Development of a modified van der Waals-type equation of state for pure and mixture of ionic liquids

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ABSTRACT

The main aim of the present study is to modify the attractive part of van der Waals-type EOS to model the volumetric ionic liquids and their mixtures. The present study uses the Carnahan–Starling (CS) repulsion term and also focuses on introducing a variable parameter in the attractive term of modified vdW-type EOS. Investigation of the results obtained revealed that this variable is a function of temperature. Our results also show that employment of CS repulsion term together with an appropriately chosen exponent in the attractive term of EOS will greatly improve the accuracies of the calculated densities of various ionic liquids. The average absolute deviation (AAD) of the calculated densities from the experimental ones for 848 data points of pure ionic liquids was found to be 0.36. Further, in the case of mixtures, for 1014 data points the AAD was 0.20.

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1. Introduction

Ionic liquids (ILs) usually refer to room-temperature molten salts, comprising at least one large and asymmetric organic cation or anion. They are liquids that consist exclusively or almost exclusively of ions and therefore they exhibit ionic conductivity. Since the late 1990s, ionic liquids have attracted the attention of chemists around the world for various reasons [1].

The important properties include high heat capacity, high density, extremely low volatility, non-flammability, high thermal stability, wide temperature range for liquid, many variations in compositions, low surface tension and a large number of possible variations in cation and anion conformation, allowing fine-tuning of the IL properties for specific applications [2–16]. A major reason for the interest in ILs is their negligible vapor pressure, which decreases the risk of technological exposure, explosion, and the loss of solvent to the atmosphere.

The science of ionic liquids is a fledgling science. The determination of the properties of ionic liquids and the trends in these properties is critical in the design of ionic liquid for specific applications. ILs are entirely composed of ions and therefore, their physical properties depend on both the type of cation/anion pair and the alkyl chain of the anion [17]. Moreover, their properties can be significantly tuned by appropriate modifications of the cation, anion, or both for a specific application.

Recently, Quijano et al. presented a state-of-the-art review on the applications of ILs in bioreactor technologies [18]. Key properties potentially affecting the performance of bioreactors such as viscosity, density, surface tension and gas absorption are summarized. Also, an overview for the specific chemical and physical properties of ILs was given by Keskin et al. [19]. To understand more about the nature of ionic liquids and rationally expand their applications, knowledge of their pressure–volume–temperature (PVT) properties is required. In fact, the design of industrial processes and new products based on ILs can only be achieved when their thermophysical properties are exactly known [20]. The two most commonly used methods of calculating PVT properties are equation-of-state (EOS) and PVT correlations. Recently, several models have been proposed for predicting densities of this class of fluids. The equations in common use can be classified as belonging to the van der Waals (vdW) family of cubic equations, the extended family of virial equations, or equations based more closely on the results from statistical mechanics and computer simulations.

Several works have been done on modification of the vdW-type equations of state (EOSs) to improve their ability to predict thermophysical properties of fluid and fluid mixtures [21]. In the case of the cubic-type EOS, 24 and 26 different forms of, respectively the volume-dependence and temperature-dependence of the attractive part "a(T)" of the EOS have been reported [22]. Also, there are many modifications on van der Waals-type equations of state through choosing expressions other than the van der Waals one for the repulsive term [21,23–28]. Papari and his coworkers [29] have studied the most commonly used repulsion terms including the well known Carnahan–Starling (CS) [24] and Scott [30] repulsion terms instead of the van der Waals one in van der Waals-family equations of state. It has been identified that, in

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Table 1
The constant of Eq. (3).

Pure Ionic liquid	a_0	a_1	a_2
[C$_2$mim][CF$_3$SO$_3$]	2.1545×10^{-1}	6.8800×10^{-4}	5.1400×10^{-7}
[C$_3$mpy][NTf$_2$]	-9.7324×10^{-2}	5.0835×10^{-4}	-1.9305×10^{-7}
[C$_4$mpyr][NTf$_2$]	-1.8365×10^{-1}	5.9900×10^{-4}	8.3600×10^{-8}
[Omim][BF$_4$]	9.7778×10^{-1}	-1.0700×10^{-3}	9.9100×10^{-6}
[Bmim][BF$_4$]	9.1701×10^{-1}	-4.0316×10^{-3}	1.7500×10^{-5}
[C$_2$mim][MeSO$_4$]	-3.8991×10^{-1}	2.0250×10^{-4}	9.3973×10^{-7}
[C$_2$eim][Tf$_2$N]	-1.7632×10^{-1}	5.4169×10^{-4}	-4.7103×10^{-7}
[C$_2$mim][NTf$_2$]	-1.0349×10^{-1}	-1.6774×10^{-4}	8.3560×10^{-7}
[bmim][CF$_3$SO$_3$]	2.3660×10^{-1}	-1.0174×10^{-3}	3.3085×10^{-6}
[omim][PF$_6$]	-1.0828×10^{-1}	-1.1023×10^{-4}	1.1500×10^{-6}
[hmim][PF$_6$]	3.7338	-1.1887×10^{-2}	2.6268×10^{-5}
[bmmim][PF$_6$]	5.3207×10^{-1}	-2.0730×10^{-3}	5.3400×10^{-6}

general, the van der Waals-type equations of state using the repulsion term proposed by Carnahan–Starling [24] give better results than those obtained based on the van der Waals repulsion term [31–33]. The replacement of the van der Waals term by the Carnahan–Starling (CS) expression leads to a new class of EOSs which are of the fifth or higher degree. Furthermore, Papari et al. [29] showed that the Scott repulsion term is superior with respect to CS and vdW repulsion terms. In 2011, Papari et al. [34] presented a new version of perturbed hard sphere equation of state by imposing a parameter in the attraction term of the EOS. They obtained the parameters of the EOS in terms of critical parameters by imposing the critical conditions.

Further, a perturbed hard-sphere equation of state has been employed to predict the pressure–volume–temperature properties of some pure and mixture of ionic liquids [35–38]. Also, they predicted the volumetric properties of ILs using Ihm–Song–Mason (ISM) [39] and Tao–Mason [40] equations of state.

In the present study, the new version of modified perturbed hard sphere developed by Papari et al. [34] was extended to mixtures and tested by ionic liquid mixtures.

2. Theory

2.1. Equation of state for pure ILs

As mentioned above, the general frame of the EOS developed by Papari [34] known as vdW–CS-β equation takes the following form. This equation consists of two terms: 1, the Carnahan–Starling (CS) hard-sphere repulsion term and 2, the van der Waals attractive term modified by introducing a power law of the form $T^{-(\beta + 1)}$ [34]:

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{a(T)\rho}{RT^{(\beta + 1)}} \tag{1}$$

where Z is the compressibility factor, ρ is the number (molar) density, R is the gas constant, $a(T)$ reflects the strengths of attractive forces between the spheres, η is packing fraction defined as:

$$\eta = \frac{b(T)\rho}{4}. \tag{2}$$

In this equation b is the van der Waals co-volume.

We found empirically that the β parameter that appeared in Eq. (1) is actually temperature dependent. This parameter was correlated with the simple Eq. (3) using the PVT data.

$$\beta = a_0 + a_1 T + a_2 T^2 \tag{3}$$

The constants a_0, a_1, and a_2 for several ILs have been listed in Table 1. The coefficients in Eq. (3) have been determined by a fitting procedure by taking the experimental data of ILs including: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [C$_2$mim][CF$_3$SO$_3$], 3-methyl-1-propylpyridinium bis(trifluoromethylsulfonyl) imide [C$_3$mpy][NTf$_2$], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide [C$_4$mpyr][NTf$_2$], 1-butyl-3-methylimidazoliumtetrafluoroborate [Bmim][BF$_4$], 1-methyl-3-octylimidazolium tetrafluoroborate [Omim][BF$_4$], 1-ethyl-3-methyl-imidazolium bis-(trifluoromethylsulfonyl)imide [C$_2$mim][NTf$_2$], 1,3-diethylimidazolium bis-(trifluoromethylsulfonyl) imide [C$_2$eim][Tf$_2$N], 1-ethyl-3-methylimidazolium methylsulfate [C$_2$mim][MeSO$_4$], 1-butyl-2,3-dimethylimidazolium hexafluorophosphate [bmmim][PF$_6$], 1-butyl-3-methylimidazolium trifluoromethanesulfonate [bmim][CF$_3$SO$_3$], 1-hexyl-3-methylimidazolium hexafluorophosphate [hmim][PF$_6$], and 1-octyl-3-methylimidazolium hexafluorophosphate [omim][PF$_6$]. Their experimental data provided us with a nearly wide PVT space for fitting procedure.

Several procedures have been proposed to evaluate two temperature dependent parameters $a(T)$ and $b(T)$ that appeared in Eqs. (1) and (2). We have determined these parameters by applying the two constraints at the critical point to Eq. (1) (i.e. the first and second derivatives of pressure with respect to volume are equal to zero). Therefore, the expressions for $a(T)$ and $b(T)$ in terms of critical properties are as follows:

$$a = 0.496388 \frac{R^2 T_C^{(2+\beta)}}{P_C} \tag{4}$$

$$b = 0.187294 \frac{RT_C}{P_C}. \tag{5}$$

Here P_C is the critical pressure and T_C is the critical temperature.

Table 2
The constant of Eq. (12).

Mixture ionic liquid	m_0	m_1	m_2
[C$_2$mim][CF$_3$SO$_3$] + acetone	5.354×10^{-1}	-6.0000×10^{-4}	1.0400×10^{-4}
[C$_2$mim][CF$_3$SO$_3$] + methyl acetate	1.585×10^{-1}	6.1000×10^{-3}	-1.1100×10^{-5}
[C$_2$mim][CF$_3$SO$_3$] + methanol	1.6891	-2.5000×10^{-3}	3.2100×10^{-6}
[C$_2$mim][CF$_3$SO$_3$] + ethanol	1.8817	-2.5000×10^{-3}	2.6600×10^{-6}
[C$_2$mim][CF$_3$SO$_3$] + water	3.4990×10^{-1}	-1.9000×10^{-3}	2.8000×10^{-6}
[Bmim][PF$_6$] + benzene	1.5173	-2.8000×10^{-3}	3.3100×10^{-6}
[Bmim][PF$_6$] + acetonitrile	1.7601	6.0000×10^{-3}	-7.7500×10^{-6}
[Bmim][BF$_4$] + acetonitrile	2.9336	9.5000×10^{-3}	-1.400×10^{-5}
[Bmim][BF$_4$] + benzene	7.3092	-8.1000×10^{-3}	7.8900×10^{-6}
[Bmim][BF$_4$] + water	7.8024	-2.0100×10^{-2}	3.0700×10^{-5}
[BuPy][BF$_4$] + water	-3.1800×10^{-2}	2.5700×10^{-2}	-4.4200×10^{-5}
[Omim][BF$_4$] + ethanol	1.7377×10^{-1}	-1.7500×10^{-2}	1.7000×10^{-5}