.118</td>
<td>0.6182</td>
<td>112.089</td>
</tr>
<tr>
<td>$b = 0.0449$ kg$^2$ dm$^{-3}$</td>
<td>1.3046</td>
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<td>0.9779</td>
<td>88.282</td>
<td>1.0861</td>
<td>99.529</td>
<td>1.7167</td>
<td>110.813</td>
</tr>
<tr>
<td>$b = 0.0439$ kg$^2$ dm$^{-3}$ mol$^{-1}$</td>
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<td>6.8990</td>
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<td>7.0330</td>
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<td>94.548</td>
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<td>82.639</td>
<td>14.143</td>
<td>93.480</td>
<td>20.093</td>
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<td>81.729</td>
<td>17.579</td>
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<td>91.799</td>
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<td>b = 0.0414 kg(^2)dm(^{-3})</td>
<td>b = 0.0407 kg(^2)dm(^{-3})mol(^{-1})</td>
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</table>
The densities, viscosities, and relative water’s permittivity were taken from ref. [20].

To convert molality, \( m \), (moles of electrolyte per kilogram of solution) into molarity, \( c \), the values of density gradients, \( b \), have been determined independently and used in the equation

\[
c / m = \rho = \rho_o + b \ m
\]  

(1a)

where \( \rho_o \) is the density of the solvent. Molar concentrations, \( c \), were necessary to use the conductibility equation. The density gradients and the molar conductances of the ILs in solution, \( \Lambda \), as a function of IL molality, \( m \), (moles of electrolyte per kilogram of solvent) and temperature are presented in Table 2. The relationship among \( m \), \( \tilde{m} \), and \( c \) is the following

\[
\tilde{m} = c / \rho = 1 / (1 + mM)
\]  

(1b)

where \( M \) is the molar mass of electrolyte.

The plot of molar conductances, \( \Lambda \), versus the square root of the molar concentration, \( c^{1/2} \), for the investigated systems monotonically decreases as shown in Figures 1 and 2, respectively over the temperature range from 318.15 to 283.15 K.

The conductivity data were analyzed in the framework of the low concentration Chemical Model (lcCM) [21]. This approach uses the set of equations

\[
\Lambda = \alpha \left[ \Lambda_o - S(ac)^{1/2} + E(ac)\ln(ac) + J(ac) + J_{3/2}(ac)^{3/2} \right]
\]  

(2)

\[
K_A = (1 - \alpha) / (\alpha^2 cy_{\pm}^2)
\]  

(3)

and

\[
\ln y_{\pm} = - (Aa^{1/2} c^{1/2}) / (1 + BRa^{1/2} c^{1/2})
\]  

(4)
Figure 1. Molar conductance, $\Lambda$, of aqueous [emim]BF$_4$ solutions versus $c^{1/2}$ at experimental temperatures; ○, 283.15 K; ■, 288.15 K; ×, 293.15 K; +, 298.15 K; •, 303.15 K; ●, 308.15 K; ♦, 313.15 K; ▲, 318.15 K. The lines represent the calculations according to Eqs (2) through (4).

Figure 2. Molar conductance, $\Lambda$, of aqueous [bmim]BF$_4$ versus $c^{1/2}$ at experimental temperatures; ○, 283.15 K; ■, 288.15 K; ×, 293.15 K; +, 298.15 K; •, 303.15 K; ●, 308.15 K; ♦, 313.15 K; ▲, 318.15 K. The lines represent the calculations according to Eqs (2) through (4).

In these equations, $\Lambda_o$ is the limiting molar conductance; $\alpha$ is the dissociation degree of an electrolyte; $K_A$ is the ionic association constant; $R$ is the distance parameter of ions; $y_\pm$ is the activity coefficient of ions on the molar scale; $A$ and $B$ are the Debye–Hückel equation coefficients. The analytical form of the parameters $S$, $E$, $J$, and $J_{3/2}$ was presented previously [21]. The values of $\Lambda_o$, $K_A$, and $R$ were obtained using the well-known procedure given by Fuoss [22] and are collected in Table 3.
Table 3. Limiting molar conductances, $\Lambda_o$, association constants, $K_A$, distance parameters, $R$, and standard deviations, $\sigma(\Lambda)$, for the investigated electrolytes in water at different temperatures

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$\Lambda_o$/S cm$^2$ mol$^{-1}$</th>
<th>$K_A$/dm$^3$ mol$^{-1}$</th>
<th>$R$/nm</th>
<th>$\sigma(\Lambda)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[emim][BF$_4$]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>283.15</td>
<td>79.39 ± 0.01</td>
<td>1.36</td>
<td>7.98</td>
<td>0.02</td>
</tr>
<tr>
<td>288.15</td>
<td>90.38 ± 0.02</td>
<td>1.01</td>
<td>7.42</td>
<td>0.04</td>
</tr>
<tr>
<td>293.15</td>
<td>102.01 ± 0.02</td>
<td>0.85</td>
<td>7.20</td>
<td>0.04</td>
</tr>
<tr>
<td>298.15</td>
<td>114.27 ± 0.01</td>
<td>0.89</td>
<td>6.91</td>
<td>0.04</td>
</tr>
<tr>
<td>303.15</td>
<td>127.17 ± 0.02</td>
<td>0.92</td>
<td>6.92</td>
<td>0.03</td>
</tr>
<tr>
<td>308.15</td>
<td>140.66 ± 0.02</td>
<td>1.06</td>
<td>6.78</td>
<td>0.04</td>
</tr>
<tr>
<td>313.15</td>
<td>154.86 ± 0.01</td>
<td>1.39</td>
<td>6.62</td>
<td>0.03</td>
</tr>
<tr>
<td>318.15</td>
<td>169.61 ± 0.01</td>
<td>1.59</td>
<td>6.70</td>
<td>0.03</td>
</tr>
<tr>
<td>[bmim][BF$_4$]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>283.15</td>
<td>74.93 ± 0.01</td>
<td>1.87</td>
<td>7.81</td>
<td>0.01</td>
</tr>
<tr>
<td>288.15</td>
<td>84.73 ± 0.01</td>
<td>0.60</td>
<td>7.50</td>
<td>0.02</td>
</tr>
<tr>
<td>293.15</td>
<td>95.57 ± 0.01</td>
<td>0.21</td>
<td>7.21</td>
<td>0.02</td>
</tr>
<tr>
<td>298.15</td>
<td>107.39 ± 0.01</td>
<td>0.16</td>
<td>7.18</td>
<td>0.02</td>
</tr>
<tr>
<td>303.15</td>
<td>120.21 ± 0.01</td>
<td>0.59</td>
<td>6.92</td>
<td>0.03</td>
</tr>
<tr>
<td>308.15</td>
<td>134.02 ± 0.01</td>
<td>1.06</td>
<td>7.24</td>
<td>0.04</td>
</tr>
<tr>
<td>313.15</td>
<td>148.78 ± 0.02</td>
<td>1.54</td>
<td>7.78</td>
<td>0.04</td>
</tr>
<tr>
<td>318.15</td>
<td>164.54 ± 0.02</td>
<td>2.17</td>
<td>8.41</td>
<td>0.04</td>
</tr>
</tbody>
</table>

As seen from Table 3, both ionic liquids are practically fully dissociated in water. In DMF the values of association constants are also very small [14], but slightly higher than in water, whereas in 1-propanol both ILs were highly associated [15]. This may mean that an essential role in the ionic association process plays the relative permittivity of the solvent.

One should pay attention to the fact that the values of association constants for various ionic liquids in water are also very small as reported previously [4, 8, 10, 11], which confirms that the ionic liquids exist as free ions in aqueous solution. The values of $K_A$ (and $\Lambda_o$) differ considerably from those of Wang et al. [1] who reported for [bmim][BF$_4$] at 298.15 K association constant of ~100 dm$^3$ mol$^{-1}$. Such a large value of the association constant is surprising given by the high permittivity of water. Wang et al. presented values of $K_A$ and $\Lambda_o$ in various solvents which also differ from other literature data [12, 13, 23, 24]. In turn, Katsuta et al. [3] illustrated for [bmim][BF$_4$] at 298.15 K an association constant of ~5 dm$^3$ mol$^{-1}$. This value also differs slightly from ours, which may result from another research method (capillary electrophoresis).

The limiting molar conductances increase as the temperature increases since the mobility of free ions is higher. The values of $\Lambda_o$ for [emim][BF$_4$] are higher compared to those values for [bmim][BF$_4$], because the $\Lambda_o$ values increase with decreasing alkyl chain length of the ILs.
From the temperature dependence of $\Lambda_o$, the Eyring activation enthalpy of charge transport, $\Delta H^\dagger$, was obtained by using equation 5

$$\ln \Lambda_o + 2/3 \ln \rho_o = - \frac{\Delta H^\dagger}{RT} + D \quad (5)$$

where $D$ is an empirical constant. From the slope of the linear dependencies of $\ln \Lambda_o + 2/3 \ln \rho_o$ versus the inverse of the temperature ($1/T$), which are shown in Figure 3, we obtained the following $\Delta H^\dagger$ values 16078 and 16727 J mol$^{-1}$ for [emim][BF$_4$] and [bmim][BF$_4$], respectively. For [bmim][BF$_4$], the value of $\Delta H^\dagger$ is thus higher than [emim][BF$_4$] by 649 units. It is the result of the presence of a larger substituent in the [bmim]$^+$ cation compared to [emim]$^+$.

Figure 3. Plot of $\ln \Lambda_o + 2/3 \ln \rho_o$ as a function of $1/T$ for ■, [emim][BF$_4$]; and ●, [bmim][BF$_4$] in water.

In the case of protic 1-propanol the $\Delta H^\dagger$ value for [bmim][BF$_4$] was higher than [emim][BF$_4$] by 330 units [15] and for aprotic DMF the $\Delta H^\dagger$ value for [bmim][BF$_4$] was also higher than [emim][BF$_4$], but only by 128 units [14]. It should also be noted that in the case of protic solvents (water and 1-propanol) $\Delta H^\dagger$ values are very similar and almost twice bigger than those for DMF [14, 15]. It can be concluded that the value of $\Delta H^\dagger$ depends on the formation of hydrogen bonds between molecules of the solvent and its structure.

As shown in Table 4, the association constant values, $K_A$, are very small. This means that the test electrolytes are almost completely dissociated and can be treated as strong electrolytes. For this reason, the values of thermodynamic functions of the association were not determined because of their too large uncertainties.

In the next stage of this investigation we decided to calculate the Walden products, connected with Stokes radii, often called the hydrodynamic radius (Table 4)

$$\eta \lambda_o = r_S = 8.204 z_i / r_S \quad (6)$$

where $z_i$ is the charge number of the ion, $\eta$ is the dynamic viscosity of water.
Table 4 shows the Walden products of [emim][BF$_4$] and [bmim][BF$_4$] ionic liquids which change very slightly with temperature. Similarly, small changes in the value of the products Walden can be observed for these ionic liquids in the case of N,N-dimethylformamide [14], and 1-propanol [15]. Considering equation (6) can be assumed that the temperature change in the used range does not practically affect the effective size of ions. The data contained in Table 4 and the equation (6) shows that the effective size of the ion [bmim]$^+$ are larger than those of the ions [emim]$^+$ over the range of applied temperatures. Comparing the $\Lambda_0\eta$ values from Table 4 with those given in [14, 15], can be seen that the Walden products in water, DMF and 1-propanol satisfy the following relations:

$$\Lambda_0\eta [\text{emim}] [\text{BF}_4] > \Lambda_0\eta [\text{bmim}] [\text{BF}_4]$$

and

$$\Lambda_0\eta (\text{water}) > \Lambda_0\eta (\text{DMF}) > \Lambda_0\eta (1\text{-propanol})$$

The first relationship, suggests a greater effective radius of the ion [bmim]$^+$ which corresponds well with the fact that the Eyring activation enthalpy of charge transfer is larger for this ion. However, a meaningful comparison of the effective size of ions will be possible only on the basis of values of ionic conductances and by use of equation (6).

4. CONCLUSIONS

Molar conductances of aqueous solutions of 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate have been successfully reported for the first time at $T = (283.15 \text{ to } 318.15)$ K. Conductivity data were analyzed on the basis of Barthel’s low concentration Chemical Model (lcCM) showing that these electrolytes exist as free ions in aqueous solution at used temperature range. This strategic, low cost and effective method allowed us to calculate the activation enthalpy of charge transfer and the Walden products and compared with the corresponding values for the DMF and 1-propanol.
References


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