Towards understanding the effect of electrostatic interactions on the density of ionic liquids

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Abstract

In order to have a better understanding on the electrostatic contribution to the thermodynamic property of ionic liquids (ILs), a two-parameter equation of state (EOS) is developed on the basis of hard sphere perturbation theory by accounting for the dispersion interaction with Cotterman et al.’s EOS for L-J fluid and electrostatic interaction with mean spherical approximation (MSA) approach. The EOS is applicable for the density correlation of molecular liquids, and the resulting parameters, viz. Lennard–Jones dispersive parameter $\varepsilon/k$ and soft-core diameter $\sigma$, can be used to predict the density of molecular mixtures and the corresponding ILs. The results indicate that the density of IL is always about 10% higher than the corresponding stoichiometric molecular mixture with which the IL is produced as an ionic adduct, for example, IL 1-methyl-3-methylimidazolium dimethylphosphate ([MMIM][DMP]) versus equimolar mixture of 1-methylimidazole (MIM) and trimethylphosphate (TMP). Furthermore, the density enhancement of ILs with respect to their corresponding stoichiometric molecular mixtures can be well represented by the electrostatic contribution among ionic species involved.

Keywords:
Equation of state
Ionic liquid
Thermodynamic properties
Prediction

1. Introduction

Ionic liquids (ILs) are generally defined as molten salts at ambient temperature, and many of their properties are mainly attributed to the presence of ionic species and strong electrostatic interactions, e.g., high electric and thermal conductivity, higher viscosity and density over molecular solvents and negligible volatility. As a result, studies on ILs have recently attracted much attention for the researchers in both academic and industrial areas as is shown by the drastic increase of publications and patents issued [1–5]. In fact, it is the ionic attribute that makes ILs attractive as a conductive medium for fuel cell and electrochemical processes and as a novel solvent for the separation of extraction and special distillation [6,7]. However, their ionic property is not as strong as expected in terms of their limited electric conductivity being in the order of $10^{-3}$ S/cm, and the solution behavior which only slightly deviates from the Raoults’s law as indicated by the vapor–liquid equilibrium data of many IL-containing mixtures. For this reason, ionic liquid was generally treated as a neutral molecule rather than a completely dissociated electrolyte in the modeling of gas–liquid, vapor–liquid and liquid–liquid phase equilibrium for the IL-containing systems, and almost all experimental data were correlated with traditional equation of states (EOS), e.g., SRK EOS, or excess Gibbs models of nonelectrolyte, e.g., NRTL and UNIQUAC, etc. From the practical point of view, the above empirical models without consideration of ionic properties work well, however, from the theoretical point of view it is necessary to have an insight into the electrostatic contribution on the thermodynamic properties of an IL. Toward this aim, the densities were compared between a special kind of IL and a physical mixture of two components with which the IL was produced via a nucleophilic substitution reaction, e.g. IL 1-methyl-3-methylimidazolium dimethylphosphate ([MMIM][DMP]) and its precursor, an equimolar mixture of 1-methylimidazole (MIM) and trimethylphosphate (TMP). As shown in Scheme 1, IL [MMIM][DMP] is formed as a result of transference of a methyl group from TMP to the MIM ring.

This approach is chosen due to the following facts. First, density is such a thermodynamic property that is directly related to an EOS and many experimental data have been available. Second, the density difference between a specified IL and its physical mixture can be solely ascribed to the appearance of electrostatic interaction as the physical mixture is converted to the corresponding IL, see Scheme 1, while the short range intermolecular interactions, e.g., hard sphere repulsion and dispersive interaction virtually remain unchanged. Third, the ionic characteristic of IL has been recognized and justified from both experimental observation and computer simulations [8,9].
In this work, density of a molecular liquid or its mixture is represented with an EOS constructed on the basis of perturbation theory, and the resulting EOS is further extended to IL by introducing an electrostatic term expressed by mean spherical approximation (MSA). Molecular parameters were obtained by correlating the experimental density of pure molecular liquids at atmospheric pressure and varying temperatures, and the resulting parameters were used to predict the density of the physical admixture and the corresponding ILs. The results indicate that the density enhancement of an IL with respect to its corresponding physical admixture can be satisfactorily accounted for by the electrostatic interaction involved, which suggest that IL may be treated as a completely dissociated electrolyte for the simplification of the modeling work.

2. Experimental

2.1. Chemicals

All chemical reagents used in the experiments were analytical grade without further purification. The ILs used were prepared and purified in the laboratory according to the literatures procedure [10,11], and the purity was more than 98% in terms of NMR analysis. Furthermore, the ILs were treated before use by vacuum evaporation to remove the residual volatile impurities, and the mass fraction of water was 5.2 × 10⁻⁴ as measured by the Karl Fischer method (CBS-1A).

2.2. Density measurement

In order to determine the molecular parameters as well as ionic parameters for the EOS developed hereinafter in a self-consistent way, densities in the temperature range of (293.15–323.15 K) were measured for pure molecular liquids, viz. N-methylimidazolide ([MIM]), N-ethylimidazolide ([EIM]), trimethylphosphate ([TMP]), triethylphosphate ([TEP]) and tributylphosphate ([TBP]), equimolar mixture of ([MIM] + [TMP]) and ([MIM] + [TEP]), and four ILs, viz. [MMIM][DMP], [EMIM][DEP], [EEIM][DEP] and [BMIM]DBP. The experimental density data at different temperatures were presented in Table 1.

All densities in Table 1 were measured using pycnometer method except the equimolar mixture of ([MIM] + [TMP]) and ([MIM] + [TEP]), which was measured by Anton Paar DMA 5000 digital vibrating tube densimeter. With respect to the pycnometer method, 50 ml glass pycnometers were used with their exact volume calibrated a priori with water, and the liquid mass weighted by a precision electronic balance (Brook Co. Ltd., USA, 0.001 g). The liquid temperature of the pycnometer was recorded by a platinum thermometer inside the thermostatic vibrating air oven. The uncertainty and fluctuation of the measured temperature was within 0.2 K.

3. Theoretical basis

3.1. Model

In this paper, ionic liquid is assumed to be composed entirely of organic cations and anions, which is similar to a typical 1–1 type strong electrolyte, e.g. NaCl above melting temperature. The cation is assumed as a univalent charged particle with hard sphere diameter of $d_c$ and dispersive energy of $\varepsilon_{dis}$, and similarly the anion is assumed as a univalent charged particle with hard sphere diameter of $d_a$ and dispersive energy of $\varepsilon_a$. The Helmholtz free energy for an IL system is composed of three parts, viz. hard sphere repulsion, dispersive attraction and ionic electrostatic interaction, and accordingly the system pressure, $P$, can be expressed as a sum of these contributions, i.e.

$$P = P_{hs} + P_{dis} + P_{elec}$$

The first two terms in the right hand side of Eq. (1) have been available in literature [12,13] and can be expressed as follows.

$$P_{hs} = \frac{6kT}{\pi} \left\{ \frac{\xi_0}{1 - \xi_3} + \frac{3\xi_1\xi_2}{(1 - \xi_3)^2} + \frac{(3 - \xi_3)^2}{(1 - \xi_3)^2} \right\}$$

$$P_{dis} = \frac{1}{\rho R T^2} \sum_{m=1}^{4} m A_{1m} \left( \frac{\xi_3}{\tau} \right)^m + \frac{1}{\rho R T^2} \sum_{m=1}^{4} m A_{2m} \left( \frac{\xi_3}{\tau} \right)^m$$

Table 1

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>293.15</th>
<th>298.15</th>
<th>303.15</th>
<th>308.15</th>
<th>313.15</th>
<th>318.15</th>
<th>323.15</th>
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<tr>
<td>MIM*</td>
<td>1.0370</td>
<td>1.0332</td>
<td>1.0292</td>
<td>1.0250</td>
<td>1.0207</td>
<td>1.0155</td>
<td>1.0119</td>
</tr>
<tr>
<td>EIM*</td>
<td>0.9986</td>
<td>0.9952</td>
<td>0.9913</td>
<td>0.9874</td>
<td>0.9835</td>
<td>0.9787</td>
<td>0.9748</td>
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<tr>
<td>TMP*</td>
<td>1.2171</td>
<td>1.2129</td>
<td>1.2078</td>
<td>1.2025</td>
<td>1.1980</td>
<td>1.1919</td>
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<tr>
<td>TEP*</td>
<td>1.0711</td>
<td>1.0679</td>
<td>1.0633</td>
<td>1.0589</td>
<td>1.0535</td>
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<td>0.9616</td>
<td>0.9584</td>
<td>0.9554</td>
<td>0.9496</td>
<td>0.9447</td>
<td>0.9409</td>
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<tr>
<td>[MMIM][DMP]*</td>
<td>1.2017</td>
<td>1.2583</td>
<td>1.2550</td>
<td>1.2517</td>
<td>1.2480</td>
<td>1.2451</td>
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<tr>
<td>[EMIM][DEP]*</td>
<td>1.1468</td>
<td>1.1464</td>
<td>1.1400</td>
<td>1.1365</td>
<td>1.1335</td>
<td>1.1299</td>
<td>1.1264</td>
</tr>
<tr>
<td>[EEIM][DEP]*</td>
<td>1.1272</td>
<td>1.1250</td>
<td>1.1223</td>
<td>1.1196</td>
<td>1.1155</td>
<td>1.1119</td>
<td>1.1088</td>
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<tr>
<td>[BMIM]DBP*</td>
<td>–</td>
<td>–</td>
<td>1.0410</td>
<td>1.0375</td>
<td>1.0339</td>
<td>1.0306</td>
<td>1.0272</td>
</tr>
<tr>
<td>[MIM + TMP]*</td>
<td>1.14209</td>
<td>1.13720</td>
<td>1.13239</td>
<td>1.12785</td>
<td>1.12326</td>
<td>1.11895</td>
<td>1.11306</td>
</tr>
<tr>
<td>[MIM + TEP]*</td>
<td>1.06082</td>
<td>1.05609</td>
<td>1.05120</td>
<td>1.04638</td>
<td>1.04156</td>
<td>1.03673</td>
<td>1.03132</td>
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</table>

* Measured by pycnometer method.

b Measured by Anton Paar DMA 5000 densimeter.
Table 2
Parameters of Eqs. (3) and (7).

<table>
<thead>
<tr>
<th>$A_{31}$</th>
<th>$A_{32}$</th>
<th>$A_{33}$</th>
<th>$A_{34}$</th>
<th>$A_{35}$</th>
<th>$A_{32}$</th>
</tr>
</thead>
<tbody>
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<td>$A_{31}$</td>
<td>$A_{34}$</td>
<td>$C_1$</td>
<td>$C_2$</td>
<td>$C_3$</td>
<td>$C_4$</td>
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<tr>
<td>-22.216</td>
<td>15.904</td>
<td>0.2977</td>
<td>0.33163</td>
<td>1.0477</td>
<td>$10^{-3}$</td>
</tr>
</tbody>
</table>

\[ \xi_n = \frac{n}{6} \sum \rho d_i^n \quad (n = 0, 1, 2, 3) \]  
(4)

\[ \tau = \frac{\sqrt{2}}{6} \]  
(5)

\[ \hat{\beta} = \frac{kT}{\xi} \]  
(6)

where $d_i$ is temperature dependent and related with the temperature-independent soft-core diameter of Lennard–Jones fluid $\sigma_i$ by the following equation.

\[ \frac{d_i}{\sigma_i} = \frac{1 + c_1 \hat{\beta}}{1 + c_2 \hat{\beta} + c_3 \hat{\beta}^2} \]  
(7)

The coefficients $A_{1m}$ and $A_{2m}$ of Eq. (3) and $c_1$–$c_3$ of Eq. (7) are taken from reference [13] and listed in Table 2.

The electrostatic contribution to pressure of ILs, $\rho_{\text{elec}}$, is presented by the following equation, which was derived from integral equation under mean spherical approximation (MSA) [14].

\[ \rho_{\text{elec}} = -kT \left[ \frac{\Gamma^3}{3\pi} + \frac{1}{8} \left( \frac{\rho P_n}{A} \right)^2 \right] \]  
(8)

\[ \Gamma = \frac{\alpha}{2} \sum \rho_i \left( \frac{Z_i - (\pi/2\Delta) d_i^3 P_n}{1 + \tau d_i^2} \right)^{1/2} \]  
(9)

\[ \alpha^2 = 4\pi\beta e^2 \]  
(10)

\[ P_n = \frac{1}{\sum \rho_i d_i Z_i} \]  
(11)

\[ \Omega = 1 + \frac{\pi}{2\Delta} \sum \rho_i d_i^3 \]  
(12)

\[ \Delta = 1 - \frac{\pi}{6} \sum \rho_i d_i^3 \]  
(13)

The inverse shielding length, $\Gamma$, can be obtained by simple iteration using the following initial value

\[ \Gamma = \frac{\alpha}{2} \left( \sum \rho_i Z_i^2 \right)^{1/2} \]  
(14)

Density of an IL at specified temperature can be calculated by using Eqs. (1)–(14) together with two ionic parameters, i.e. soft core diameter $\sigma_i$ and dispersive parameter $\varepsilon_i$ of ion $i$, which can be readily derived from corresponding molecular ones by using some combining rules as illustrated in the following context. It should be pointed out that Eq. (1) is also applicable to pure molecular liquids as well as their physical mixtures by simply deleting the $\rho_{\text{elec}}$ term due to the absence of electrostatic interaction in molecular liquids.

3.2. Estimation of parameters

The molecular parameters ($\sigma$ and $\varepsilon$) are determined by fitting the experimental densities of pure liquids with the least-squares method according to Eqs. (1)–(7) and the following objective function, OBF.

\[ \text{OBF} = \min \frac{1}{n} \sum \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right| \]  
(15)

The resulting parameters for MIM, EIM, TMP, TEP, TBP, dimethylsulfate (DMS), and diethylsulfate (DES) are listed in Table 3.

Densities for a physical mixture of molecular liquids at specified temperature and concentration can also be predicted with Eqs. (1)–(7) together with the following mixing rule,

\[ \varepsilon = \sum \sum x_i x_j \sqrt{\varepsilon_i \varepsilon_j} \]  
(16)

From Scheme 1, it is seen that the IL [MMIM][DMP] is formed when a methyl group is transferred from TMP to MIM. Considering the additive property of volume and dispersive energy, the ionic parameters of dispersion energy and diameter can be expressed with Eqs. (17)–(20), respectively. This means that the dispersive parameter $\varepsilon$ of [MMIM]$^+$ and [DMP]$^-$ can be derived from their corresponding molecular precursors MIM and TMP by adding and subtracting the dispersive contribution of methyl group. And similarly, the ionic diameters of [MMIM]$^+$ and [DMP]$^-$ can be calculated using Eqs. (19) and (20), respectively, where 0.996 is an adjustable constant adopted by the present authors to reflect the volume contraction of the bonded ion [MMIM]$^+$ compared to its physical group mixture of (MIM and CH$_3$). The group parameters ($\sigma$ and $\varepsilon$) of methyl and methylene are directly taken from literature [15], and listed in Table 3.

\[ \varepsilon_{[\text{MMIM}]} = \varepsilon_{\text{MIM}} + \varepsilon_{\text{CH}_3} \]  
(17)

\[ \varepsilon_{[\text{DMP}]} = \varepsilon_{\text{TMP}} - \varepsilon_{\text{CH}_3} \]  
(18)

\[ d_{[\text{MMIM}]} = 0.996 \sqrt{d_{\text{MIM}}^3 + d_{\text{CH}_3}^3} \]  
(19)

\[ d_{[\text{DMP}]} = 0.996 \sqrt{d_{\text{TMP}}^3 - d_{\text{CH}_3}^3} \]  
(20)

4. Results and discussion

Experimental densities for seven pure molecular liquids in the temperature range of (293–323 K) are correlated with the two-parameter EOS, i.e. Eqs. (1)–(7), the resulting parameters ($\varepsilon/k$, $\sigma$)

Table 3
The value of parameters ($\varepsilon/k$, $\sigma$).

<table>
<thead>
<tr>
<th>Species</th>
<th>$\varepsilon/k \text{K}^{-1}$</th>
<th>$\sigma \text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIM</td>
<td>477.168</td>
<td>4.833</td>
</tr>
<tr>
<td>EIM</td>
<td>523.767</td>
<td>5.186</td>
</tr>
<tr>
<td>TMP</td>
<td>428.055</td>
<td>5.422</td>
</tr>
<tr>
<td>TEP</td>
<td>449.895</td>
<td>6.217</td>
</tr>
<tr>
<td>TBP</td>
<td>624.984</td>
<td>7.352</td>
</tr>
<tr>
<td>DMS</td>
<td>477.704</td>
<td>5.127</td>
</tr>
<tr>
<td>DES</td>
<td>521.804</td>
<td>5.743</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>98$^a$</td>
<td>3.750$^a$</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>46$^a$</td>
<td>3.950$^a$</td>
</tr>
</tbody>
</table>

$^a$ Taking from the literature [15]
are listed in Table 3, and the average relative deviation (ARD) of the correlation listed in Table 4. The experimental density data of DMS and DES are taken from literature [16]. From Table 3, it is seen that the model parameters of dispersion and soft-core diameter increase monotonically with the alkyl group size, viz. TBP > TEP > TMP, EIM > MIM, DES > DMS, which is reasonable and coincides with the group additivity of dispersion energy and volume.

From Table 4, it is shown that the two-parameter EOS is applicable for density calculation of pure molecular liquids with average relative deviation of 0.46%. It is also noted that the density calculation accuracy monotonically decreases with the increase of the alkyl group for the same series of molecular liquids, i.e. the calculation accuracy followed the order TMP > TEP > TBP, MIM > EIM, and DMS > DES. This may be ascribed to the increasing non-sphericity of the molecules as the alkyl-chain group becomes longer, which deviates from the spherical assumption of the particles embedded in the EOS.

With the available parameters obtained from density regression of pure molecular components, as listed in Table 3, the densities of their equimolar physical mixture as well as the resulting ionic liquids can be predicted successfully. The experimental density data of [MMIM][DMP] are schematically presented in Fig. 1. From Table 4, it is seen that the model parameters of dispersion and soft-core diameter monotonically decrease with the increase of the alkyl group for the same series of molecular liquids, i.e. the calculation accuracy followed the order TMP > TEP > TBP, MIM > EIM, and DMS > DES. This may be ascribed to the increasing non-sphericity of the molecules as the alkyl-chain group becomes longer, which deviates from the spherical assumption of the particles embedded in the EOS.

According to Eq. (21), the expansivity of MIM, TMP, (MIM + TMP) and [MMIM][DMP] are calculated as 8.31 \times 10^{-4} \text{K}^{-1}, 8.48 \times 10^{-4} \text{K}^{-1}, 8.41 \times 10^{-4} \text{K}^{-1} and 5.31 \times 10^{-4} \text{K}^{-1}, respectively, which suggests that ionic liquid has the lowest expansivity in comparison with molecular liquids or their mixtures related. This highlighted the importance of the electrostatic interaction on the density enhancement and expansivity decrease of ILs with respect to their corresponding precursors of molecular mixture.

To show the overall performance of the present model, the correlated/predicted and the experimental densities are compared and plotted in Fig. 2. The results manifest the applicability of the EOS proposed for ionic liquids.

![Image](350x608 to 589x785)

**Fig. 1.** Experimental densities for some liquids as a function of temperature Experimental data: ▲ [MMIM][DMP]; ■ [TMP]; ▼ [MIM] + [TMP]; □ [MIM] — predicted; - - - correlated.

![Image](351x122 to 587x313)

**Fig. 2.** The calculated vs. experimental densities of all systems studied ▲ correlated for pure molecule components ▼ predicted for ILs and their physical mixtures.
5. Conclusions

Based on the hard sphere perturbation theory an EOS is developed for ionic liquid by accounting for the dispersive and electrostatic interaction independently. The EOS can correlate the density of molecular liquids accurately, and the resulting molecular parameters can be used to predict the density of molecular mixtures as well as their corresponding ionic liquids with good accuracy. The density enhancement of ILs versus their equimolar physical mixtures can be well described by the electrostatic contribution expressed using MSA equation, which manifests the significance of electrostatic interaction and rationality to treat ionic liquid as a molten salt in addition to a neutral molecular liquid in the modeling work.

List of symbols

- \( n \): number of data points
- \( P \): the system pressure (kPa)
- \( P_{\text{hs}} \): the pressure of hard sphere (kPa)
- \( P_{\text{dis}} \): the pressure of dispersive (kPa)
- \( P_{\text{ele}} \): the pressure of electrostatic (kPa)
- \( T \): the absolute temperature (K)
- \( d_i \): the hard-sphere diameter of species \( i \) (m)
- \( \rho_i \): the number density of species \( i \) (m\(^{-3}\))
- \( \rho_{\text{cal}} \): calculated densities (g/cm\(^3\))
- \( \rho_{\text{exp}} \): experimental densities (g/cm\(^3\))
- \( n_c \): the number of components in the mixture
- \( Z_i \): the valence of species \( i \)
- \( \sigma_i \): the soft-core diameter of species \( i \) (Å)
- \( \varepsilon \): the dispersion energy
- \( \lambda^{-1} \): the inverse shielding length
- \( k \): the Boltzmann constant
- \( \tilde{T} \): the reduced temperature

Acknowledgment

The authors are grateful to the financial support from National Science Foundation of China (20376004, 20776015) that allowed the authors to accomplish the research presented herein.

References