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Volumetric properties of ionic liquids and their binary mixtures from improved Tao–Mason equation of state

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ABSTRACT

In this work, the Tao–Mason (TM) equation of state (EOS) has been employed to model the pressure–volume–temperature (PVT) properties of ionic liquids (ILs) by the help of an alternative corresponding state correlation based on the measurable scaling constants, i.e., surface tension and liquid density both at room temperature. Performance of model has been assessed against 2207 experimental data points over a wide temperature range within 293–472 K and pressure range from ambient up to 200 MPa for 17 imidazolium-based ILs. The average absolute deviation (AAD in %) of the calculated densities from literature values was found to be 0.79%. Generally, this work shows that TM EOS based on the surface tension property of ILs outperforms the previous version of TM EOS which uses normal boiling point properties, i.e. the heat of vaporization and liquid density. Improved TM EOS has also been extended to binary systems formed by ionic liquids to predict their volumetric properties. The performance of the mixture version of improved TM EOS has been assessed against 385 experimental data points, and AAD was found to be 0.78%.

1. Introduction

The relationship between pressure, volume and temperature of ionic liquids (ILs) is one of the most fundamental and useful from both a theoretical and a practical point of view. Pressure–volume–temperature (PVT) data are particularly important to describe the thermodynamic behavior of ILs and are important for efficient design of chemical products and processes. Although some experimental data for thermophysical properties of ILs exist, prediction of their *PVT* properties is still an important task considering they have been in focus recently as new materials offering several highly promising applications [1–4]. So, the prediction of *PVT* properties of ILs is an important task. In these circumstances the development of equations of state (EOSs) and corresponding states correlation methods to predict the volumetric properties can be highly useful.

A literature survey of some previous efforts on modeling the volumetric properties of ILs can be noted below.

So far, several researchers developed the predictive methods for ILs in the literature for this purpose using a wide range of approaches starting with Gardas and Coutinho [5] to the recent work by Abildskova et al. [6]. Also, Aparicio et al. [7] have analyzed the predictive models for the thermophysical properties of ILs together with the quality of their predictions. Goharshadi and Moosavi [8] have developed another approach for the description of *PVT* properties of ILs using the linearity property. Their approach is important because it can be used for safe extrapolation in the calculation of the density.

Wang et al. [9] used a group contribution equation of state which was based on the electrolyte perturbation theory to calculate densities of ionic liquids. They divided ILs into several groups including cations, anions, and alkyl substituent groups. Shen et al. [10] predicted the densities of ILs using the Patel–Teja equation of state in conjunction with the modified Lydersen–Joback–Reid group contribution method. Machida et al. [11] modified the temperature dependence of Sanchez–Lacombe EOS to take into account the hydrogen bonding and ionic interactions that appeared in ILs.

In addition, some alternative approaches for modeling the ionic liquids data, such as those based on the statistical associating fluid theory (SAFT) EOS models have been developed in the literature from the work of Llovell et al. [12], and Rahmati-Rostami et al. [13] to the recent work by Polishuk [14]. In these studies, several SAFT-type EOSs have been developed to model the *PVT* behavior of ionic liquids and the solubility of some gases in imidazolium-based ILs.

Some assessments were made on the performance of statistical–mechanical based EOS for non-polar fluids, polar fluids and ILs in the literature. For instance, Papari et al. [15–17] have presented simplified Tao–Mason (TM) EOS [18] for the estimation of volumetric properties of refrigerant fluids. They have employed TM EOS with the three temperature-dependent parameters scaled according to the heat of vaporization and the liquid density at boiling temperature. However, their approach cannot be easily performed for ILs, neither the accurate

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vapor–pressure data nor heats of vaporization are accessible for most ILs in the literature.

Hosseini et al. [19] have previously modified a perturbed hard-sphere (PHS) EOS for ILs by the use of the surface tension and the liquid density, both at room temperature to improve the model's capability of describing the volumetric properties of ILs and their mixtures. Their method have represented an improvement from their previous works [20,21]. In this regard, we aim to utilize the work of Hosseini et al. [19] to apply the alternative corresponding states correlations to TM EOS [18] for the largest class of ILs, namely imidazolium-based ILs. The reason for selecting this approach is that the need for heat of vaporization and liquid density at boiling point, which are scarcer than surface tension data, limits the applicability of the previous model developed by Papari et al. [17].

We determine three temperature-dependent parameters that appeared in TM EOS via the extended law of corresponding states and perturbation theory of liquids. It should be mentioned that the above-mentioned parameters reflect a measure of pairwise interactions. Besides, to assess further the accuracy of the present model, our calculation results are compared with the previous models developed by Hosseini et al. [19], Papari et al. [22], Wang et al. [9] and the recent model developed by Fadaei et al. [23].

In the present work, the mixture version of improved TM EOS will also be extended to binary systems formed by ILs for predicting their volumetric properties by taking some interaction parameters between two unlike ILs. These parameters reflect somewhat non-ideal volumetric behavior in the studied binary mixtures.

2. Theory

2.1. TM EOS for pure ILs

The general frame of the TM EOS can be read as [18]:

$$\frac{P}{\rho k_B T} = 1 + \rho(B_2 - \alpha) + \frac{\alpha\rho}{1 - \lambda b\rho} + A_1 b\rho^2(\alpha - B_2)\frac{\left(e^{(\kappa/T_r)} - A_2\right)}{1 + 1.8(b\rho)^4} \tag{1}$$

where P is the pressure, ρ is the molar (number) density, $B_2(T)$ is the second virial coefficient, $\alpha(T)$ is the contribution of repulsive branch of pair potential function according to the Weeks–Chandler–Anderson approach in perturbation theory of liquids [24], b(T) reflects the van der Waals co-volume, and $k_B T$ is the thermal energy per one molecule. This is based on the recognition that the structure of a liquid is determined primarily by repulsive forces, so that fluids of hard bodies can serve as useful reference states. In Eq. (1), λ is a free parameter which can be varied to get the desired volumetric properties of dense fluids. The numerical values of A_1, A_2 and κ have been fixed by the fitting of experimental *PVT* data and vapor pressures for simple fluids as the following [18]:

$A_1 = 0.143;$

$A_2 = 1.66;$

$\kappa = 1.093.$

2.2. Parameter estimation

In this section, three temperature-dependent parameters $B_2(T)$, $\alpha(T)$ and $b(T)$ of Eq. (1) must be evaluated. These parameters reflect the second viral coefficient, contribution of repulsive branch of the pair potential and the van der Waals co-volume, respectively. In this work, we have determined the above-mentioned parameters by the help of alternative corresponding states correlations [19], i.e. the surface tension and liquid density of ILs, both at room temperature were taken as two measurable scaling constants. These correlations can be expressed by the following equations:

$$B_2(T)\rho_f = \left(0.0804 - 2.1288\,T_r^{-1} - 8.5597\,T_r^{-2} + 7.4294\,T_r^{-3} - 3.3494\,T_r^{-4}\right) \tag{2}$$

where,

$$T_r = \left(T^{3/2} \middle/ T_{ref}\,T^{*1/2}\right)^{3/4} \tag{3}$$

$T_{ref.}$ is defined as a reference temperature which contains the surface tension, γ^* and the liquid density ρ^* both at room temperature, and is defined as:

$$T_{ref.} = \gamma^* \rho^{*-2/3} N^{1/3} \Big/ R. \tag{4}$$

The parameters $\alpha(T)$ and $b(T)$ are related to the following corresponding states correlations as [19]:

$$\rho^*\alpha(T) = a_1\left[\exp(-c_1 T_r)\right] + a_2\left[1 - \exp\left(-c_2/T_r^{1/4}\right)\right] \tag{5}$$

and

$$\begin{aligned}\rho^* b(T) = {} & a_1\left[(1 - c_1 T_r)\exp(-c_1 T_r)\right] \\ & + a_2\left[1 - \left(1 + 0.25\,c_2/T_r^{1/4}\right)\exp\left(-c_2/T_r^{1/4}\right)\right]\end{aligned} \tag{6}$$

where

$a_1 = -0.01054 \qquad c_1 = 0.7613$

$a_2 = 2.9387 \qquad c_2 = 1.3227.$

2.3. Extension to binary mixtures

The mixture version of TM EOS can be read as:

$$\frac{P}{\rho k_B T} = 1 + \rho\sum_i\sum_j x_i x_j\left((B_2)_{ij} - \alpha_{ij}\right) + \sum_i\sum_j x_i x_j \alpha_{ij} G_{ij} + \rho\sum_i\sum_j x_i x_j (I_1)_{ij} \tag{7}$$

where x_i and x_j are the mole fractions of the i'th and j'th components, respectively. η is the packing fraction of mixtures of hard-spheres which is defined by the following expression [16]:

$$\eta = \frac{\rho}{4}\sum_i^m x_i\, b\,(T)_i. \tag{8}$$

In Eq. (7), G_{ij} represents the pair correlation function of hard-sphere mixture proposed by Ihm et al. [25]:

$$G_{ij} = \frac{1}{1 - \eta} - \left(\frac{b_i\, b_j}{b_{ij}}\right)^{1/3} \frac{\rho\sum_k x_k b_k^{2/3}(\lambda_k + 0.25)}{(1 - \eta)\left(1 + \rho\sum_k x_k b_k \lambda_k\right)}. \tag{9}$$

For a pure system, we have $I_1 = (\alpha - B_2)\,\zeta(T)\,\varphi(b\rho)$.