Densities and dynamic viscosities of the binary system 
(water + 1-hexyl-3-methylimidazolium bromide) at different temperatures

Ji-Guang Li, Yu-Feng Hu, Shu-Feng Sun, Yan-Sheng Liu, Zhi-Chang Liu

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China
The Centre for Biological Imaging Institute of Biophysics, Chinese Academy of Sciences, Beijing 100101, China

1. Introduction

Ionic liquids (ILs) have been recognized as novel solvents, which are liquids over a wide temperature range including room temperature [1,2]. ILs are expected to reduce or eliminate the hazards associated with volatile organic solvents and have been applied in growing applications such as solvents for organic and catalytic reactions, new material productions, solvents for separation and extraction processes, novel electrolytes for electrochemical devices and processes, and enzyme catalysis/multiphase bioprocess operations [1-5].

Generally, there are three ways to use ILs in a biocatalytic process: as a pure solvent, as a co-solvent in aqueous systems, and in a biphasic system [6]. To design any process involving ILs on an industrial scale, it is necessary to know a range of physical properties including viscosity and density. Furthermore, the presence of water in ILs can dramatically affect their physicochemical properties [7-9]. The excess thermodynamic properties are of great importance in understanding the nature of molecular aggregation that exists in the binary mixtures over the whole composition range [10].

A number of groups have studied the physicochemical properties of aqueous solutions of imidazolium-based ILs [10-14]. Ge et al. reported dynamic viscosities, densities for the binary mixtures of (water + [C6mim][TfO]) over the entire mole fraction range from (303.15 to 343.15) K [10]. Goómez et al. reported dynamic viscosities, densities of (water + [C6mim][Cl]) and (water + [C8mim][Cl]) over the entire mole fraction range from (298.15 to 343.15) K [11]. Brennecke and Rodríguez reported dynamic viscosities, densities of (water + [C2mim][EtSO4]), (water + [C2mim][TfO]), and (water + [C2mim][TFA]) over the entire mole fraction range [12]. Shekaari and Mousavi reported osmotic coefficients, mean activity coefficients, vapor pressure data, and excess Gibbs free energies $\Delta G^\circ$ of aqueous solutions of [Cn mim][Br] \((n = 3, 5, 6)\) [15a]. Wang et al. measured the densities, conductivities, and polarity indexes of pyrene for aqueous solutions of a series of [Cn mim][Br] \((n = 4, 6, 8, 10, 12)\) and [Cn mim][BF4] at 298.15 K, and discussed the aggregation behaviors of these aqueous IL solutions [15b]. However, relative few references have been made on the binary systems (water + [Cn mim][Br]) \((n = 1, 2, \ldots, m)\) [15a,b], and no reference on the transport properties depending on the whole composition range and/or temperature. Therefore, in this work the densities and dynamic viscosities were measured for pure [C6mim][Br] and the binary system (water + [C6mim][Br]) in the (293.15 to 333.15) K range and at atmospheric pressure over the whole.
composition range. Excess molar volumes and viscosity deviations over the entire composition range were obtained from the experimental data and correlated by Redlich–Kister polynomial [16].

### TABLE 1

Densities and viscosities of pure [C₆mim][Br] in the (293.15 to 333.15) K range.

<table>
<thead>
<tr>
<th>T/K</th>
<th>ρ/(g cm⁻³)</th>
<th>η/(mPa S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>1.2274</td>
<td>6936</td>
</tr>
<tr>
<td>298.15</td>
<td>1.2235</td>
<td>3986</td>
</tr>
<tr>
<td>303.15</td>
<td>1.2201</td>
<td>2239</td>
</tr>
<tr>
<td>308.15</td>
<td>1.2159</td>
<td>1386</td>
</tr>
<tr>
<td>313.15</td>
<td>1.2133</td>
<td>851.65</td>
</tr>
<tr>
<td>318.15</td>
<td>1.2057</td>
<td>3986</td>
</tr>
<tr>
<td>323.15</td>
<td>1.2075</td>
<td>512.14</td>
</tr>
<tr>
<td>328.15</td>
<td>1.2022</td>
<td>412.18</td>
</tr>
<tr>
<td>333.15</td>
<td>1.1986</td>
<td>350.69</td>
</tr>
</tbody>
</table>

### TABLE 2

Experimental densities ρ, excess molar volumes V^E, dynamic viscosities η, and viscosity deviations Δη for the binary system (water (1) + [C₆mim][Br] (2)) in the (293.15 to 333.15) K range.

<table>
<thead>
<tr>
<th>x₂</th>
<th>ρ/(g cm⁻³)</th>
<th>η/(mPa S)</th>
<th>V^E/(cm³ mol⁻¹)</th>
<th>Δη/(mPa S)</th>
<th>ρ/(g cm⁻³)</th>
<th>η/(mPa S)</th>
<th>V^E/(cm³ mol⁻¹)</th>
<th>Δη/(mPa S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.2274</td>
<td>6936</td>
<td>0.019</td>
<td>1.2201</td>
<td>2239</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.1225</td>
<td>1.2334</td>
<td>3519</td>
<td>0.171</td>
<td>2567</td>
<td>1.2161</td>
<td>1255</td>
<td>0.183</td>
<td>709.84</td>
</tr>
<tr>
<td>0.2196</td>
<td>1.2204</td>
<td>1578</td>
<td>0.180</td>
<td>3835</td>
<td>1.2132</td>
<td>695.45</td>
<td>0.186</td>
<td>1052</td>
</tr>
<tr>
<td>0.2978</td>
<td>1.2179</td>
<td>776.62</td>
<td>0.134</td>
<td>4094</td>
<td>1.2108</td>
<td>395.49</td>
<td>0.135</td>
<td>1177</td>
</tr>
<tr>
<td>0.3480</td>
<td>1.2163</td>
<td>507.80</td>
<td>0.072</td>
<td>4015</td>
<td>1.209</td>
<td>265.62</td>
<td>0.101</td>
<td>1194</td>
</tr>
<tr>
<td>0.4166</td>
<td>1.2134</td>
<td>313.52</td>
<td>0.122</td>
<td>3733</td>
<td>1.2062</td>
<td>168.31</td>
<td>0.046</td>
<td>1138</td>
</tr>
<tr>
<td>0.5940</td>
<td>1.2087</td>
<td>173.73</td>
<td>0.039</td>
<td>3267</td>
<td>1.2016</td>
<td>98.93</td>
<td>0.016</td>
<td>1012</td>
</tr>
<tr>
<td>0.8191</td>
<td>1.2039</td>
<td>111.42</td>
<td>0.006</td>
<td>2871</td>
<td>1.1968</td>
<td>65.77</td>
<td>0.039</td>
<td>897.35</td>
</tr>
<tr>
<td>0.6405</td>
<td>1.1969</td>
<td>70.83</td>
<td>0.074</td>
<td>2423</td>
<td>1.1899</td>
<td>43.45</td>
<td>0.044</td>
<td>762.11</td>
</tr>
<tr>
<td>0.7285</td>
<td>1.1843</td>
<td>36.40</td>
<td>0.076</td>
<td>1848</td>
<td>1.1773</td>
<td>22.54</td>
<td>0.035</td>
<td>586.08</td>
</tr>
<tr>
<td>0.8160</td>
<td>1.1637</td>
<td>18.13</td>
<td>0.066</td>
<td>1259</td>
<td>1.1569</td>
<td>12.10</td>
<td>0.022</td>
<td>400.69</td>
</tr>
<tr>
<td>0.9048</td>
<td>1.1236</td>
<td>6.655</td>
<td>0.051</td>
<td>654.83</td>
<td>1.1173</td>
<td>4.764</td>
<td>0.009</td>
<td>209.29</td>
</tr>
<tr>
<td>0.9241</td>
<td>1.1094</td>
<td>4.951</td>
<td>0.046</td>
<td>522.7</td>
<td>1.1036</td>
<td>3.619</td>
<td>0.013</td>
<td>167.25</td>
</tr>
<tr>
<td>0.9440</td>
<td>1.0912</td>
<td>3.480</td>
<td>0.044</td>
<td>386.17</td>
<td>1.0854</td>
<td>2.622</td>
<td>0.005</td>
<td>123.71</td>
</tr>
<tr>
<td>0.9613</td>
<td>1.0709</td>
<td>2.438</td>
<td>0.039</td>
<td>267.24</td>
<td>1.0657</td>
<td>1.860</td>
<td>0.008</td>
<td>85.75</td>
</tr>
<tr>
<td>0.9899</td>
<td>1.0226</td>
<td>1.342</td>
<td>0.019</td>
<td>70.00</td>
<td>1.0192</td>
<td>1.047</td>
<td>0.011</td>
<td>22.56</td>
</tr>
<tr>
<td>1</td>
<td>0.9982</td>
<td>1.304</td>
<td>0</td>
<td>0</td>
<td>0.9956</td>
<td>1.002</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### 2. Experimental section

The deionized water was distilled in a quartz still, and its conductivity is 0.8–1.2 × 10⁻⁴ S cm⁻¹. All chemicals used in this study were of reagent grade with the claimed purity more than 99%. N-methylimidazole and n-C₆H₁₃Br were supplied by Shanghai Jiachen Chemical Ltd. All chemicals used were refined by the traditional methods before use. [C₆mim][Br] was prepared with well-established procedures by our previous works [17a,b]. The resulting after purification was dried under vacuum over CaCl₂ for days at 70 °C. It was further dried with 3 Å molecular sieve for days immediately before use. ¹H NMR (600 MHz, d₆-DMSO) for [C₆mim][Br] agrees well with literature [17c]. The water content after drying, measured by Karl–Fisher titration, was within 0.012 wt%.
3. Apparatus and procedure

The experimental procedures are similar to those used in our previous studies [18,19] and are described briefly as follows. The binary aqueous solutions were prepared by syringing weighed amounts of the pure liquids into stoppered bottles in glove box using a Sartorius CT225D balance with the precision of ±5 × 10⁻⁵ g. The solutions were placed into stoppered bottles and stirred for 2h, and all solutions were made in glass flasks and measurements were carried on one week after preparation to assure complete dissolution and aggregation. All the samples were prepared immediately before the density and viscosity measurements to prevent possible loss of water due to evaporation. Densities of solutions were measured with a KEM oscillating-tube digital densimeter (DA-505) thermostated to better than ±0.01 K. All measurements were performed at atmospheric pressure. The temperature in the measuring cell was monitored with a digital thermometer. The densimeter was calibrated by double-distilled water and dry air at the temperatures ranging from (283.15 to 323.15) K prior to its use. The experimental uncertainty was less than ±5 × 10⁻³ K.

All measurements were carried out at the temperatures ranging from (283.15 to 333.15) K, 313.15 K; 323.15 K; and 333.15 K. The symbols represent experimental values, and the solid curves represent the corresponding correlations by the Redlich–Kister equation:

\[
\ln \rho = a + bT
\]

where \( \rho \) is the density, \( T \) is the absolute temperature, \( a \) and \( b \) are fitting parameters. The measured densities can be well described by equation (1), with \( R^2 = 0.99927 \). The coefficient of thermal expansion for \([\text{C}_6\text{mim}][\text{Br}]\), \( \xi_p \), is defined by the following equation:

\[
\xi_p = 1/V(\partial V/\partial T)_p = -\langle \partial \ln \rho / \partial T \rangle_p
\]

where \( V \) is the molar volume of pure IL. Then, \( \xi_p = -b = 5.90 \times 10^{-4} \pm 0.06 \, K^{-1} \) for \([\text{C}_6\text{mim}][\text{Br}]\) is obtained from the slope of the fitting line. Generally, the practical IL use was under 373.15 K, with a straight line for \( \ln \rho \) versus \( T \) in this temperature range, so thermal expansion for each typical IL could be considered as a constant. Thermal expansion for \([\text{C}_6\text{mim}][\text{Br}]\) is in the common range for typical ILs [11, 12, 21], and is much lower than conventional molecular solvents [22].

The viscosities of pure \([\text{C}_6\text{mim}][\text{Br}]\) at the temperatures ranging from (293.15 to 333.15) K were fitted to the Vogel–Fulcher–Tamman (VFT) [23, 24]:

\[
\eta = A T^{-\alpha} \exp \left( \frac{k}{T - T_0} \right)
\]

where \( \eta \) is the dynamic viscosity, \( T \) is the absolute temperature, \( A, k, \) and \( T_0 \) are adjustable parameters. The parameter \( T_0 \) is the “ideal glass transition temperature”, and it should be slightly below the experimental glass transition temperature \( T_g \) [12]. The measured viscosities can be well described by equation (3), with \( R^2 = 0.99875 \), while \( T_0 = 216.2 \pm 13.8 \) is slightly higher than the experimental data for \([\text{C}_6\text{mim}][\text{Br}]\) with \( T_g = 224 \, K [25] \). We can consider VFT equation as an empirical equation to correlate the transport properties just as originally proposed, with \( T_0 \) close to glass transition temperature.

4. Results and discussion

4.1. Pure component

The measured densities and viscosities of pure \([\text{C}_6\text{mim}][\text{Br}]\) in the (293.15 to 333.15) K range are shown in Table 1. The measured densities at (293.15 and 303.15) K were in good agreement with the data reported in literature [20], while no viscosity data were referred for pure \([\text{C}_6\text{mim}][\text{Br}]\) in literature by our search. Experimental values of \( \ln \rho \) for pure \([\text{C}_6\text{mim}][\text{Br}]\) in the temperature were fitted to the following equation:

\[
\ln \rho = a + bT
\]

The measured densities and viscosities at the temperatures ranging from (293.15 to 333.15) K are shown in Table 2. The measured viscosities can be well described by equation (3), with \( R^2 = 0.99875 \), while \( T_0 = 216.2 \pm 13.8 \) is slightly higher than the experimental data for \([\text{C}_6\text{mim}][\text{Br}]\) with \( T_g = 224 \, K [25] \). We can consider VFT equation as an empirical equation to correlate the transport properties just as originally proposed, with \( T_0 \) close to glass transition temperature.

4.2. Binary system

The dynamic viscosities and densities of the system (water + \([\text{C}_6\text{mim}][\text{Br}]\)) in the (293.15 to 333.15) K range and at 0.1 MPa are shown in Table 2. It is clear that their densities and dynamic viscosities decrease with increasing the temperature and the mole fraction of water and that the decreases are more notable for the dynamic viscosities. The measured densities and viscosities of water shown in Table 2 were in good agreement with the values reported in the literature [26].

The excess molar volumes and viscosity deviations are calculated from the experimental data by the following equations:

\[
\langle \chi_i > = \sum_{i=1}^{N} x_i M_i (\rho_i^{-1} - \rho^{-1}),
\]

\[
\Delta \eta = \eta - \sum_{i=1}^{N} x_i \eta_i.
\]

where \( \rho_i \) and \( \rho \) are the density of the binary system and the density of the pure component, respectively. \( x_i \) and \( M_i \) represent the mole fraction and the molar mass of the \( i \) component. \( \eta_i \) and \( \eta \) are the dynamic viscosity of the binary system and the pure component, respectively.

The excess molar volumes and viscosity deviations for the binary system (water + \([\text{C}_6\text{mim}][\text{Br}]\)) in the (293.15 to 333.15) K range and at 0.1 MPa are also shown in Table 2. The excess molar volumes and viscosity deviations at each temperature were fitted to a Redlich–Kister [16] equation:

\[\text{FIGURE 1.} \quad \text{Excess mole volumes } V^e \text{ versus mole fraction of water for the binary system (water (1) + [C_6mim][Br] (2)) at different temperatures: ○, 293.15 K; ▲, 303.15 K; □, 313.15 K; ○, 323.15 K; ●, 333.15 K. The symbols represent experimental values, and the solid curves represent the corresponding correlations by the Redlich–Kister equation.}

\[\text{FIGURE 2.} \quad \text{Viscosity deviation } \Delta \eta \text{ versus mole fraction of water for the binary system (water (1) + [C_6mim][Br] (2)) at different temperatures: ○, 293.15 K; ▲, 303.15 K; □, 313.15 K; ○, 323.15 K; ●, 333.15 K. The symbols represent experimental values, and the solid curves represent the corresponding correlations by the Redlich–Kister equation.} \]
when the anion is [HCOO]−, negative values were observed even for the pyrrolidinium cation [28]. For binary systems (water + [Pyr][HSO4]) and (water + [Pyr][NO3]), the maximum \( x_1 = 0.5 \) was formed by H-bonds breaking up [28]. The formation of strong H-bonds between water and ions leads to an increase in the volume occupied by ions or molecules. From comparing the \( V_e \) for ([water + [C4Py][BF4]]) and ([water + [C4Py][Br]]), ([water + [C4mim][Br]]), and ([water + [C4mim][TFO]] and [water + ([C4mim][TFO])]), respectively, we can conclude that, \( V_e \) values increase in the magnitude with increasing the alkyl chain length of the imidazolium and pyridinium cations for ILS with the same anions [10–12]. In the general, the anion can greatly influence on the excess molar volume for (water + IL) systems, and they can follow the hydrophilic order of anion for the IL with the same cation [10–12].

The comparisons of the experimental viscosity deviations with those obtained from the Redlich–Kister polynomial equation for the system (water + [C4mim][Br]) are illustrated in figure 2. Negative deviations are observed over the whole temperature and composition ranges. The minimum deviation always appears at \( x_1 \approx 0.3 \).

The viscosity deviations decrease with increasing of water mole fraction up to \( x_1 \approx 0.3 \) for (water + [C4mim][Br]). This behavior becomes reversed for this system at higher mole fractions of water. The similar phenomenon appeared in other (water + IL binary) systems [9–11], with the minimum deviation \( x_1 \approx 0.3 \) for (water + [C4Py][BF4]) or [C4Py][Br]) [9]. \( x_1 \approx 0.2 \) for (H2O + [C4mim][TFO]) [10], and \( x_1 \approx 0.2 \) for (water + [C4mim][Cl]) or ([C4mim][Cl]) [11], and no further explanations were revealed in this references [9–11]. We think that the structures of aqueous solutions somehow changed at \( x_1 \approx 0.3 \), but we did not have direct evidence to approve our views. With the development of molecular dynamics simulation [30,31] and spectra measurements, more information will be obtained about the structure of IL aqueous solution. Increasing the temperature diminishes the viscosity deviations progressively from \( T = 293.15 \) to 333.15 K.

5. Conclusions

The densities and viscosities of the pure [C4mim][Br] were measured in the (293.15 to 333.15) K range and at atmospheric pressure. The densities and viscosities of the binary system (water + [C4mim][Br]) in (293.15 to 333.15) K range were also determined over the whole composition range. The excess molar volumes and viscosity deviations for the binary system were calculated from the experimented data. The excess molar volumes of the system (water + [C4mim][Br]) are positive at higher temperatures, whereas negative deviations from the ideality is observed at 293.15 K as the \( x_1 \) exceeds 0.4 to 0.5. Contrarily, the system shows the negative viscosity deviations over the whole temperature and composition ranges.

Acknowledgement

The authors thank the National Natural Science Foundation of China (40673043 and 20976189), and the Program for New Century Excellent Talents in University of Ministry of Education of China (NCTE-06-0088) for financial supports.
References


JCT 09-146