



Modeling High-Pressure Densities of Ionic Liquids

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Abstract

Accurate knowledge of liquid density is necessary for the development of industrial processes involving ionic liquids (ILs). In this work, a group contribution approach based on statistical associating fluid theory (SAFT- γ) is used to predict the high-pressure densities of some ILs. The SAFT- γ parameters of some imidazolium-based ionic liquids with either [MeSO₃], [MeSO₄], [EtSO₄] and [CF₃SO₃] anions are optimized to experimental data within a temperature range of 293.15-393.15 K and pressures up to 35 or 60 MPa. Moreover, by using the optimized group parameters, the performance of the model is examined by predicting the density of some IL systems not included in the optimization database. The results show good agreement with experimental data.

Keywords: Ionic liquids, Statistical associating fluid theory (SAFT), Thermodynamic modeling, Density

Introduction

Ionic Liquids (ILs) have superb physicochemical properties including potential of dissolving a vast variety of compounds, recyclability, suitable chemical and thermal stability, wide liquid and electrochemical range and insignificant volatility. These properties make them interesting to replace traditional organic solvents in many processes. Some industrial examples of ILs applications include preparation of a media for CO₂ absorption, and separation of heavy metal ions from aqueous solutions, sulfur mixtures from gasolines and paraffins from aromatics [1, 2]

Accurate knowledge of physicochemical properties are necessary for the development of industrial processes involving ILs. In the midst of all ILs properties, density is crucial in thermodynamic and thermophysical calculations. Nonetheless, the accurate understanding of density is still lacking or at least scarce due to the unfeasibility of density measurement for a large number of nearly 10¹⁸ possible ILs [1, 2].

Bulk of literature studies have been focused on prediction and correlation of ILs densities via techniques such as empirically derived correlations [3], intelligent models [2], quantitative structure-property relationships (QSPRs) [4], group contribution (GC) methods [5] and the calculations based on equation of state (EoS) [6]. Most of literature studies are established for a specific operational condition in which their applications for other conditions and other types of ILs may lead to considerable deviations from actual data [2].



Since the huge family of ILs, similar to hydrocarbons, has many groups in common among its various members, using GC methods and intelligent methods can be a suitable tool to predict the phase behavior of many ILs. This only requires the determination of some parameters for a number of functional groups. This procedure will then allow the prediction of properties and phase behavior of even those IL members that have not been considered, as long as their constituent groups are in common with previously studied ILs [7].

In this study, we deal with the modeling of density of some ILs using the SAFT- γ group contribution method under wide temperature ranges and high pressures. The density of imidazolium-based ILs consisting of 1-ethyl-3-methylimidazolium methanesulfonate [emim][MeSO₃], 1-ethyl-3-methylimidazolium methylsulfate [emim][MeSO₄], 1-ethyl-3-methylimidazolium ethylsulfate [emim][EtSO₄] and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [emim][CF₃SO₃] are correlated to the experimental data within the temperature range of 293.15-393.15 K and up to high pressures (35 or 60 MPa). Moreover, the prediction ability of model is checked for some IL systems not included in the optimization database.

Model

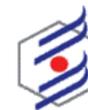
In this study, we chose to divide the IL molecule into several groups consisting of CH₃, CH₂, the cation head, and the anion. Each of these groups is considered to be made of only one segment. By considering association sites on the anion and cation head groups, it is possible to account for the association interactions between these groups. Generally, two types are taken into account to describe the association sites: type *a* (electronegative atoms or electron ion pairs) and type *b* (electropositive atoms) [8].

In the following, the subscripts *i* and *j* express a component (running from 1 to *NC*, the number of components), *k* and *l* express groups (running from 1 to *NG*, the number of group types) and the subscripts *a* and *b* express site types (running from 1 to *NST*, the number of site types on a segment of a group type *k*) [8]. In the SAFT- γ group contribution method, a group of type *k* is composed of v_k^* identical fused segments. Each fused segment on group *k* is determined by four individual parameters: a shape factor S_k , a diameter σ_{kk} , a dispersive energy ε_{kk} , and range λ_{kk} . The number of site types NST_k on a group of type *k* is also specified. If NST_k is non-zero, the number of sites of each type n_{ka} ($a = 1, \dots, NST_k$) is then set. Unlike potential parameters also have to be determined to characterize the interactions of a segment of a group of type *k* with a segment of a group of type *l* (σ_{kl} , ε_{kl} , λ_{kl}). The interactions on each *a*-site on a group of type *k* with a *b*-site on a group of type *l* (ε_{klab}^{HB} and r_{klab}^c , $a = 1, \dots, NST_k$; $b = 1, \dots, NST_l$) also must be determined.

The SAFT approach for a mixture of associating chain molecules is given in the form of Helmholtz free energy *A* by [8]:

$$\frac{A}{Nk_B T} = \frac{A^{IDEAL}}{Nk_B T} + \frac{A^{MONO}}{Nk_B T} + \frac{A^{CHAIN}}{Nk_B T} + \frac{A^{ASSOC}}{Nk_B T} \quad (1)$$

In Eq. (1), *N* is the total number of molecules in the mixture, *T* is the temperature and k_B is the Boltzmann constant. The terms A^{IDEAL} and A^{MONO} refer, respectively, to the ideal free energy of the molecules and the residual monomer free-energy contribution related to hard-sphere repulsion and dispersive attractive interactions between segments. The term A^{CHAIN}



takes into account the contribution due to the formation of molecules comprising the heteronuclear segments, and the term A^{ASSOC} deals with the associative contribution related to bonding between sites on associating segments [8]. In what is to follow, the association term is defined, while the other terms are provided in our previous publication [7].

The free energy contribution related to association between sites on segments of the groups is expressed in the usual Wertheim form as [8]:

$$\frac{A^{ASSOC}}{Nk_B T} = \sum_{i=1}^{NC} x_i \sum_{k=1}^{NG} v_{k,i} \sum_{a=1}^{NST_i} n_{ka} \left(\ln X_{ika} + \frac{1 - X_{ika}}{2} \right) \quad (2)$$

X_{ika} is the fraction of component i not bonded at site type a , that is placed on a group of type k . These fractions are determined by solving the following system of non-linear equations [8]:

$$X_{ika} = \frac{1}{1 + \sum_{j=1}^{NC} \sum_{l=1}^{NG} \sum_{b=1}^{NST_j} \rho x_j v_{l,j} n_{lb} X_{jlb} \Delta_{ijklab}} \quad (3)$$

In Eq. (3), ρ is the number density of the system and Δ_{ijklab} is a function that depends on the association strength between sites a and b placed on segments of groups k and l of components i and j , and was expressed in our previous publication [7].

In this paper, to reduce the number of parameters which must be optimized, the values obtained by Lympieriadis et al. [9] for σ , ε , λ , and S of CH_3 and CH_2 functional groups are applied. In addition, arithmetic relations fix the cross energy parameters (ε_{kl}), unlike diameters (σ_{kl}) and attractive range parameters (λ_{kl}) [8]. Also, the segment parameters of the cation head were optimized in our previous work [7]. Therefore, in this paper, the parameters of anion group are determined by optimization. Also, the site-site energy parameters (ε^{HB}) and cut-off distance parameters (r^c) need to be optimized. Twenty anion parameters and eight binary parameters between anions and cation head group are optimized by using the Differential Evolution (DE) [10] algorithm in MATLAB programming. The objective function that is minimized during the optimization step is given as follows:

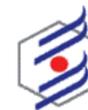
$$Obj. Func = \frac{1}{ND} \times \sqrt{\sum_{i=1}^{ND} \left(\frac{\rho_{L,i}^{Exp.} - \rho_{L,i}^{Calc.}}{\rho_{L,i}^{Exp.}} \right)^2} \quad (4)$$

Where ND is the number of experimental data points and $\rho_{L,i}^{Exp.}$ and $\rho_{L,i}^{Calc.}$ are experimental and calculated liquid densities, respectively.

In this work, first, the optimization was carried out for ILs of [emim][MeSO₃], [emim][MeSO₄], [emim][EtSO₄] and [emim][CF₃SO₃] using the available experimental data [11-13] and then by applying the obtained parameters, the accuracy of the model was checked for some IL systems not included in the optimization database.

Results and discussion

Table 1 shows the optimized individual group parameters for the SAFT- γ group contribution method. In this study, the dispersive energy parameter (ε) of the cation head and the anion groups were considered temperature-dependent according to Eq. (5). The optimized constants



of this equation are given in Table 2. Binary parameters between the cation head and the anions are shown in Table 3.

$$\frac{\epsilon}{k_B} = c_1 + c_2 T \quad (5)$$

Table 1- Optimized pure group parameters of the SAFT- γ equation of state

Groups	$\sigma(A^\circ m)$	λ	S	$\epsilon/k_B (K)$
CH ₃ [*]	3.8100	1.4130	0.6670	252.6010
CH ₂ [*]	4.0270	1.6610	0.3330	240.4820
[-imi] [#]	3.614372	1.250259	0.184091	Eq.(5)
[MeSO ₃]	6.583003	1.347813	0.685366	Eq. (5)
[MeSO ₄]	6.920209	1.326256	0.628394	Eq.(5)
[EtSO ₄]	6.791496	1.598666	0.671096	Eq.(5)
[CF ₃ SO ₃]	7.192268	1.365038	0.632250	Eq.(5)

* The pure group parameters of CH₃ and CH₂ are taken from Lymperiadis et al. [9].

[-imi] indicates the imidazolium cation head. Group parameters of [-imi] are taken from our previous publication [7]

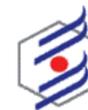
Table 2- The optimized constants of Eq. (5) for calculation of ϵ/k_B

Groups	c_1	c_2
[-imi]	-1945	9.8760
[MeSO ₃]	4571.883653	-5.520149
[MeSO ₄]	5522.112995	-7.015009
[EtSO ₄]	5639.601387	-8.467509
[CF ₃ SO ₃]	5229.471022	-7.415304

Table 3- Optimized binary parameters (ϵ^{HB} and r^c) between the cation head and the anion groups

Groups	$\epsilon^{HB}/k_B (K)$	$r^c (A^\circ m)$
[-imi]- [MeSO ₃]	2049.488941	3.126568
[-imi]- [MeSO ₄]	2152.013711	2.721497
[-imi]- [EtSO ₄]	2801.490570	2.632598
[-imi]- [CF ₃ SO ₃]	2472.816851	2.904673

Table 4 presents the average absolute relative deviation between experimental and calculated liquid densities (AARD% in L) of some ILs. To examine the predictive ability of model, some other imidazolium-based ILs with available experimental density data (including dimethylimidazolium methylsulfate [mmim][MeSO₄], 1-butyl-3-methylimidazolium methylsulfate [bmim][MeSO₄], 1-hexyl-3-methylimidazolium methylsulfate [hmim][MeSO₄], 1-butyl-3-methylimidazolium ethylsulfate [bmim][EtSO₄], 1-hexyl-3-methylimidazolium ethylsulfate [hmim][EtSO₄], 1-octyl-3-methylimidazolium methylsulfate [omim][EtSO₄] and 1-butyl-3-methylimidazolium trifluoromethanesulfonate [bmim][CF₃SO₃]) which had not been used in the optimization process were considered at some temperatures and pressures. The average absolute deviation between experimental and predicted density for these systems are also given in Table 4. According to this table, correlation errors in density are under 0.2% and the prediction errors are mostly under 2%. These results indicate the reliable predictive power of the model for the systems considered without the use of any adjustable parameters. Therefore, it can be concluded that the SAFT- γ group contribution method with the optimized



parameters in this study can predict with good certainty, the density of imidazolium-based ILs with different chain lengths of the cation within a range of temperatures between 293.15 and 393.15 K and at different pressures up to 35 or 60 MPa. Based on the results, it may also be expected that this equation will give relatively precise predictions even for systems for which no experimental data are available.

Table 4- AARD% in liquid density of ILs

IL	Temperature (K)	Pressure (MPa)	AARD %	No. ⁺	Reference
[emim][MeSO ₃]	293.15-393.15	0.1-60	0.1128*	54	Safarov et al. [12]
[emim][MeSO ₄]	293.15-393.15	0.1-35	0.0781*	60	Tome et al. [13]
[emim][EtSO ₄]	293.15-393.15	0.1-35	0.1563*	60	Tome et al. [13]
[emim][CF ₃ SO ₃]	293.15-393.15	0.1-35	0.1720*	65	Gardas et al. [11]
[bmim][CF ₃ SO ₃]	293.15-393.15	0.1-10	0.7330 [#]	42	Gardas et al. [14]
[mmim][MeSO ₄]	313.15-333.15	0.1-25	0.8960 [#]	34	Goldon et al. [15]
[bmim][MeSO ₄]	298.15-348.15	0.1	1.7978 [#]	9	Fernandez et al. [16]
[hmim][MeSO ₄]	298.15, 313.15	0.1	1.7382 [#]	2	Torrecilla et al. [17]
[bmim][EtSO ₄]	298.15, 313.15	0.1	0.7297 [#]	2	Torrecilla et al. [17]
[hmim][EtSO ₄]	298.15, 313.15	0.1	2.1423 [#]	2	Torrecilla et al. [17]
[omim][EtSO ₄]	298.15, 313.15	0.1	2.7813 [#]	2	Torrecilla et al. [17]

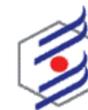
⁺ Number of data points, * Correlated by the SAFT- γ model, [#] Predicted by the SAFT- γ model

Conclusions

In this work, a group contribution approach was used to correlate and predict the density of IL systems based on the statistical associating fluid theory, SAFT- γ . In this model, the IL molecule was divided into several groups consisting of CH₃, CH₂, the cation head, and the anion. To account for the association between the cation head and the anion group, appropriate association sites were considered on these groups. Then, by fitting to experimental data, the SAFT- γ parameters of the imidazolium-based ionic liquids with [MeSO₃], [MeSO₄], [EtSO₄] and [CF₃SO₃] anions were optimized. Twenty anion group parameters and eight binary parameters between anions and cation head group were obtained, which can be added to the SAFT- γ group contribution data bank of Lympieriadis et al. [8, 9]. Moreover, predictive ability of model was examined by using the optimized group parameters to predict the liquid density of IL systems not included in the optimization database. The results showed good agreement with experimental data, with correlation and prediction errors in density respectively never exceeding 0.2% and 2.8%. So, it is expected that this equation will give relatively precise predictions, even for other systems within these homologous families for which no experimental data are available.

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