Thermodynamic modeling of CO₂ solubility in ionic liquid with heterosegmented statistical associating fluid theory

Xiaoyan Ji^{a,*}, Hertanto Adidharma^b

^a Division of Energy Engineering, Luleå University of Technology, 97187 Luleå, Sweden

^b Soft Materials Laboratory, Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 82071-3295, USA

ARTICLE INFO

Article history:

Received 14 October 2009

Received in revised form 16 February 2010

Accepted 19 February 2010

Available online 1 March 2010

Keywords:

Ionic liquid

Solubility

CO₂

SAFT

ABSTRACT

Heterosegmented statistical associating fluid theory is used to represent the CO₂ solubility in ionic liquids. As in our previous work, ionic liquid molecule is divided into several groups representing the alkyls, cation head, and anion. The cation of ionic liquid is modeled as a chain molecule that consists of one spherical segment representing the cation head and groups of segments of different types representing different substituents (alkyls). The anion of ionic liquid is modeled as a spherical segment of different type. To account for the electrostatic/polar interaction between the cation and anion, the spherical segments representing cation head and anion each have one association site, which can only cross associate. Carbon dioxide is modeled as a molecule with three association sites, two sites of type O and one site of type C, where sites of the same type do not associate with each other. The parameters of CO₂ are obtained from the fitting of the density and the saturation vapor pressure of CO₂. For the CO₂-ionic liquid systems, cross association between site of type C in CO₂ and another association site in anion is allowed to occur to account for the Lewis acid–base interaction. The parameters for cross association interactions and the binary interaction parameters used to adjust the dispersive interactions between unlike segments are obtained from the fitting of the available CO₂ solubility in ionic liquids. The model is found to well represent the CO₂ solubility in the imidazolium ionic liquids from 283 to 415 K and up to 200 bar.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids (ILs) are organic salts that are liquids at ambient temperature. Unlike other common liquids, ILs have negligible vapor pressure and a stable and wide liquid range of over 300 K. Their densities are greater than that of water. They are also good solvents for many organic and inorganic compounds. These fluids have been proposed as attractive alternatives to volatile organic compounds for green processes.

ILs have recently gained great attention in a variety of chemical processes. A potential application of ILs is in the gas and liquid separation processes. The non-volatility of ILs would not cause any contamination to the gas stream, and thus this feature gives ILs a big advantage over conventional solvents that are commonly used for absorbing gases. To select an effective IL for use as a gas separating agent, it is necessary to know the solubility of the gas in the IL.

The solubilities of gases in ILs have been measured by many researchers [1–20]. However, due to the vast number of ILs that can be tailored the number of experimental investigations needed

is less than adequate. Not to mention that the experimental measurement is expensive and time-consuming, and in some cases, dangerous. Therefore, it is highly desirable to have predictive methods for calculating gas solubilities in ILs.

Different models have been proposed for this purpose, such as irregular ionic lattice model [21], regular solution theory [22], and cubic equations of state (EOS) [5,23]. However, these models have some limitations. In the irregular ionic lattice model, the irregular ionic structure breaks down in the limiting case of pure CO₂. In the regular solution theory, a melting point is needed but many ILs do not have one. In the cubic EOS, the critical parameters needed are not available for ILs. In addition, the assumption of one single neutral molecule to represent IL containing large and charged cation and anion is unreasonable.

Recently, statistical associating fluid theory (SAFT) EOS [24,25] has been extended to describe the gas solubility in ILs [26,27], where an IL molecule was modeled as a neutral ion pair with one set of parameters. In the models of hetero-nuclear square-well chain fluids [28], group-contribution non-random lattice fluid equation of state [29], and group-contribution equation of state [30], the imidazolium ring-anion pair was modeled as one segment or functional group. As can be concluded from those works, all of these models utilize model parameters that are not completely transferable.

* Corresponding author. Tel.: +46 920 492837; fax: +46 920 491074.

E-mail address: xiaoyan.ji@ltu.se (X. Ji).

Fig. 1. Scheme of molecular models for [bmim][PF₆].

In our previous work [31], a heterosegmented SAFT has been used to describe the IL density. One set of transferable parameters was obtained to describe the densities of three important series of imidazolium-based ILs, i.e., [C_nmim][Tf₂N], [C_nmim][BF₄], and [C_nmim][PF₆]. The model was found to well represent the densities of these ionic liquids from 293.15 to 415 K and up to 650 bar, and well capture the effects of temperature, pressure, and alkyl types on density. In this paper, the model is extended to describing the CO₂ solubility in the related ILs.

2. Modeling

The heterosegmented SAFT is defined in terms of the dimensionless residual Helmholtz free energy as follows

$$\tilde{a}^{res} = \tilde{a}^{hs} + \tilde{a}^{disp} + \tilde{a}^{chain} + \tilde{a}^{assoc} \quad (1)$$

where the superscripts on the right side refer to terms accounting for the hard-sphere, dispersion, chain, and association interactions, respectively. The hard-sphere, dispersion, and chain terms have been described in detail elsewhere [32,33], while the association term for heterosegmented molecule has been proposed in our previous work [31]. For completeness, we summarize all terms in Appendix A.

CO₂ is a linear molecule with a large quadrupole moment, which allows CO₂ to associate. The CO₂ dimer is believed to have a slipped-parallel (offset face to face) geometry where the O atom of the first molecule is nestled against the C atom of the second molecule [34,35]. The T-shaped dimer (the first molecule perpendicular to the axis of the second molecule) is believed to be less stable (metastable). Thus, as in our previous work [36], CO₂ is modeled as a molecule with one type of segment having three association sites, two sites of type O and one site of type C, where sites of the same type do not associate with each other.

Generally, ionic liquid consists of a large organic cation and a weakly coordinating inorganic or organic anion. The large organic cation consists of a cation head and several alkyls. It has been stated that ionic liquid dissociates into cation and anion, and the strong interaction between the cation and anion makes the ionic liquid molecules take the form of ionic pairs [37,38]. Following our previous work [31], IL molecule is divided into several groups representing the alkyls, cation head, and anion. The cation of IL is modeled as a chain molecule that consists of one spherical segment representing the cation head and groups of segments of different types representing different substituents (alkyls). The anion of IL is modeled as a spherical segment of different type. To account for the electrostatic/polar interaction between the cation and anion, the spherical segments representing cation head and anion each have one association site, which can only cross associate with each other. For example, ionic liquid [bmim][PF₆], as shown in Fig. 1,

Table 1
Parameters for CO₂.

Parameter	Value	Parameter	Value
m	1.3513	λ	1.422
v^{00} (cc/mol)	11.137	ε^{CO}/k (K)	217.7834
u^0/k (K)	219.992	κ^{CO}	0.18817

consists of [bmim]⁺ (cation) and [PF₆][−] (anion). The cation consists of three groups with different types of segments representing butyl (A), methyl (B), and imidazolium cation head (C). The anion is assumed to be a single segment representing [PF₆][−] as a whole (D). The spherical segments representing cation head (C) and anion (D) each have one association site, which can only cross associate with each other. In our previous work [31], one set of transferable parameters has been obtained to describe the densities of three important series of imidazolium-based ILs, i.e., [C_nmim][Tf₂N], [C_nmim][BF₄], and [C_nmim][PF₆] from 293.15 to 415 K and up to 650 bar. These parameters are also summarized in Tables A3 (for the alkyls) and A4 (for the imidazolium cation head and the anions) of Appendix A, and will be used in this work.

For CO₂(1)–IL(2), evidence of a strong association between the CO₂ and anion of the IL was found [39]. Kazarian et al. [40] found that this association was probably the result of a Lewis acid–base interaction between CO₂ and the anions of ILs, where CO₂ acts as a Lewis acid and anions of the ILs act as Lewis bases. Therefore, we assign another type of association site in the anion of IL and allow cross association between this association site and site of type C in CO₂ to account for this Lewis acid–base interaction. Two parameters, i.e., ε_L and κ_L , are used to describe this cross association.

To capture the effect of temperature on the phase equilibria of CO₂–IL systems, a temperature-dependent binary interaction parameter $k_{\alpha\beta}$ is used to adjust the dispersive energy between the segment of CO₂ (α) and the segment of cation head or anion (β):

$$u_{\alpha\beta} = u_{\beta\alpha} = \sqrt{u_{\alpha}u_{\beta}}(1 - k_{\alpha\beta}) \quad (2)$$

$$k_{\alpha\beta} = c_1 + c_2T + c_3T^2 \quad (3)$$

To adjust the dispersive energy between the segment of CO₂ (α) and the segment of alkyl in the cation (β), temperature-independent binary interaction parameter $k_{\alpha\beta}$ is used:

$$k_{\alpha\beta} = c_1 \quad (4)$$

Since the available experimental data [41] reveals that the content of IL in the vapor phase is very low at the temperature and pressure of interest, in this work we assume that only CO₂ exists in the vapor phase.

3. Parameter fitting

3.1. CO₂

In our previous work [36], SAFT1 was used to describe the properties and phase equilibria of CO₂–H₂O system, and the parameters of pure CO₂ were fitted to its vapor pressure and saturated liquid density from 218 to 302 K [42]. In this work, the same experimental data are used for heterosegmented SAFT. The fitted parameters are listed in Table 1 and the average relative deviations (ARDs) for the vapor pressure and liquid density are 0.22% and 1.33%, respectively.

3.2. CO₂ + IL

The binary interaction parameters $k_{\text{CO}_2\text{-alkyl}}$, $k_{\text{CO}_2\text{-cation head}}$, and $k_{\text{CO}_2\text{-anion}}$ along with the cross association parameters ε_L and κ_L are fitted to the CO₂ solubility in ILs in a wide temperature and pressure range. The experimental data used in parameter fitting are

Table 2
Experimental CO₂ solubility data in imidazolium-based IL.

IL	Data at high pressures	Data at low pressures
[C ₂ mim][Tf ₂ N]	Schilderman et al. [4] Shin et al. [20]	Kim et al. [3]
[C ₄ mim][Tf ₂ N]	Lee and Outcalt [8] Aki et al. [13] Oh and Lee [19] Shin et al. [20]	Anthony et al. [14]
[C ₆ mim][Tf ₂ N]	Kumelan et al. [10] Aki et al. [13] Shin et al. [20]	Kim et al. [3] Shiflett and Yokozeki [15] Muldoon et al. [16]
[C ₈ mim][Tf ₂ N]	Aki et al. [13] Shin et al. [20]	
[C ₂ mim][BF ₄]		Kim et al. [3]
[C ₄ mim][BF ₄]	Kroon et al. [7] Aki et al. [13]	Shiflett and Yokozeki [5] Anthony et al. [14]
[C ₆ mim][BF ₄]	Costantini et al. [6]	Kim et al. [3]
[C ₈ mim][BF ₄]	Blanchard et al. [11] Gutkowski et al. [18]	
[C ₄ mim][PF ₆]	Shariati et al. [1] Liu et al. [2] Kumelan et al. [9] Aki et al. [13]	Kim et al. [3] Shiflett and Yokozeki [5] Anthony et al. [14]
[C ₆ mim][PF ₆]	Shariati and Peters [17]	Kim et al. [3]
[C ₈ mim][PF ₆]	Blanchard et al. [11]	

Table 3
Cross association parameters ε_L and κ_L between CO₂ and anion.

	ε_L	κ_L
C-Tf ₂ N	894.1751	0.057747
C-BF ₄	1298.5604	0.040840
C-PF ₆	1057.0701	0.190719

Table 4
Coefficients of Eqs. (3) and (4) for calculating $k_{\alpha\beta}$.

	c_1	$10^4 c_2$	$10^6 c_3$
CO ₂ -imi	0.4733	-5.73946	-1.25361
CO ₂ -Tf ₂ N	1.6140	-97.23875	15.94551
CO ₂ -BF ₄	0.0715	10.39087	-3.19146
CO ₂ -PF ₆	-0.5315	33.70713	-8.42553
CO ₂ -methyl	-0.0802	-	-
CO ₂ -ethyl	0.0061	-	-
CO ₂ -butyl	0.0166	-	-
CO ₂ -hexyl	0.0690	-	-
CO ₂ -octyl	0.0546	-	-

listed in Table 2 and the fitting results are listed in Tables 3 and 4, and the average absolute deviation in CO₂ solubility is 0.015. We find that Eq. (3) with the obtained coefficients yields segment energy that is reasonable at least from room temperature up to 415 K. Of course, beyond this temperature range, one should use Eq. (3) with care.

4. Comparison and discussion

The CO₂ solubility in ILs has been measured extensively and most of the experimental data are for solubility at high pressures. In the existing models [26–28], to represent the CO₂ solubility in ILs, the adjustable binary interaction parameter $k_{\alpha\beta}$ between CO₂ and another segment and cross association parameters were fitted to the experimental data at high pressures only. However, we find that the use of the experimental data throughout the whole pressure range is vital for obtaining a set of reasonable parameters, especially

Fig. 2. CO₂ solubility in [C₂mim][Tf₂N] at 363.15, 344.55, 324.15, and 293.15 K (from left to right). $\diamond$, experimental data [4]; $\circ$, experimental data [20]; —, calculated.

the cross association parameters ε_L and κ_L .

To show the representation of the model, with the parameters obtained, the calculated solubility using the model is compared with the available experimental data both at high and low pressures. In this work, we will focus on the CO₂ solubility in ILs at temperatures and pressures up to 423 K and 200 bar, respectively, because ILs have proven to be a promising solvent to separate CO₂ from flue gas or synthesis gas, in which the temperature is generally lower than 423 K and the pressure is lower than 200 bar.

4.1. Results at high pressures

The CO₂ solubility in [Tf₂N] series of ILs has been measured extensively at high pressures in a wide temperature range. Schilderman et al. [4] measured the CO₂ solubility in [C₂mim][Tf₂N] at temperatures from 313.15 to 363.15 K, and Shin et al. [20] measured the CO₂ solubility in the same IL at 293, 303, 324, 334, and 344 K. The comparison of the calculated CO₂ solubility in [C₂mim][Tf₂N] with those experimental data [4,20] at 293.15, 324.15, 344.55, and 363.15 K is shown in Fig. 2. The experimental data from these two sources are consistent and the calculated CO₂ solubility agrees well with the experimental data.

For the CO₂ solubility in [C₄mim][Tf₂N], Lee and Outcalt [8] measured at temperatures from 280 to 340 K, Aki et al. [13] measured at temperatures from 298 to 333 K, Oh and Lee [19] measured at temperatures from 297 to 344 K, and Shin et al. [20] measured at temperatures from 293 to 343 K. The comparison of the calculated solubility with the available experimental data at 280, 298, 313, and 344 K is shown in Fig. 3. At 313 K, the CO₂ solubility data from Aki et al. [13] (Δ) are lower than those from Oh and Lee [19] (∇) and Shin et al. [20] ($\circ$), and the calculated CO₂ solubility agrees well with the experimental data from Oh and Lee [19] and Shin et al. [20]. At 344.5 K, the calculated CO₂ solubility agrees well with experimental data from Oh and Lee [19] and Shin et al. [20] at high pressures, but at low pressures (<30 bar), the solubility data from both of these two sources are higher than the calculated results.

Kumelan et al. [10] measured the CO₂ solubility in [C₆mim][Tf₂N] at 293.15, 333.15, 373.2, and 413.2 K, and pressures up to 100 bar. For the same system, Aki et al. [13] measured at 298, 313, and 333 K, and pressures up to 120 bar, and Shin et al. [20] measured at temperatures from 298 to 343 K and pressures up to 200 bar. Fig. 4 shows the comparison of the calculated and the experimental data at 293.15, 334.35, 344.55, 373.2, and 413.2 K

Fig. 3. CO₂ solubility in [C₄mim][Tf₂N] at 344.5, 313, 298, and 280 K (from left to right). $\diamond$, experimental data [8]; Δ , experimental data [13]; ∇ , experimental data [19]; $\circ$, experimental data [20]; —, calculated.

Fig. 4. CO₂ solubility in [C₆mim][Tf₂N] at 413.2, 373.2, 344.55, 334.35, and 293.15 K (from left to right). $\diamond$, experimental data [10]; $\circ$, experimental data [13]; $\triangleright$, experimental data [20]; —, calculated.

with good agreement throughout the whole temperature and pressure range.

Aki et al. [13] measured the CO₂ solubility in [C₈mim][Tf₂N], at temperatures of 298.2, 313.3 and 333.3 K, and Shin et al. [20] measured the CO₂ solubility in the same IL at 300, 304, 314, 324, 334, and 344 K, and pressures up to 200 bar. The comparison of the calculated and experimental CO₂ solubility in [C₈mim][Tf₂N] at 298, 314, and 334 K is shown in Fig. 5. At temperatures less than or equal to 314 K, the experimental solubility data from Aki et al. [13] ($\diamond$) are higher than those from Shin et al. [20] ($\blacklozenge$), and the calculated solubility seems to agree with the average of the experimental data from these two sources.

The CO₂ solubility in [BF₄] series of ILs has been measured but the available experimental data are much less than those in [Tf₂N] series of ILs, and the experimental data of CO₂ solubility in [C₂mim][BF₄] at high pressures are not available. Kroon et al. [7] measured CO₂ solubility in [C₄mim][BF₄] at temperatures from 278 to 368 K. The comparison of the calculated solubility with the data from

Fig. 5. CO₂ solubility in [C₈mim][Tf₂N] at 334.35, 314.05, and 298 K (from left to right). $\blacklozenge$, experimental data [20]; $\diamond$, experimental data [13]; —, calculated.

Kroon et al. [7] at 278.5, 298.15, 323.15, 348.15, and 368.15 K is shown in Fig. 6(a) with good agreement up to 129 bar. Aki et al. [13] also measured the CO₂ solubility in [C₄mim][BF₄] at 298.2, 313.3, and 333.3 K, and the calculated solubility also agrees with this group of data, as shown in Fig. 6(b).

Costantini et al. [6] measured CO₂ solubility in [C₆mim][BF₄] at temperatures from 293 to 368 K. The comparison of the calculated solubility with the data from Costantini et al. [6] at 293.15, 333.15, and 368.15 K is shown in Fig. 7, and the calculated CO₂ solubility agrees well with the experimental data throughout the whole temperature and pressure range.

Blanchard et al. [11] measured CO₂ solubility in [C₈mim][BF₄] at temperatures of 313.15, 323.15, and 333.15 K, and Gutkowski et al. [18] measured CO₂ solubility in the same IL at temperatures from 308 to 363 K. It has been stated [13] that the CO₂ solubility in [C₄mim][PF₆] from Blanchard et al. [11] is not reliable, i.e., the experimental CO₂ solubility at high pressures is higher than the results from other sources. As shown in Fig. 8, the CO₂ solubility in [C₈mim][BF₄] from Blanchard et al. [11] is also higher than those from Gutkowski et al. [18]. Unfortunately, there are no other experimental data available for further verification. The calculated solubility in [C₈mim][BF₄] at 308.15, 333.15 and 363.15 K is compared with these two groups of data, as also shown in Fig. 8. The calculated solubility agrees with the experimental data at lower pressures, but there are some discrepancies at pressures higher than 60 bar, especially from the experimental data of Blanchard et al. [11]. At high pressure, the calculated solubility is higher than the experimental data from Gutkowski et al. [18] ($\diamond$) but lower than the experimental data from Blanchard et al. [11] ($\blacklozenge$).

CO₂ solubility in [PF₆] series of ILs has been measured experimentally but most of the available experimental data are for CO₂ solubility in [C₄mim][PF₆]. Shariati et al. [1] measured CO₂ solubility in [C₄mim][PF₆] at temperatures from 313 to 363 K, Liu et al. [2] measured at 313.15, 323.15, and 333.15 K, Kumelan et al. [9] measured at 293.55, 313.75, 334.05, 354.35, 374.7, and 395.05 K, and Aki et al. [13] measured at 298.2, 313.3, and 333.3 K. In addition, Blanchard et al. [11] also measured the CO₂ solubility in [C₄mim][PF₆], but it was declared that the experimental data were not reliable [13], and this group of data is excluded in the parameter fitting and not compared.

The comparison results at 293, 313, 333, 354, and 395 K are shown in Fig. 9. At 293 K, the experimental data are from Shariati et al. [1] ($\diamond$) and Liu et al. [2] (+). The experimental data are consis-

Fig. 6. CO₂ solubility in [C₄mim][BF₄]. $\diamond$, experimental data, (a) from Kroon et al. [7] at 368.15, 348.15, 323.15, 298.15, 278.5 K (from left to right); (b) from Aki et al. [13] at 333.3, 313.3, 298.2 K (from left to right); —, calculated.

Fig. 7. CO₂ solubility in [C₆mim][BF₄] at 368.15, 333.15, 293.15 K (from left to right). $\diamond$, experimental data [6]; —, calculated.

Fig. 8. CO₂ solubility in [C₈mim][BF₄] at 363.15, 333.15, and 308.15 K (from left to right). $\diamond$, experimental data [18]; $\blacklozenge$, experimental data [11]; —, calculated.

Fig. 9. CO₂ solubility in [C₄mim][PF₆] at 395.05, 354.35, 333.3, 313.3, and 293.55 K (from left to right). $\diamond$, experimental data [1]; +, experimental data [2]; Δ , experimental data [9]; ∇ , experimental data [13]; —, calculated.

tent and the calculated solubility agrees well with the experimental data. At 313 K, the experimental data are from four sources, and the solubility measured by Kumelan et al. [9] (Δ) and Aki et al. [13] (∇) are higher than those by Shariati et al. [1] ($\diamond$) and Liu et al. [2] (+), especially at high pressures. The solubility calculated with the model is lower than the experimental solubility of Kumelan et al. [9] (Δ) and Aki et al. [13] (∇) but higher than the experimental solubility of Shariati et al. [1] ($\diamond$) and Liu et al. [2] (+). At 333 K, the experimental solubility from Kumelan et al. [9] (Δ) is higher than those from Shariati et al. [1], Liu et al. [2], and Aki et al. [13], and the calculated CO₂ solubility agrees well with the experimental data of Shariati et al. [1], Liu et al. [2] and Aki et al. [13]. At 354 and 395 K, the experimental data of CO₂ solubility from different sources are consistent and the CO₂ solubility calculated with the model agrees with the experimental results.

Shariati and Peters [17] measured CO₂ solubility in [C₆mim][PF₆] at temperatures from 298 to 363 K. The comparison with the calculated solubility at 303.35, 333.3, and 363.4 K is shown in Fig. 10. Throughout the whole temperature and pressure range, the calculated solubility agrees with the experimental results.

Fig. 10. CO₂ solubility in [C₆mim][PF₆] at 363.4, 333.3, and 303.35 K (from left to right). $\diamond$, experimental data [17]; —, calculated.

Blanchard et al. [11] measured the CO₂ solubility in [C₈mim][PF₆] at 313.15, 323.15, and 333.15 K. We find that the experimental CO₂ solubility is higher than the calculated solubility at high pressures, which is consistent with the case for [C₄mim][PF₆] and [C₈mim][BF₄]. Shariati and Peters [43] measured the CO₂ solubility in [C₂mim][PF₆] experimentally from 313 to 353 K. However, the calculated CO₂ solubility is always lower than the experimental results and the inclusion of these experimental data in the parameter fitting does not improve the results of the model. Since there are no other experimental data available to verify either the model or the experimental data, this group of data is excluded in the parameter fitting.

4.2. Results at pressures lower than 20 bar

The CO₂ solubility in imidazolium-based ILs has also been determined experimentally at pressures lower than 20 bar by Kim et al. [3], Shiflett and Yokozeki [5], Anthony et al. [12], Anthony et al.

Fig. 11. CO₂ solubility in ILs at 298.15 K. $\diamond$, experimental data in [C₂mim][Tf₂N]; Δ , experimental data in [C₂mim][BF₄]; $\circ$, experimental data in [C₆mim][BF₄]; ∇ , experimental data in [C₆mim][PF₆]; —, calculated.

Fig. 12. CO₂ solubility in [C₄mim][Tf₂N] at 323.15, 298.15, and 283.15 K (from left to right). $\diamond$, experimental data [14]; —, calculated.

[14], Shiflett and Yokozeki [15], and Muldoon et al. [16]. It should be noted that the CO₂ solubility in [C₄mim][PF₆] measured by Anthony et al. [12] was repeated by Anthony et al. [14] with almost the same results, and only the data from Anthony et al. [14] were used for comparison in this section.

Fig. 11 shows the CO₂ solubility in [C₂mim][Tf₂N], [C₂mim][BF₄], [C₆mim][BF₄], and [C₆mim][PF₆] at 298.15 K. The calculated solubility agrees with the experimental data of Kim et al. [3]. This figure also shows the effects of anion and the length of alkyl on the CO₂ solubility, and the model captures the effects.

Anthony et al. [14] measured the CO₂ solubility in [C₄mim][Tf₂N] at 283.15, 298.15, and 323.15 K. The comparison of the calculated solubility with the experimental results is shown in Fig. 12. The comparison shows that the calculated solubility is higher than the experimental data. However, as shown in Fig. 3, for the same system, at 298.15 K, the comparison with the experimental data of different sources up to high pressures shows that the calculated solubility agrees well with the experimental data, even at pressures lower than 20 bar.

Fig. 13. CO₂ solubility in [C₆mim][Tf₂N] at 348, 323, 298, and 283 K (from left to right). $\diamond$, experimental data [3]; $\circ$, experimental data [15]; ∇ , experimental data [16]; —, calculated.

Fig. 14. CO₂ solubility in [C₄mim][BF₄] at 348, 323, 298, and 283 K (from left to right). ◇, experimental data [14]; ○, experimental data [5]; —, calculated.

The CO₂ solubility in [C₆mim][Tf₂N] at 298.15 K was measured by Kim et al. [3], by Shiflett et al. [15] at 283, 298, 323, and 348 K, and by Muldoon et al. [16] at 283, 298, and 323 K. The calculated solubility and all of these experimental data are shown in Fig. 13, which demonstrates the good representation of the model.

The CO₂ solubility in [C₄mim][BF₄] was measured by Shiflett and Yokozeki [5], and Anthony et al. [14] at temperatures of 283, 298, 323, and 348 K. The comparison of the calculated and experimental CO₂ solubility shown in Fig. 14 reveals again the good representation of the model.

The solubility of [C₄min][PF₆] has been measured by Kim et al. [3] at 298.15 K, Shiflett and Yokozeki [5] at 283, 298, 323, and 348 K, and Anthony et al. [14] at 283, 298, and 323 K. The comparison of the calculated solubility with the available experimental data is shown in Fig. 15, the available experimental data from different sources are consistent, and the calculated solubility agrees well with the available experimental data.

Fig. 15. CO₂ solubility in [C₄min][PF₆] at 348, 323, 298, and 283 (from left to right). ◇, experimental data [3]; ○, experimental data [5]; ▷, experimental data [14]; —, calculated.

5. Conclusion

The CO₂ solubility in ILs is represented with heterosegmented SAFT, in which the cation of IL is modeled as a chain molecule that consists of one spherical segment representing the cation head and groups of segments of different types representing different substituents (alkyls) and the anion of IL is modeled as a spherical segment of different type. The spherical segments representing cation head and anion each have one association site and they can only cross associate with each other. Carbon dioxide is modeled as a molecule with three association sites, i.e., two sites of type O and one site of type C, where the association is only between two sites of different type.

For the CO₂-IL systems, we assign another type of association site in the anion of IL and allow cross association between this association site and site of type C in CO₂ to account for the Lewis acid–base interaction. A temperature-dependent binary interaction parameter is used to adjust the dispersive energy between the segment of CO₂ and the segment of cation head or anion, and a temperature-independent binary interaction parameter is used to adjust the dispersive energy between the segment of CO₂ and the segment of alkyl in the cation.

The parameters of CO₂ are obtained from the fitting of the density and saturation vapor pressure of CO₂. The parameters for cross association interactions and the binary interaction parameters used to adjust the dispersive interactions between unlike segments are obtained from the fitting of the available CO₂ solubility in ionic liquids. The model is found to well represent the CO₂ solubility in the imidazolium ILs at temperatures from 283 to 415 K and pressures up to 200 bar and well capture the effects of anion and the length of alkyl on the CO₂ solubility.

Acknowledgments

X. Ji thanks Prof. Marcus Öhman for his valuable suggestions and assistance on this work, and thanks the Swedish Research Council and Luleå University of Technology for the financial support.

Appendix A.

A.1. Hard-sphere term $\tilde{a}^{hs}$

The calculation of $\tilde{a}^{hs}$ in heterosegmented SAFT is the same as that in homosegmented SAFT [44], that is

$$\tilde{a}^{hs} = \frac{6}{\pi \rho_m N_{Av}} \left[\frac{(\zeta_2)^2 + 3\zeta_1\zeta_2\zeta_3 - 3\zeta_1\zeta_2(\zeta_3)^2}{\zeta_3(1-\zeta_3)^2} - \zeta_0 - \frac{(\zeta_2)^3}{(\zeta_3)^2} \ln(1-\zeta_3) \right] \quad (A1)$$

where ρ_m is the molar density and

$$\zeta_k = \frac{\pi}{6} N_{Av} \rho_m \sum_i X_i m_i \sum_{\alpha} X_{\alpha} (\sigma_{\alpha})^k \quad (A2)$$

where N_{Av} is the Avogadro number, σ_{α} is the diameter of segment α , and X_{α} is the segment fraction defined as

$$X_{\alpha} = \frac{\text{number of moles of segments } \alpha}{\text{number of moles of all segments}} \quad (A3)$$

We notice that Eq. (A2) in reference [30] was incorrectly typed and should be replaced by Eq. (A2) in this work. All of the calculation results presented in reference [30] were correct.

A.2. Dispersion term $\tilde{a}^{disp}$

The dispersion term is calculated from

$$\tilde{a}^{disp} = \frac{1}{k_B T} a_1^{disp} + \frac{1}{(k_B T)^2} a_2^{disp} + \tilde{a}^t \quad (A4)$$

Table A1The universal coefficients c_{ij} .

i/j	1	2	3	4	5	6
1	−0.010 348 412 43	5.012 940 585	−46.069 085 85	271.226 970 3	−645.515 037 9	605.117 779 9
2	0.034 371 512 70	−45.703 391 47	391.844 391 2	−2296.265 301	5430.859 895	−5087.008 598
3	0.046 688 853 54	161.837 063 5	−1267.473 745	7368.693 459	−17,288.510 83	16,217.305 15
4	−0.286 193 974 80	−276.070 506 3	1903.020 452	−10,912.042 77	25,296.495 02	−23,885.063 01
5	0.679 398 501 40	224.732 718 6	−1256.163 441	7025.297 671	−15,911.317 81	15,336.690 52
6	−1.380 935 033	−69.715 059 55	242.462 559 3	−1282.236 283	2690.356 186	−2828.288 422

where k_B is the Boltzmann constant, T is the temperature in Kelvin, and

$$a_1^{disp} = \sum_{\alpha} \sum_{\beta} X_{\alpha} X_{\beta} a_{1,\alpha\beta}^{disp} \quad (A5)$$

where α and β are the segment types, and $a_{1,\alpha\beta}^{disp}$ is the first-order binary term for α – β segment interaction given by

$$a_{1,\alpha\beta}^{disp} = -4 \left(\frac{\pi}{6} \sigma_{\alpha\beta}^3 N_{Av} \rho_m \right) u_{\alpha\beta} (\lambda_{\alpha\beta}^3 - 1) g_{\alpha\beta}^{hs} (\sigma_{\alpha\beta}, \zeta_{3,eff}) \quad (A6)$$

In Eq. (A6), $\sigma_{\alpha\beta}$ is the distance between centers of segment α and β at contact, $u_{\alpha\beta}$ is the well depth of square-well potential for the α – β interaction, and $\lambda_{\alpha\beta}$ is the reduced range of the potential well for the α – β interaction. The combining rules used for $\sigma_{\alpha\beta}$ and $u_{\alpha\beta}$ are,

$$\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_{\alpha} + \sigma_{\beta}) \quad (A7)$$

$$u_{\alpha\beta} = u_{\beta\alpha} = \sqrt{u_{\alpha} u_{\beta}} (1 - k_{\alpha\beta}) \quad (A8)$$

where u_{α} is the segment energy of segment α and $k_{\alpha\beta}$ is the binary interaction parameter. A simple arithmetic-mean combining rule is used for $\lambda_{\alpha\beta}$, analogous to that for the segment diameters:

$$\lambda_{\alpha\beta} = \frac{1}{2}(\lambda_{\alpha} + \lambda_{\beta}) \quad (A9)$$

where λ_{α} is the reduced range of the potential well of segment α .

The radial distribution function for a mixture of hard spheres is calculated using Carnahan-Starling's equation but evaluated at the effective reduced variable $\zeta_{k,eff}$,

$$g_{\alpha\beta}^{hs}(\sigma_{\alpha\beta}, \zeta_{3,eff}) = \frac{1}{1 - \zeta_{3,eff}} + \frac{3\sigma_{\alpha}\sigma_{\beta}}{\sigma_{\alpha} + \sigma_{\beta}} \frac{\zeta_{2,eff}}{(1 - \zeta_{3,eff})^2} + 2 \left(\frac{\sigma_{\alpha}\sigma_{\beta}}{\sigma_{\alpha} + \sigma_{\beta}} \right)^2 \frac{(\zeta_{2,eff})^2}{(1 - \zeta_{3,eff})^2} \quad (A10)$$

In the range of $1.0 < \lambda_{\alpha\beta} \leq 2.5$, the effective reduced variable $\zeta_{3,eff}$ is approximated from

$$\zeta_{3,eff}(\lambda_{\alpha\beta}, \zeta_3) = \zeta_3 [1 + \delta(\lambda_{\alpha\beta}, \zeta_3)] \quad (A11)$$

where

$$\delta(\lambda_{\alpha\beta}, \zeta_3) = \lambda_{\alpha\beta}^{5.397} (\lambda_{\alpha\beta} - 1) (1 - 0.59\zeta_3) \sum_{i=1}^6 \sum_{j=1}^6 c_{ij} \frac{\zeta_3^{i-1}}{\lambda_{\alpha\beta}^{j-1}} \quad (A12)$$

and c_{ij} 's are universal constants listed in Table A1.

In Eq. (A10), the effective reduced variable $\zeta_{2,eff}$ is calculated from

$$\zeta_{2,eff} = \frac{\zeta_2}{\zeta_3} \zeta_{3,eff} \quad (A13)$$

The term a_2^{disp} in Eq. (A4) has the same form as the term a_1^{disp} ,

$$a_2^{disp} = \sum_{\alpha} \sum_{\beta} X_{\alpha} X_{\beta} a_{2,\alpha\beta}^{disp} \quad (A14)$$

Table A2The universal coefficients D_{mn} .

n/m	2	3	4	5
1	−2.420747	−4.151326	2.501130	−0.462574
2	9.955897	−1.520369	0	0

Table A3Parameters v^{oo} , u/k , and λ for alkyis.

n	MW (g/mol)	v^{oo} (cc/mol)	u/k (K)	λ
1	15.035	16.9740	194.6721	1.5628
2	29.062	19.7362	227.0978	1.5666
3	43.088	21.1998	238.8779	1.5846
4	57.115	21.8387	247.2764	1.5897
5	71.142	22.4333	253.2574	1.5897
6	85.169	22.8280	256.9062	1.5910
7	99.196	23.1253	259.1726	1.5926
8	113.222	23.4905	262.1160	1.5908
9	127.249	23.4833	267.4389	1.5832
11	155.303	23.9364	271.5238	1.5802
13	183.356	24.1598	271.7395	1.5829
15	211.410	24.1988	271.0103	1.5872
19	267.517	24.4288	273.4217	1.5865

where $a_{2,\alpha\beta}^{disp}$ is related to $a_{1,\alpha\beta}^{disp}$ as follows:

$$a_{2,\alpha\beta}^{disp} = \frac{1}{2} u_{\alpha\beta} \rho_m \frac{\partial a_{1,\alpha\beta}^{disp}}{\partial \rho_m} \left(\frac{\zeta_0(1 - \zeta_3)^4}{\zeta_0(1 - \zeta_3)^2 + 6\zeta_1\zeta_2(1 - \zeta_3) + 9\zeta_3^2} \right) \quad (A15)$$

The term $\tilde{a}_t$ in Eq. (A4) is calculated from

$$\tilde{a}_t = \sum_{m=2}^5 \sum_{n=1}^2 D_{mn} \left(\frac{u}{kT} \right)^m \left(\frac{\zeta_3}{\tau} \right)^n \quad (A16)$$

where D_{mn} 's are universal constants listed in Table A2, τ is the close-packed reduced density ($=2^{1/2} \pi/6$), and u/kT is evaluated in the spirit of the van der Waals one fluid theory (Tables A3 and A4)

$$\frac{u}{kT} = \frac{\sum_{\alpha} \sum_{\beta} X_{\alpha} X_{\beta} \left(\frac{u_{\alpha\beta}}{kT} \right) v_{\alpha\beta}}{\sum_{\alpha} \sum_{\beta} X_{\alpha} X_{\beta} v_{\alpha\beta}} \quad (A17)$$

where

$$v_{\alpha\beta} = \left[\frac{(v_{\alpha})^{1/3} + (v_{\beta})^{1/3}}{2} \right]^3 \quad (A18)$$

The molar volume of segment α (v_{α}) is related to the segment diameter as follows:

$$v_{\alpha} = \frac{\pi}{6\tau} \sigma_{\alpha}^3 N_{Av} \quad (A19)$$

A.3. Chain term $\tilde{a}^{chain}$

The chain term is calculated by [33]

$$\tilde{a}^{chain} = - \sum_i X_i (m_i - 1) [\ln \tilde{g}_i^{SW}(\sigma_{\alpha\beta}) - \ln \tilde{g}_{0,i}^{SW}(\sigma_{\alpha\beta})] \quad (A20)$$

Table A4Parameters for imidazolium cation head (imi⁺), Tf₂N⁻, BF₄⁻, and PF₆⁻.

	imi ⁺	Tf ₂ N ⁻	BF ₄ ⁻	PF ₆ ⁻
ν^{oo} (cm ³ /mol)	22.1794	78.7377	22.7970	34.9781
λ	2.3089	1.6373	1.1014	1.1071
n_B	1.2922	0	0	0
c_1^a (K)	1 007.7533	1 048.7711	352.2533	-344.5960
c_2^a	-8.595206	-1.882762	-0.768297	4.477235
c_3^a (K ⁻¹)	0.0260940286	-	-	-
ε (K)	1 633.7442	1 788.8889	1 208.1711	8 873.4790
$10^4\kappa$	2.060446	2.423795	5.203447	52.882628

^a These constants are used to calculate the temperature-dependent segment energy of cation head and anion.

and

$$\ln \tilde{g}_i^{\text{SW}}(\sigma_{\alpha\beta}) = \sum_{\beta \geq \alpha} B_{\alpha\beta,i} \ln g_{\alpha\beta}^{\text{SW}}(\sigma_{\alpha\beta}) \quad (\text{A21})$$

where X_i is the mole fraction of component i , m_i is the number of segment of component i , $B_{\alpha\beta,i}$ is the bond fraction of type $\alpha\beta$ in component i and $g_{\alpha\beta}^{\text{SW}}(\sigma_{\alpha\beta})$ is the square-well radial distribution function calculated at contact, and $\tilde{g}_0^{\text{SW}}$ is $\tilde{g}^{\text{SW}}$ evaluated at zero density. The square-well radial distribution is determined using Barker-Henderson's perturbation theory of the first order [45].

A.4. Association term $\tilde{a}^{\text{assoc}}$

The association term is calculated by

$$\tilde{a}^{\text{assoc}} = \sum_i X_i \sum_{\alpha} \left[\sum_{A_{\alpha i}} \left(\ln X^{A_{\alpha i}} - \frac{X^{A_{\alpha i}}}{2} \right) + \frac{n(\Gamma_{\alpha i})}{2} \right] \quad (\text{A22})$$

where X_i is the mol fraction of component i , $n(\Gamma_{\alpha i})$ is the number of association sites on segment α in molecule i , and $X^{A_{\alpha i}}$ is the mole fraction of molecule i not bonded at side A of segment α calculated from:

$$X^{A_{\alpha i}} = \frac{1}{1 + \rho_n \sum_j X_j \sum_{\beta} \sum_{B_{\beta j}} X^{B_{\beta j}} \Delta^{A_{\alpha i} B_{\beta j}}} \quad (\text{A23})$$

where ρ_n is the number density and $\Delta^{A_{\alpha i} B_{\beta j}}$ is the association given by

$$\Delta^{A_{\alpha i} B_{\beta j}} = F^{A_{\alpha i} B_{\beta j}} e^{\alpha(\rho)(u_{\alpha\beta}/kT)} g_{\alpha\beta}^{\text{hs}}(\sigma_{\alpha\beta}) (\sigma_{\alpha\beta}^3 \kappa^{A_{\alpha i} B_{\beta j}}) \quad (\text{A24})$$

where

$$F^{A_{\alpha i} B_{\beta j}} = \exp \left(\frac{\varepsilon^{A_{\alpha i} B_{\beta j}}}{kT} \right) - 1 \quad (\text{A25})$$

and

$$\alpha(\rho) = 1 + 0.1044\rho^* - 2.8469(\rho^*)^2 + 2.3787(\rho^*)^3 \quad (\text{A26})$$

where ρ^* is the reduced density calculated from

$$\rho^* = \frac{6}{\pi} \zeta_0 \sum_{\alpha} \sum_{\beta} X_{\alpha} X_{\beta} \sigma_{\alpha\beta}^3 \quad (\text{A27})$$

The pair distribution function in Eq. (A24) is given by the Carnahan-Starling equation for a mixture of hard spheres. The Lorentz and Berthelot combining rules are used for the size and

energy parameters, i.e.

$$\begin{cases} \sigma_{\alpha\beta} = \frac{\sigma_{\alpha} + \sigma_{\beta}}{2} \\ \sigma_{\alpha} = \left(\frac{\sqrt{2} \nu^{\text{oo}}}{N_{\text{Av}}} \right)^{1/3} \\ \varepsilon^{A_{\alpha i} B_{\beta j}} = \sqrt{\varepsilon^{A_{\alpha i}} \varepsilon^{B_{\beta j}}} \\ \kappa^{A_{\alpha i} B_{\beta j}} = \frac{1}{\sigma_{\alpha\beta}^3} \left[\frac{(\sigma_{\alpha}^3 \cdot \kappa^{A_{\alpha i}})^{1/3} + (\sigma_{\beta}^3 \cdot \kappa^{B_{\beta j}})^{1/3}}{2} \right]^3 \end{cases} \quad (\text{A28})$$

A.5. Parameters for [C_nmim][Tf₂N], [C_nmim][BF₄], and [C_nmim][PF₆]

$$m = \frac{n+1}{3} \quad (\text{A29})$$

$$n_B = \frac{2n-1}{6} \quad (\text{A30})$$

References

- [1] A. Shariati, K. Gutkowski, C.J. Peters, AIChE J. 51 (2005) 1532–1540.
- [2] Z.M. Liu, W.Z. Wu, B.X. Han, Z.X. Dong, G.Y. Zhao, J.Q. Wang, T. Jiang, G.Y. Yang, Chem. Eur. J. 9 (2003) 3897–3903.
- [3] Y.S. Kim, W.Y. Choi, J.H. Jang, K.P. Yoo, C.S. Lee, Fluid Phase Equilib. 228 (2005) 439–445.
- [4] A.M. Schilderman, S. Raeissi, C.J. Peters, Fluid Phase Equilib. 260 (2007) 19–22.
- [5] M.B. Shiflett, A. Yokozeki, Ind. Eng. Chem. Res. 44 (2005) 4453–4464.
- [6] M. Costantini, V.A. Toussaint, A. Shariati, C.J. Peters, I. Kikic, J. Chem. Eng. Data 50 (2005) 52–55.
- [7] M.C. Kroon, A. Shariati, M. Costantini, J. Van Spronsen, G.J. Witkamp, R.A. Sheldon, C.J. Peters, J. Chem. Eng. Data 50 (2005) 173–176.
- [8] B.C. Lee, S.L. Outcalt, J. Chem. Eng. Data 51 (2006) 892–897.
- [9] J. Kumelan, A.P.S. Kamps, D. Tuma, G. Maurer, J. Chem. Eng. Data 51 (2006) 1802–1807.
- [10] J. Kumelan, I.P.S. Kamps, D. Tuma, G. Maurer, J. Chem. Thermodyn. 38 (2006) 1396–1401.
- [11] L.A. Blanchard, Z.Y. Gu, J.F. Brennecke, J. Phys. Chem. B 105 (2001) 2437–2444.
- [12] J.L. Anthony, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 106 (2002) 7315–7320.
- [13] S. Aki, B.R. Mellein, E.M. Saurer, J.F. Brennecke, J. Phys. Chem. B 108 (2004) 20355–20365.
- [14] J.L. Anthony, J.L. Anderson, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 109 (2005) 6366–6374.
- [15] M.B. Shiflett, A. Yokozeki, J. Phys. Chem. B 111 (2007) 2070–2074.
- [16] M.J. Muldoon, S. Aki, J.L. Anderson, J.K. Dixon, J.F. Brennecke, J. Phys. Chem. B 111 (2007) 9001–9009.
- [17] A. Shariati, C.J. Peters, J. Supercrit. Fluids 30 (2004) 139–144.
- [18] K.I. Gutkowski, A. Shariati, C.J. Peters, J. Supercrit. Fluids 39 (2006) 187–191.
- [19] D.J. Oh, B.C. Lee, Kor. J. Chem. Eng. 23 (2006) 800–805.
- [20] E.K. Shin, B.C. Lee, J.S. Lim, J. Supercrit. Fluids 45 (2008) 282–292.
- [21] M.R. Ally, J. Braunstein, R.E. Baltus, S. Dai, D.W. Depaoli, J.M. Simonson, Ind. Eng. Chem. Res. 43 (2004) 1296–1301.
- [22] P. Scovazzo, D. Camper, J. Kieft, J. Poshusta, C. Koval, R. Noble, Ind. Eng. Chem. Res. 43 (2004) 6855–6860.
- [23] A. Shariati, C.J. Peters, J. Supercrit. Fluids 25 (2003) 109–117.
- [24] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, Ind. Eng. Chem. Res. 29 (1990) 1709–1721.
- [25] S.H. Huang, M. Radosz, Ind. Eng. Chem. Res. 29 (1990) 2284–2294.
- [26] E.K. Karakatsani, L.G. Economou, M.C. Kroon, C.J. Peters, G.J. Witkamp, J. Phys. Chem. C 111 (2007) 15487–15492.
- [27] J. Andreu, L. Vega, J. Phys. Chem. C 111 (2007) 16028–16034.

- [28] T.F. Wang, C.J. Peng, H.L. Liu, Y. Hu, J.W. Jiang, *Ind. Eng. Chem. Res.* 46 (2007) 4323–4329.
- [29] Y.S. Kim, J.H. Jang, B.D. Lim, J.W. Kang, C.S. Lee, *Fluid Phase Equilib.* 256 (2007) 70–74.
- [30] B. Breure, S.B. Bottini, G.J. Witkamp, C.J. Peters, *J. Phys. Chem. B* 111 (2007) 14265–14270.
- [31] X. Ji, H. Adidharma, *Chem. Eng. Sci.* 64 (2009) 1985–1992.
- [32] X.Y. Ji, H. Adidharma, *Ind. Eng. Chem. Res.* 46 (2007) 4667–4677.
- [33] H. Adidharma, M. Radosz, *Fluid Phase Equilib.* 158 (1999) 165–174.
- [34] G. Steinebrunner, A.J. Dyson, B. Kirchner, H. Huber, *J. Chem. Phys.* 109 (1998) 3153–3160.
- [35] J. Kolafa, I. Nezbeda, M. Lisal, *Mol. Phys.* 99 (2001) 1751–1764.
- [36] X.Y. Ji, S.P. Tan, H. Adidharma, M. Radosz, *Ind. Eng. Chem. Res.* 44 (2005) 8419–8427.
- [37] Z. Meng, A. Dölle, W.R. Carper, *J. Mol. Struct. (Theochem.)* 585 (2002) 119–128.
- [38] J.H. Antony, D. Mertens, T. Breitenstein, A. Dölle, P. Wasserscheid, W.R. Carper, *Pure Appl. Chem.* 76 (2004) 255–261.
- [39] C. Cadena, J.L. Anthony, J.K. Shah, T.I. Morrow, J.F. Brennecke, E.J. Maginn, *J. Am. Chem. Soc.* 126 (2004) 5300–5308.
- [40] S.G. Kazarian, B.J. Briscoe, T. Welton, *Chem. Comm.* (2000) 2047–2048.
- [41] P. Wasserscheid, *Nature* 439 (2006) 797–1797.
- [42] E.W. Lemmon, M.O. McLinden, D.G. Friend, Thermophysical properties of fluid systems in NIST Chemistry WebBook, in: NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, March 2003 (<http://webbook.nist.gov>).
- [43] A. Shariati, C.J. Peters, *J. Supercrit. Fluids* 29 (2004) 43–48.
- [44] H. Adidharma, M. Radosz, *Ind. Eng. Chem. Res.* 37 (1998) 4453–4462.
- [45] A. Gilvillegas, A. Galindo, P. Whitehead, S. Mills, G. Jackson, A. Burgess, *J. Chem. Phys.* 106 (1997) 4168–4186.