Acoustic and volumetric properties of aqueous solutions of imidazolium based ionic liquids at 298.15 K

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Abstract

The experimental measurements of the speed of sound and density of aqueous solutions of imidazolium based ionic liquids (IL) in the concentration range of 0.05 mol·kg⁻¹ to 0.5 mol·kg⁻¹ at T = 298.15 K are reported. The data are used to obtain the isentropic compressibility (βS) of solutions. The apparent molar volume (ΔV) and compressibility (βS) of ILs are evaluated at different concentrations. The data of limiting partial molar volume and compressibility of IL and their concentration variation are examined to evaluate the effect due to IL–water and IL–IL interactions. The results have been discussed in terms of hydrophobic hydration, hydrophobic interactions, and water structural changes in aqueous medium.

Keywords: Ionic liquids; Density; Speed of sound; Apparent molar volume; Isentropic compressibility

1. Introduction

The rapid growth in the ionic liquid (IL) literature shows that they attract much attention of both industry and academia as negligible vapor pressure alternatives to traditional organic solvents, the ability to solubilize an enormous variety of compounds, a wide liquid range, and the possibility to tailor their chemical structure at will to better match a given target are particularly noteworthy. While applications of ILs in a diverse range of fields, such as electrochemistry, separation processes, synthesis, and catalysis, have begun to be explored, still much research is needed towards the understanding of molecular interactions of ILs with water. The most widely studied ILs are comprised of bulky, asymmetric N-containing organic cations (e.g., imidazole, pyrrole, pyridine, etc.) in combination with any wide variety of anions, ranging from simple inorganic ions (e.g., halides) to more complex organic species (e.g., triflate). The nature of the anion is considered to be primarily responsible for many of the physical properties of ionic liquids, such as their miscibility with conventional solvents and hygroscopicity [1]. Simple changes in the cation and anion combinations or the nature of the moieties attached to each ion allow the physical properties of ionic liquids such as hydrophobicity, viscosity, and density to be designed for specific applications [2].

While ILs cannot contribute to air pollution due to their negligible vapour pressures, they may hold a significant solubility in water and go into aqueous streams what leads to an environmental problem, besides the costs due to the ionic liquid loss and the additional separation and purification steps required. Furthermore, once in the environment, the IL ecotoxicity depends directly on their lipophilicity [3–6]. The knowledge of the ILs solubilities in water can thus be an accurate way to predict the IL toxicity in the overall ecosystem.

The knowledge of thermophysical properties of binary mixtures of water and hydrophilic ILs is required for the development of practical applications and design of processes...
using (water + IL) systems. To date, a number of papers have studied the thermophysical properties of these binary systems: some of them report values for dilute aqueous solutions of ILs [7–11] or, in the other extreme, the effect of water content in “pure” ILs or binary mixtures with low fractions of water [12–18] whereas only few works present measurements covering the whole composition range [19–29].

In this work, the experimental measurements of the speed of sound and density of aqueous solutions of imidazolium chloride ([Im][Cl]), 1-methyl imidazolium chloride ([Mim][Cl]), and 1-butyl-3-methyl imidazolium chloride ([Bmim][Cl]) in the concentration range of 0.05 mol·kg⁻¹ to 0.5 mol·kg⁻¹ at 298.15 K are reported. The data are used to obtain the isentropic compressibility (βₚ) of solutions. The apparent molar volume (φᵥ) and compressibility (φᵥ/φᵥ) of IL are evaluated at different concentrations. The data of limiting partial molar volume and compressibility of IL and their concentration variation are examined to study the effect due to IL–water and IL–IL interactions.

2. Experimental

[Im][Cl] and [Mim][Cl] were acquired from Solcher with a purity greater than 98% and [Bmim][Cl] of purity >99% was obtained from Merck. The concentrations of the ILs solutions in water were prepared on a molality basis. The water used for the solutions was freshly prepared, doubly quartz distilled. The uncertainty in composition was found to be of the order of ±1·10⁻⁴ mol·kg⁻¹. The water content in the ILs was determined using a microprocessor based automatic Karl–Fischer Titrator, TKF-55, Chemito from the M/s Toshniwal company. Pyridine free Aquanil-5 Karl–Fischer reagent of Thomas Baker was used for analysis. The water content was standardized with a solution of water in methanol. The instrument is able to detect the water content on the order of ±2 ppm in organic solvents. The water content found for [Im][Cl], [Mim][Cl] and [Bmim][Cl] were of 3.06%, 1.24%, and 0.94% by mass, respectively. This water content in the ILs was taken into account during the preparation of the aqueous solutions of ILs.

The densities of aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] were measured at T = 298.15 K using a high precision Anton PAAR (DMA 60/602) digital density meter. The temperature constancy of the vibrating tube was better than ±0.02 K as it is maintained constant by circulating water through a Julabo cryostat having a temperature stability of ±0.01 K. After applying humidity and laboratory pressure corrections the accuracy in the density values is found to be of the order of ±5·10⁻³ kg·m⁻³. The reliability of the density data obtained is ascertained by making measurements of aqueous binary solutions of alkali halides and comparing the data with the literature [30] (figure 1). Similarly, the calculated apparent molar volume (φᵥ) of NaCl or KCl in aqueous solutions at T = 298.15 K, plotted in the form of φᵥ − 1.868√c against the concentration of salt (c) in mol·L⁻¹, when extrapolated to infinite dilution yield limiting apparent molar volumes which are in excellent agreement with the literature data [31]. The concentration of IL in molality units are converted to molarity scale as and when required using density data.

The speed of sound measurements were carried out for aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] at T = 298.15 ± 0.02 K at a fixed frequency of 2 MHz (M/s Mittle Enterprises). Good quality thermostating (temperature inside the cell ±0.05 K) to maintain constant temperature was achieved by circulating water by means of a Julabo thermostat having an accuracy of ±0.02 K around the cell. The reliability of the measurements were checked by obtaining sound velocity data for water at T = 298.15 K (1497.6 m·s⁻¹) which agree well with the reported literature data [32]. The standard deviation in speed of sound measurement values are found to be of the order of ±0.3 m·s⁻¹ obtained after repeated measurements.

3. Results

The speed of sound and density data of aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] in the concentration range of 0.05 mol·kg⁻¹ to 0.5 mol·kg⁻¹ at T = 298.15 K are reported in table 1. The variations of the speed of sound parameter (∆u = u_solution − u_solvent) as a function of the molality of ILs in water are shown in figure 2. Isentropic compressibility (βₚ) of solvents and solutions were obtained using the Laplace equation βₚ = 1/ (ρu²). The variations of βₚ values with the molality of water are shown in figure 3. The uncertainty in βₚ values was obtained using method of propagation of errors and standard deviations obtained for the experimental parameters including concentration and density of pure solvent; the corresponding equation obtained as
Density, speed of sound, compressibility, apparent, and partial molal properties of aqueous solutions of ionic liquids at $T = 298.15$ K

<table>
<thead>
<tr>
<th>$m$/mmol$^{-1}$</th>
<th>$\rho$/kg m$^{-3}$</th>
<th>$u$/m s$^{-1}$</th>
<th>$10^{-3}\cdot\phi_{V}$/mm$^3$mol$^{-1}$</th>
<th>$10^{-3}\cdot\Delta V$/mm$^3$mol$^{-1}$</th>
<th>$10^{11}\cdot\beta_{S}$/Pa$^{-1}$</th>
<th>$\phi_{Ks}$/mm$^3$MPa$^{-1}$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00000</td>
<td>997.05</td>
<td>1497.6</td>
<td>104.40</td>
<td>–</td>
<td>18.068</td>
<td>44.72</td>
</tr>
<tr>
<td>0.04296</td>
<td>998.24</td>
<td>1500.1</td>
<td>104.70</td>
<td>104.69</td>
<td>18.068</td>
<td>44.52</td>
</tr>
<tr>
<td>0.10274</td>
<td>999.89</td>
<td>1503.8</td>
<td>104.52</td>
<td>104.35</td>
<td>18.068</td>
<td>44.23</td>
</tr>
<tr>
<td>0.15300</td>
<td>1001.26</td>
<td>1507.0</td>
<td>104.38</td>
<td>104.05</td>
<td>18.069</td>
<td>43.98</td>
</tr>
<tr>
<td>0.19764</td>
<td>1002.47</td>
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<td>103.77</td>
<td>18.070</td>
<td>43.77</td>
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<tr>
<td>0.24165</td>
<td>1003.72</td>
<td>1512.4</td>
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<td>18.071</td>
<td>43.56</td>
</tr>
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<td>103.20</td>
<td>18.072</td>
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<td>102.83</td>
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<td>103.45</td>
<td>101.82</td>
<td>18.083</td>
<td>42.40</td>
</tr>
</tbody>
</table>

$^a$ Extrapolated values to infinite dilution.
were estimated using the same method used for estimation of the uncertainty in $\beta_S$. The data of $\phi_V$ and $\phi_{K_S}$ along with their uncertainties are shown in Table 1. The uncertainties in the derived apparent quantities are estimated to be of the order of $\pm 0.23 \cdot 10^3 \text{ mm}^3 \cdot \text{mol}^{-1}$ for $\phi_V$ and $\pm 4 \text{ mm}^3 \cdot \text{MPa}^{-1} \cdot \text{mol}^{-1}$ for $\phi_{K_S}$ at the lowest concentration studied.

The $\phi_V$ and $\phi_{K_S}$ data of aqueous solutions of studied ILs as a function of IL molarity at $T = 298.15$ K are shown in Figures 4 and 5, respectively. The $\phi_V$ and $\phi_{K_S}$ can also be expressed as

$$\phi_V = \phi_V^0 + S_V \sqrt{c} + B_V c$$

$$\phi_{K_S} = \phi_{K_S}^0 + S_K \sqrt{c}$$

(4)

(5)

where $S_V$ is the Debye–Hückel limiting slope ($S_V = 1.868 \cdot 10^3 \text{ mol} \cdot \text{mm}^{-3} \cdot \text{m}^{-1/2}$) for aqueous solutions of 1:1 electrolytes at 298.15 K) and $S_K$ is the experimental limiting slope whereas $B_V$ is the deviation parameter. The smooth extrapolations of the $\phi_V$ and $\phi_{K_S}$ data to infinitely dilute solutions enabled us to obtain limiting apparent molar volume ($\phi_V^0$) and compressibility ($\phi_{K_S}^0$) of ILs as shown in Figures 4 and 5. Experimental slopes of $\phi_{K_S}$ ($S_K$ values) for aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] are found to be $(-0.8 \pm 2.3) \cdot 10^3$, $(5.3 \pm 2.2) \cdot 10^3$, and $(6.2 \pm 2.4) \cdot 10^3$ in mm$^3$/mol$^{-1/2}$, respectively. $B_V$ values for aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] are found to be $(-4.7 \pm 0.5) \cdot 10^3$, $(-4.6 \pm 0.4) \cdot 10^3$, and $(-4.1 \pm 0.5) \cdot 10^3$ in mm$^6$·mol$^{-2}$, respectively. The data of $\phi_V$ were further used to calculate the partial molar volumes of solute ($\bar{V}_2$) and solvent ($\bar{V}_1$) using the standards equations [33] and that are reported in Table 1. The dependence of partial molar volume of solute ($\bar{V}_2$) as a function of molarity of IL is shown in Figure 6. The partial molar volume of solute ($Y$) displays a very good linear relationship with the molarity of IL ($X$) as equations (6)–(8), respectively, for aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] at 95% level of confidence:

$$Y = (-6.3258 \pm 0.0524)X + (105.00 \pm 0.02) \quad (R^2 = 0.9995)$$

$$Y = (-6.1729 \pm 0.0356)X + (119.07 \pm 0.01) \quad (R^2 = 0.9997)$$

$$Y = (-5.3107 \pm 0.0500)X + (175.37 \pm 0.02) \quad (R^2 = 0.9993)$$

(6)

(7)

(8)
The molecule. Small negative deviations from limiting law the deviations increasing with the hydrocarbon portion of negative deviation from the Debye–Huckel limiting law, molar volume as a function of salt concentration exhibit molar volume has been illustrated previously [35–37]. Cabani vent structure brought about by neutral or charged solute solutions as a useful tool for elucidating local changes of sol-

4. Discussion

It is observed from figure 2 that speed of sound increases as the imidazolium ring is substituted at the N centers by methylene groups and a butyl chain. This is also reflected in decrease of adiabatic compressibility as the salt concentra-

The isentropic compressibility \( \phi_{ks} \) is related to the second pressure differential of the partial molar free energy of the solute and has proved to be very sensitive to changes in solvation, H-bond and water structural changes in the aqueous medium. The limiting apparent molar compressibilities (\( \phi_{ks}^{\circ} \)) are generally negative for electrolytes in aqueous solutions [48]. The magnitude depends upon the charges of cations (electrostriction). The negative values are attributed to hydration of cations (water loosing compressibility due to coloumbic attraction). The hydration number for the ions has been calculated by using Passynski’s equation [49].

A distinction has also been made between compressibility changes due to electrostriction (high charge density) and similar changes which arise for large \( \text{R}_2\text{N}^+ \) ions [50] but for completely different reasons associated with hydrophobic structure promotion. Seen in this light, the limiting apparent molar compressibility (table 1) for the studied ILs are all negative but they are of much smaller magnitude than those for 1:1 electrolytes but similar to \( \text{R}_2\text{N}^+\text{X} \) solutes. Thus the \( \phi_{ks}^{\circ} \) values indicate that the imidazolium cations are sol-

The calculations of \( \overline{V}_2 \) and \( \overline{V}_1 \), i.e., partial molar vol-

FIGURE 6. The dependence of partial molar volume of solute (\( \overline{V}_2 \)) as a function of concentration of ionic liquids (m) at \( T = 298.15 \text{ K} \). [Im][Cl], ●; [Mim][Cl], ■; [Bmim][Cl], ▲.
due to less electrostriction and increased H-bonding amongst the water molecules in the water clusters around cation (structure making effect) resulting in very small negative $\phi_{K_s}^c$ values. The large negative $\phi_{K_s}^c$ values are observed in case of usual metal halides where the electrostriction is large and the hydration sheath around the cation is less compressible if the charge density is high [53]. It has also been questioned about the compressibility of the ions itself. However, it can be resolved if the compressibility of the salts are known in pure liquid state or in CCl$_4$ solutions [54].

The Debye–Hückel theory requires $\phi_{K_s}$ to be linear in $m^{1/2}$ (or $c^{1/2}$), so that equation (5) has a limiting slope $S_K^0$. The limiting slope $S_K^0$ is not known precisely as its calculation requires the dielectric constant data at different pressures. We observed from figure 5 that $\phi_{K_s}$ increases linearly with square root of concentration; giving small positive values of $S_K^0$ parameter. We do not compare these with the literature values of $S_K$ for variety of electrolytes, since our data are of limited accuracy and the concentration range is also above Debye–Hückel limiting region. However, the small positive values of $S_K^0$ do indicate that the water structure around these imidazolium cations is affected by the pressure effect giving support to the hypothesis of soft and hydrophobic structures around the cations.

5. Conclusions

The variations of the speed of sound parameter ($\Delta \nu = \nu_{\text{solution}} - \nu_{\text{solvent}}$) as a function of the molality of studied ILs in water increases with the insertion of methylene groups or butyl chain at the N centers of ILs; and the reverse is observed in case of isentropic compressibility. For the studied systems, the solvent induced solute core–sphere over-lap effect (i.e., increase of solute–solvent interaction along with water structure making effect) is observed and the extent of the effect is more important in case of [Bmim][Cl]. Studied imidazolium cations are solvated by hydrophobic hydration in water and charge density of the hydrated sheath is small and they are not compressible to significant extent. The water structure around the imidazolium cation is less compressible due to less electrostriction and increased H-bonding amongst the water molecules in the water clusters around cation (structure making effect) resulting in the small negative $\phi_{K_s}^c$ values.

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