Modeling imidazolium-based ionic liquids with ePC-SAFT. Part II. Application to H₂S and synthesis-gas components

Xiaoyan Ji^{a,*}, Christoph Held^{b,**}, Gabriele Sadowski^b

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

^b Department for Biochemical and Chemical Engineering, TU Dortmund, Dortmund, Germany

ARTICLE INFO

Article history:

Received 6 August 2013

Received in revised form 5 November 2013

Accepted 11 November 2013

Available online 20 November 2013

Keywords:

PC-SAFT

Gas solubility

Ionic liquid

Synthesis gas

H₂S

ABSTRACT

ePC-SAFT was used to model the gas solubility in ionic liquids (ILs). The gases under consideration were CO, H₂, H₂S and O₂, and the imidazolium-based ILs studied were [C_nmim][Tf₂N], [C_nmim][PF₆] and [C_nmim][BF₄] (*n* = 2, 4, 6 and 8). For the ePC-SAFT modeling, each IL was considered to be completely dissociated into a cation and an anion. Each ion was modeled as a non-spherical species exerting repulsive, dispersive and Coulomb forces. CO, H₂ and O₂ were modeled as non-spherical molecules exerting repulsive and dispersive forces, and H₂S was modeled as a non-spherical, associating molecule. ePC-SAFT reasonably predicts the gas solubility in the considered gas/IL mixtures. In order to describe the experimental gas solubilities quantitatively in a broad temperature and pressure range, one ion-specific binary interaction parameter between the IL-anion and the gas was applied, which was allowed to depend linearly on temperature.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

CO₂ separation plays an important role in CO₂ emission mitigation, bio-fuel production via biomass gasification as well as in biogas upgrading. For example, CO₂ needs to be removed from synthesis gas (CO and H₂ with impurities of CH₄ and O₂) after biomass gasification in order to get valuable products and to improve the efficiency of the subsequent processes [1]. Biogas upgrading is a process of CO₂ removal from the biogas CH₄ with H₂S being the main gaseous impurity [2].

However, the CO₂ separation in general consumes a lot of energy, and exploring low-cost CO₂-separation technologies is still a hot research topic. Recent research reveals that ionic liquids (ILs) are promising liquid absorbents for CO₂ separation. This is mainly due to the extremely low vapor pressure of pure ILs leading to low energy requirements for regeneration steps. In addition, the properties of ILs can be “tailored” by different combinations of cation and anion, and then it is feasible to design a task-specific IL for CO₂ separation purposes [3,4].

The investigation of IL-based CO₂ separation technologies requires knowledge of gas solubilities (CO₂, CH₄, H₂, CO, O₂ and H₂S) in ILs as well as understanding the dependence of these

solubilities on microscopic structures (IL-anion and IL-cation including the length of the alkyl substituents). In addition, the removal of H₂S from industrial gas and oil streams is an essential step because of its undesirably high toxicity and corrosiveness [5]; thus, the application of ILs for H₂S removal purposes requires knowledge of the H₂S solubility in ILs. Although experimental measurements are broadly available and can already provide some insights into the understanding of gas solubility in ILs [5–15], such measurements are often difficult, time-consuming and expensive. It is thus desirable to develop theoretical models that are able to estimate the gas solubility in ILs over a wide range of system conditions. Such predictive model estimations should agree at least qualitatively with experimental observations. In addition, thermodynamic modeling gives insight into fundamental factors that control the gas solubility and selectivity, and it is required for performing process simulation, design and optimization.

Thermodynamic models representing gas solubilities in ILs have already been proposed earlier [16], and Statistical Associating Fluid Theory (SAFT)-type models were recommended due to their physical background. Several SAFT-type models have been developed to represent the gas solubility in imidazolium-based ILs, for example, truncated Perturbed-Chain Polar SAFT (tPC-PSAFT) [17,18], PC-SAFT [19], soft-SAFT [20–22], heterosegmented SAFT [23–25], SAFT-γ [26] as well as ePC-SAFT [6]. Most of them require binary fitting parameters, which are usually adjusted to gas-solubility data in order to represent gas solubilities quantitatively.

In contrast, the modeling strategy within ePC-SAFT developed in our previous work [6] could be used to predict CO₂ solubilities

* Corresponding author. Tel.: +46 920492837.

** Corresponding author. Tel.: +49 231 755 2086.

E-mail addresses: xiaoyan.ji@ltu.se (X. Ji), christoph.held@bci.tu-dortmund.de (C. Held).

Table 1
ePC-SAFT parameters of IL-ions determined in [6] and used in this work.

IL-ion	[C ₂ mim] ⁺	[C ₄ mim] ⁺	[C ₆ mim] ⁺	[C ₈ mim] ⁺	[BF ₄] [−]	[PF ₆] [−]	[Tf ₂ N] [−]
<i>M</i> (g mol ^{−1})	111.168	139.221	167.275	195.328	86.809	144.973	280.145
<i>m</i> ^{seg}	1.4872	2.4805	3.4131	4.2977	3.8227	4.2771	6.0103
<i>σ</i> (Å)	3.5926	3.6371	3.6781	3.7187	3.5088	3.5889	3.7469
<i>u/k_B</i> (K)	206.49	218.144	230.00	242.00	496.12	492.28	375.65

quantitatively in ILs between 293 and 450 K up to 950 bar. Further, the much lower solubility of CH₄ compared to CO₂ was obtained predictively. The goal of this work is to study the solubility of H₂, CO, O₂ and H₂S in ILs with ePC-SAFT using a modeling strategy developed in our previous work [6]. The ILs of interest in this work are imidazolium-based and contain one of the anions [BF₄][−], [PF₆][−] and [Tf₂N][−].

2. Theory

2.1. ePC-SAFT

Within ePC-SAFT, the dimensionless residual Helmholtz energy is obtained as the sum of contributions accounting for the hard-chain, dispersive, associative, ionic and polar interactions. As described in our previous work [6], polar interactions can be neglected for modeling gas solubilities in imidazolium-based ILs, and thus the Helmholtz-energy contributions considered within ePC-SAFT in this work are:

$$a^{\text{res}} = a^{\text{hc}} + a^{\text{disp}} + a^{\text{assoc}} + a^{\text{ion}} \quad (1)$$

where the terms of hard-chain (a^{hc}), dispersion (a^{disp}) and association (a^{assoc}) were already described elsewhere [27–30], and the ionic term (a^{ion}) is represented with the Debye–Hückel theory [31] expressed as

$$a^{\text{ion}} = -\frac{\kappa}{12\pi \cdot \epsilon} \cdot \sum_j x_j q_j^2 \chi_j \quad (2)$$

where x_j and q_j are the mole fraction and the charge of ion j , respectively, ϵ is the dielectric constant of the medium, and κ is the inverse Debye-screening length. The quantities κ and χ_j were applied as defined in the original ePC-SAFT publication [31].

In ePC-SAFT, three parameters are generally used to model a pure non-associative substance i , namely the segment number m_i^{seg} , the segment diameter σ_i and the dispersion-energy parameter between two segments u_i/k_B in which k_B is the Boltzmann constant. For associative substances i , additionally N association sites per molecule are characterized by the association-energy parameter $\epsilon^{\text{AiBi}}/k_B$ and the association-volume parameter κ^{AiBi} .

The ePC-SAFT parameters of a pure component are usually determined from the fitting to density and/or vapor-pressure data of the pure component. As the vapor pressure of most pure ILs is negligibly small below 100 °C, the parameters of ILs are most often fitted to liquid densities only, with pressures ranging from atmospheric up to elevated pressures [6]. Other strategies applied in the literature include fitting the ePC-SAFT parameters of an IL to activity coefficients at infinite dilution [32], to finite activity coefficients [33], or to high-temperature vapor-liquid equilibrium (VLE) data [34].

For modeling mixtures, Lorentz–Berthelot-combining rules used in this work are

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (3)$$

$$u_{ij} = \sqrt{u_i u_j (1 - k_{ij})} \quad (4)$$

where k_{ij} is a binary parameter between two components i and j to adjust the cross-dispersion energy if required. It is usually

determined by fitting to binary data, e.g. to the gas solubility in ILs. For the case that very accurate model descriptions are desired, the k_{ij} is allowed to depend on temperature [35].

2.2. Gas solubility

Following our previous work [6], it was assumed in this work too that the IL does not vaporize into the gas phase due to the extremely low vapor pressure of the ILs at the temperatures considered in this work. Therewith, the phase-equilibrium relation for the solubility of one gas in one IL is:

$$\phi_j^{\text{V}}(T, v^{\text{V}}) = x_j \phi_j^{\text{L}}(T, v^{\text{L}}, x), \quad (j \text{ is a component other than IL}) \quad (5)$$

where x is the mole-fraction-based composition of a mixture of gas and IL, and T is the temperature. Molar volumes (v^{V} and v^{L}) and fugacity coefficients ϕ_j^{V} and ϕ_j^{L} of component j in the vapor phase (V) and in the liquid (L) phase were calculated applying the ePC-SAFT equation of state.

2.3. Modeling strategy and model parameters

As described in our previous work [6], ILs were considered to be completely dissociated into a cation and an anion. Each IL-ion was modeled as a non-spherical species exerting repulsive, dispersive and Coulomb forces. According to our previous work [6], dispersion among all IL-ions was allowed in this work. The set of ePC-SAFT parameters for the IL-ions [C₂mim]⁺, [C₄mim]⁺, [C₆mim]⁺, [C₈mim]⁺, [Tf₂N][−], [PF₆][−] and [BF₄][−] was obtained by fitting to reliable density data of pure ILs up to 1000 bar in our previous work [6]. For the sake of completeness, these parameters are summarized in Table 1.

The components CO, H₂ and O₂ were modeled as non-polar and non-associative molecules, and the parameters of each pure component were taken from the literature. The parameters of CO and O₂ had been obtained by fitting to liquid densities and vapor-pressure data [27,36]. The parameters of H₂ were determined together with the binary adjustable parameters via the simultaneous regression of only a mixture of VLE data of H₂ + alkane (C₃, C₇, C₁₀ and C₂₀) systems [48]. Pure VLE data for H₂ were excluded from the regressed database, because they correspond to a very low temperature (<33 K), i.e., where the ortho/para ratio of H₂ is very different from that of the conditions of interest for industrial purposes [48]. As suggested in the work by Tang and Gross [37], H₂S was modeled as an associative molecule without polar interactions. The parameters of CO, H₂, O₂ and H₂S used in this work are summarized in Table 2.

The application of ePC-SAFT requires the use of a dielectric constant (Eq. (2)). Due to the dissolution of a gas in an IL, the dielectric

Table 2
PC-SAFT parameters for CO [27], H₂ [48], O₂ [36] and H₂S [37] used in this work.

	<i>M</i> (g mol ^{−1})	<i>m</i> ^{seg}	<i>σ</i> (Å)	<i>u/k_B</i> (K)	$\epsilon^{\text{AiBi}}/k_B$ (K)	κ^{AiBi}
CO	28.01	1.3097	3.2507	92.15	–	–
H ₂	2.016	1.3060	2.6010	23.42	–	–
O ₂	32.00	1.0740	3.2598	117.73	–	–
H ₂ S	34.08	1.6490	3.0550	229.84	536.6 ^a	0.001

^a H₂S was modeled via a 2B association scheme.

Table 3
Relative dielectric constant (ϵ_r) of H₂S [38] as function of temperature.

T (K)	169.6	174	177.6	183.7	187.4	187.7	283
ϵ_r	11.25	11.05	10.92	10.72	10.57	10.53	5.93

constant of the medium will change from the vacuum value (for a pure IL) to a certain value, which is related to the amount of gas dissolved in the IL. As the relative dielectric constant of pure CO, H₂ or O₂ is roughly unity and the relative dielectric constant for an IL is also unity, the relative dielectric constant of IL + CO, IL + H₂ and IL + O₂ mixtures were also set to unity in this work. In contrast, the influence of H₂S on the dielectric constant of IL + H₂S mixtures cannot be neglected. This is due to the fact that the relative dielectric constant of H₂S at atmospheric pressure has a value of 11.25 at 170 K and 5.93 at 283 K, respectively [38]. In this work, the dielectric constant of the medium (mixture of IL and H₂S) was set equal to the value of H₂S at the same temperature. Since no experimental investigation of the effect of pressure on the dielectric constant of H₂S is available, the dielectric constant was assumed to be pressure-independent in this work. The temperature dependence of the relative dielectric constant of H₂S was measured between 169.6 K and 283 K [38] and is listed in Table 3. These experimental data were correlated by the following equation with T given in Kelvin:

$$\epsilon_r = 19.299 - 0.0472 \cdot T \quad (6)$$

3. Gas-solubility data

CO₂ solubilities in imidazolium-based ILs were measured extensively, and reliable experimental data were summarized in our previous work [6]. CH₄ solubilities in such ILs were also determined, which was also summarized in our previous work [6]. However, compared to CO₂ solubilities in ILs, experimental CH₄ solubilities in ILs are available to a much lower extent. The solubilities of CO, O₂, H₂ and H₂S in ILs are also reported in the literature and are summarized in Table 4.

Table 4
Available experimental data sources for the solubility of H₂, CO, O₂ and H₂S in imidazolium-based ILs.

	T (K)	$P_{\max}$ (bar)	Ref.
H ₂			
[C ₂ mim][Tf ₂ N]	283–343	1	[39]
[C ₈ mim][Tf ₂ N]	283–343	1	[40]
[C ₄ mim][PF ₆]	283–343	1	[41]
[C ₄ mim][BF ₄]	283–341	1	[42]
[C ₆ mim][Tf ₂ N]	293–413	95	[7]
	300–370	120	[8]
[C ₄ mim][PF ₆]	333–373	90	[9]
CO			
[C ₄ mim][PF ₆]	283–343	1	[41]
[C ₄ mim][BF ₄]	283–341	1	[42]
[C ₆ mim][Tf ₂ N]	293–413	90	[10]
[C ₄ mim][PF ₆]	293–373	90	[11]
O ₂			
[C ₄ mim][PF ₆]	283–323	13	[43]
	298–323	13	[44]
[C ₆ mim][Tf ₂ N]	293–413	98	[10]
[C ₄ mim][PF ₆]	293–373	90	[12]
H ₂ S			
[C ₂ mim][Tf ₂ N]	333–363	20	[5]
[C ₄ mim][Tf ₂ N]	303–343	10	[13]
[C ₆ mim][Tf ₂ N]	303–343	11	[14]
[C ₆ mim][Tf ₂ N]	303–353	20	[15]
[C ₈ mim][Tf ₂ N]	303–353	20	[15]
[C ₂ mim][PF ₆]	333–363	20	[5]
[C ₄ mim][PF ₆]	303–343	10	[13]
[C ₆ mim][PF ₆]	303–343	11	[14]
[C ₄ mim][BF ₄]	303–343	10	[13]
[C ₆ mim][BF ₄]	303–343	11	[14]

For H₂, CO and O₂, the amount of available experimental is much smaller compared to that for CO₂ solubility in ILs. Most of the measured data at high pressures are taken from the research group of Maurer et al. [7,9–12], whereas only one data set stems from the research group of Peters and co-workers [8]. In addition, experimental data for higher pressures (higher than atmospheric pressure) are only available for [C₆mim][Tf₂N] and [C₄mim][PF₆], and the effect of alkyl length on the experimental solubility of H₂, CO and O₂ in ILs at elevated pressures has not yet been well studied. The main reason might be the low gas solubility in ILs, which requires a very high accuracy of the experimental set-up.

The solubility of H₂S in ILs was measured extensively. The effect of temperature, pressure, IL-cation, IL-anion as well as of the IL-cation's alkyl length on H₂S solubilities in ILs was studied, and the available experimental data sources are also listed in Table 4. Compared to the solubility of other gases (CO₂, H₂, CO and O₂) in ILs, the experimental H₂S solubility data were measured only at pressures up to 20 bar. The high H₂S solubility in ILs and the corrosiveness of highly concentrated H₂S solutions might be the reasons for this limitation.

The solubility of the gases H₂, CO, CH₄ and O₂ in the ILs under consideration is rather low. Among these poorly soluble gases, the solubility of CH₄ is the highest. In contrast, the solubility of H₂S and CO₂ in the same ILs is much higher, and H₂S has the highest solubility in all the ILs studied in this work. For example, at 303.15 K and 15 bar, the CO₂ solubility in [C₈mim][Tf₂N] is around 0.385 (mole fraction), while for H₂S it is almost 0.74.

In order to give an overview of pure-gas solubilities in the ILs, the solubilities of H₂S, CO₂, CH₄, O₂, CO and H₂ in [C₆mim][Tf₂N] at 333 K are illustrated in Fig. 1. The experimental sequence of gas solubilities in this IL is $x_{\text{H}_2\text{S}} > x_{\text{CO}_2} > x_{\text{CH}_4} > x_{\text{O}_2} > x_{\text{CO}} > x_{\text{H}_2}$; further, it can be observed that the solubilities of H₂S and CO₂ are much higher than those of CH₄, O₂, CO and H₂. All these observations are generally valid, i.e. also at other temperatures and in other ILs. The solubility of the other gases considered in this work also depends non-linearly on pressure.

4. Modeling results and discussion

4.1. ePC-SAFT predictions

Using the model parameters listed in Tables 1 and 2 as well as the information on the dielectric constant of the medium in Table 3, the gas solubility in ILs can be predicted with ePC-SAFT (the modeling is based on pure component parameters only and the binary

Fig. 1. Gas solubilities in [C₆mim][Tf₂N] at 333 K. Gray circles: H₂; black squares: CO; gray triangles: O₂; black circles: CH₄; gray squares: CO₂; black triangles: H₂S. The solubility of H₂, CO, O₂ and H₂S in [C₆mim][Tf₂N] are taken from sources listed in Table 4. The solubility data of CH₄ stem from [45] and those for CO₂ from [46]. Curves will guide the reader's eye.

Fig. 2. Solubility of H₂S in ILs. (a) H₂S in [C₈mim][Tf₂N] at 353.15, 323.15 and 303.15 K from left to right; (b) H₂S in [C₂mim][PF₆] at 363.15, 343.15 and 333.15 K from left to right. Symbols: experimental data (references in Table 4); curves: ePC-SAFT prediction.

parameter k_{ij} in Eq. (4) is set at zero). In this work, the solubility of H₂, CO, O₂ and H₂S in ILs was predicted and compared with the available experimental data from sources listed in Table 4.

To illustrate the accuracy of the ePC-SAFT predictions, a comparison between prediction and experimental solubility data for H₂S in [C₈mim][Tf₂N], [C₂mim][PF₆] and [C₆mim][BF₄] is shown in Figs. 2a, b and 3a, respectively. Although model parameters have not been fitted to binary data, ePC-SAFT provides qualitatively good predictions of the H₂S solubility in these ILs.

Additionally, the system O₂ + [C₄mim][PF₆] is shown in Fig. 3b as an example of the prediction of the solubility of O₂ in ILs. It can be observed from Fig. 3 that without using a binary fitting parameter, ePC-SAFT predicts correctly that H₂S is much more soluble in ILs compared to O₂. Moreover, the temperature dependence of the H₂S solubilities in ILs can be predicted reasonably with ePC-SAFT. The experimental temperature influence on O₂ solubilities (Fig. 3b) is much less pronounced than for H₂S solubilities (Figs. 2a, b and 3a). The model also captures this phenomenon qualitatively correct; however, the accuracy of the predicted temperature influence on O₂ solubilities is less good than for the H₂S systems.

Besides the reasonable prediction of the systems shown in Figs. 2 and 3, ePC-SAFT also captures well the much lower gas solubility of H₂ and CO in ILs compared to H₂S and CO₂. This is illustrated in Fig. 4. Fig. 4(a) represents experimental and predicted solubilities of H₂ and H₂S in [C₆mim][Tf₂N] at 333 K, and Fig. 4(b) compares the solubility of CO and H₂S in [C₄mim][PF₆] at 313 K. To further compare the solubility of different gases in ILs, the CO₂ solubility is also illustrated in Fig. 4 in which the model results were taken from our previous work [6]. The experimental H₂ and CO solubilities in ILs are very low (10 times lower than those for CO₂ and H₂S at 100 bar), which is captured correctly by applying ePC-SAFT in a predictive way ($k_{ij} = 0$).

Fig. 3. Solubility of H₂S in ILs and of O₂ in ILs. (a) H₂S in [C₆mim][BF₄] at 343.15, 323.15 and 303.15 K from left to right; (b) O₂ in [C₄mim][PF₆] at 293.2 K (squares, solid curve) and 373.1 K (circles, dashed curve). Symbols: experimental data (references in Table 4); curves: ePC-SAFT prediction.

To sum up, ePC-SAFT can be used to predict quantitatively the CO₂ solubility and predict qualitatively the H₂S and O₂ solubility in imidazolium-based ILs based on pure-IL parameters (obtained from fitting to pure-IL density) and pure-gas parameters (taken from the literature). Using ePC-SAFT further allows predicting a much lower CO and H₂ solubility in imidazolium-based ILs compared to the solubility of CO₂ and H₂S.

However, the accuracy of the ePC-SAFT predictions for the systems IL + CO and IL + H₂ (systems with low gas solubility in ILs) is not high enough for a quantitatively correct representation of the experimental data. This cannot be explained by the uncertainty of experimental data as the relative uncertainty in the experimentally determined mole fraction of dissolved CO is maximum 0.5%, and the relative uncertainty in the observed pressure is less than 2% [11]. Meanwhile, ePC-SAFT cannot quantitatively represent the temperature-effect on the O₂ solubility in [C₆mim][Tf₂N]. In order to improve the modeling results, binary interaction parameters between different species might be introduced, which are usually fitted to experimental data. This is shown in the following chapter.

4.2. ePC-SAFT correlations

The accuracy of the modeling results can be improved by introducing a binary interaction parameter k_{ij} between an IL-ion and the gas. Since the modeling approach within ePC-SAFT is IL-ion specific, k_{ij} values between the gas and IL-cation ($k_{\text{gas-cation}}$) or between the gas and IL-anion ($k_{\text{gas-anion}}$) can be applied. Since it is known from previous works [44] that the high gas solubility of CO₂ in ILs is mainly determined by the interactions between the gas and the IL-anion, k_{ij} s between gases and IL-cations were set at zero

Fig. 4. Gas solubilities in ILs. (a) Solubility of H₂, CO₂ and H₂S in [C₆mim][Tf₂N] at 333 K; (b) solubility of CO, CO₂ and H₂S in [C₄mim][PF₆] at 313 K. The solubilities of H₂ (a) and CO (b) are enlarged and illustrated in the inserted figures. Symbols: experimental data (references in Table 4; triangles: CO₂, diamonds: H₂S, circles: H₂, squares: CO), curves: ePC-SAFT predictions (from this work and from our previous work [6]).

while temperature-dependent k_{ij} s between the gas and IL-anion were introduced in this work according to:

$$k_{\text{gas-anion}} = C_1 + C_2 T \quad (7)$$

Setting C_2 in Eq. (7) equal to zero yields a temperature-independent k_{ij} .

$k_{\text{gas-anion}}$ values were fitted to solubility data of H₂, CO and O₂ in ILs at pressures up to 120 bar and to all solubility data of H₂S in ILs from sources listed in Table 4. The H₂ solubility in [C₆mim][Tf₂N] at elevated pressures was determined by two research groups with very good consistency and the C_1 and C_2 values were fitted to the data from Ref. [7]. The results are listed in Table 5.

As listed in Table 5, the adjusted k_{ij} values are generally small between H₂S and the IL-anion as well as O₂ and the IL-anion, which confirms the observation that the model already provides good predictions of the solubility of these two gases in the considered ILs. The k_{ij} s between CO and the IL-anion was found to be in the order of

Table 5
Results for the coefficients C_1 and C_2 for the calculation of k_{ij} s according to Eq. (7).

$k_{\text{gas-anion}}$	C_1	C_2
$k_{\text{H}_2\text{S-Tf}_2\text{N}}$	3.022×10^{-4}	0
$k_{\text{H}_2\text{S-PF}_6}$	6.976×10^{-3}	0
$k_{\text{H}_2\text{S-BF}_4}$	-4.944×10^{-3}	0
$k_{\text{H}_2\text{-Tf}_2\text{N}}$	-0.2625	0
$k_{\text{H}_2\text{-PF}_6}$	-0.3104	0
$k_{\text{CO-Tf}_2\text{N}}$	-2.1213×10^{-1}	3.0741×10^{-4}
$k_{\text{CO-PF}_6}$	-0.1371	0
$k_{\text{O}_2\text{-Tf}_2\text{N}}$	-1.5646×10^{-1}	4.9689×10^{-4}
$k_{\text{O}_2\text{-PF}_6}$	1.490×10^{-2}	0

Table 6

ARDs between ePC-SAFT modeled and experimental data from sources listed in Table 4.

System	ARD (%)	System	ARD (%)
H ₂ S-[C ₂ mim][Tf ₂ N]	6.4	H ₂ -[C ₆ mim][Tf ₂ N]	2.5
H ₂ S-[C ₄ mim][Tf ₂ N]	3.4	H ₂ -[C ₄ mim][PF ₆]	1.6
H ₂ S-[C ₆ mim][Tf ₂ N]	13.9	CO-[C ₆ mim][Tf ₂ N]	1.6
H ₂ S-[C ₈ mim][Tf ₂ N]	9.5	CO-[C ₄ mim][PF ₆]	5.4
H ₂ S-[C ₂ mim][PF ₆]	7.4	O ₂ -[C ₆ mim][Tf ₂ N]	1.1
H ₂ S-[C ₄ mim][PF ₆]	9.3	O ₂ -[C ₄ mim][PF ₆]	6.4
H ₂ S-[C ₆ mim][PF ₆]	21.5		
H ₂ S-[C ₄ mim][BF ₄]	7.1		
H ₂ S-[C ₄ mim][BF ₄]	6.2		

–0.1. The k_{ij} values for H₂ and IL-anions, however, are very negative, and this might be related to the dispersion energy of H₂. The dispersion energy parameter u_{H_2}/k_B is only 23.42 K as listed in Table 2, which is an extremely small value compared to those of the other components considered in this work. Such small values cause the need for very negative k_{ij} values. The pure-component parameters of H₂ were determined [48] by fitting to binary VLE data in the systems H₂ + alkane (C₃, C₇, C₁₀ and C₂₀). We nevertheless decided to use these H₂ parameters as they were also applied in an ongoing research work on phase equilibria of syngas systems [47].

Furthermore, temperature-independent k_{ij} values were used for most of the systems, while for modeling the solubility of CO and O₂ in [C₆mim][Tf₂N] temperature-dependent k_{ij} s were used; a detailed discussion is given below.

The deviations between experimental and modeled gas solubilities in ILs are listed in Table 6 in terms of the absolute relative deviations ARD in %, calculated by:

$$\text{ARD} = 100 \frac{1}{\text{NP}} \sum_{i=1}^{\text{NP}} \left| 1 - \frac{p_i^{\text{calc}}}{p_i^{\text{exp}}} \right| \quad (8)$$

where NP is the number of experimental data points, and the superscripts “calc” and “exp” are the calculation results and experimental data, respectively. The different systems will be discussed in the following.

4.2.1. H₂S solubility in ILs

The results of the investigation in Table 6 show that ePC-SAFT with temperature-independent k_{ij} values can reliably describe the solubility of H₂S in ILs for most of the considered systems with ARD values < 10%. The relative deviations of experimental pressures stemming from different sources [13] are < 9%; thus, ARD values between ePC-SAFT calculations and experimental data of < 10% are reasonable.

The ARDs for H₂S-[C₆mim][Tf₂N] and H₂S-[C₆mim][PF₆] are higher than for the other systems studied in this work. For these systems the comparison between the modeling results and experimental data is illustrated in Fig. 5. The experimental H₂S solubilities in [C₆mim][Tf₂N] stem from two sources, from which some discrepancies can be observed (e.g. at 303.15 K in Fig. 5(a)). The model represents the experimental data with reasonable accuracy. The H₂S solubility in [C₂mim][PF₆] and [C₄mim][PF₆] at 343.15 K is also shown in Fig. 5(b), which implies that it is represented well with ePC-SAFT. But the H₂S solubility in [C₆mim][PF₆] is underestimated compared to the experimental data.

In order to further improve the modeling of the H₂S-[C₆mim][PF₆] system, a temperature-dependent k_{ij} was applied yielding an ARD of around 12%. As only one group of experimental data for H₂S-[C₆mim][PF₆] is available, it is hard to state whether the experimental data or the model is inaccurate for the H₂S-[C₆mim][PF₆] system. Therefore, in this work, we chose the

Fig. 5. H₂S solubility in ILs. (a) ln [C₆mim][Tf₂N] at 353.15, 323.15 and 303.15 K from left to right, black symbols: experimental data from [14]; gray symbols: experimental data from [15]; (b) in [C₂mim][PF₆] (squares, solid curve), [C₄mim][PF₆] (circles, dotted curve) and [C₆mim][PF₆] (triangles, dashed curve) at 343.15 K. Curves: modeling results using ePC-SAFT with temperature-independent k_{ij} s.

temperature-independent k_{ij} for representing H₂S solubility data in ILs.

Note that the results shown in Fig. 5 are not representative for modeling gas solubilities in ILs with ePC-SAFT. It is rather the illustration of the two worst cases for H₂S solubility in ILs considered in this work, and the model performance for all other systems is much better compared to these two systems.

4.2.2. H₂ solubility in ILs

As mentioned before, the solubility of H₂ is much lower than that of H₂S and CO₂. The solubility of H₂ in [C₆mim][Tf₂N] and [C₄mim][PF₆] behaves abnormally compared to most gases in solution, i.e. the H₂ solubility increases with increasing temperature. Applying ePC-SAFT with temperature-independent k_{ij} values (Table 6) captures both quantitatively, the very low H₂ solubility as well as the abnormal temperature phenomenon, and the ARDs are less than 2.5%. The results are shown in Fig. 6, which illustrates the abnormal temperature behavior and the good agreement between model and data.

4.2.3. CO and O₂ solubility in ILs

The solubility of CO and O₂ in ILs is much lower compared to H₂S and CO₂ but higher than that of H₂ in ILs. Furthermore, the temperature dependence of the solubility of these two pure gases in ILs is much less pronounced compared to the other gases considered in this work, as shown in Fig. 7. In addition, the CO and O₂ solubilities in [C₄mim][PF₆] show the same abnormal phenomenon as that for H₂, i.e. the gas solubility increases with increasing temperature. Applying ePC-SAFT and again temperature-independent k_{ij} s allows for capturing this abnormal phenomenon and for quantitatively representing the CO and O₂ solubilities in [C₄mim][PF₆] (results

Fig. 6. H₂ solubility in [C₆mim][Tf₂N] at 293.2, 313.2, 373.15 and 413.15 K from left to right. Symbols: experimental data (references in Table 4), curves: modeling results using temperature-independent k_{ij} s.

not shown graphically). The ARDs for CO and O₂ solubilities in [C₄mim][PF₆] are only 5.4 and 6.4%, respectively.

In contrast to the accurate model performance shown until here, the application of ePC-SAFT with temperature-independent k_{ij} s cannot describe the temperature behavior of CO + [C₆mim][Tf₂N] and O₂ + [C₆mim][Tf₂N]. Experimental CO and O₂ solubilities in [C₆mim][Tf₂N] show the classical temperature dependence of gas solubilities in solvents, i.e. the solubility decreases with increasing temperature. However, this temperature dependence is only very weak. ePC-SAFT applied with temperature-independent k_{ij} values overestimates this behavior. In order to capture the temperature effect of the CO and O₂ solubilities in [C₆mim][Tf₂N] correctly, temperature-dependent k_{ij} values had to be introduced, represented by the constant C_2 in Eq. (7). Applying ePC-SAFT with these temperature-dependent k_{ij} values provides very accurate results compared to the available experimental data (see Table 6 and Fig. 7). The need for a temperature-dependent k_{ij} between O₂ or CO and a Tf₂N-based IL might be related to the pure-component parameters for the Tf₂N-anion. Compared to the other IL-anions considered in this work, the segment diameter of [Tf₂N][−] is higher, and the dispersion-energy parameter is lower.

To sum up, using adjustable binary parameters k_{ij} between the gas and IL-anion can be used to improve the model performance in order to represent quantitatively the gas solubility in ILs in a broad temperature and pressure range. Applying temperature-independent k_{ij} s allows for representing quantitatively the experimental data for most of the gas + IL systems under investigation. Among the considered gas + IL systems, temperature-dependent k_{ij} values had only to be introduced to represent quantitatively the CO and O₂ solubility in [C₆mim][Tf₂N] in a broad

Fig. 7. CO (squares) and O₂ (triangles) solubilities in [C₆mim][Tf₂N] at 413 K (black symbols) and 293 K (gray symbols) from left to right. Symbols: experimental data (references in Table 4), curves: modeling results using ePC-SAFT and temperature-dependent k_{ij} s.

temperature and pressure range. This was due to the fact that the solubility only marginally depends on the temperature for these gases in Tf₂N-based ILs.

5. Conclusion

In this work, ePC-SAFT [6] was used to model the solubility of H₂S, O₂, CO and H₂ in [C_nmim][Tf₂N], [C_nmim][PF₆] and [C_nmim][BF₄] with 2 ≤ *n* ≤ 8. The investigation shows that the model can predict qualitatively the solubility of H₂S in these ILs at temperatures from 303.15 to 353.15 K and pressures up to 20 bar. ePC-SAFT can also predict qualitatively the much lower gas solubility of O₂, CO and H₂ in ILs compared to those for CO₂ and H₂S. Further, by applying temperature-independent model parameters it was possible for most of the considered systems to predict the experimentally observed abnormal temperature-dependence of gas solubilities in ILs (increasing solubility with increasing temperature).

Applying *k_{ij}* values allows for representing quantitatively the solubility of ILs for most of the gases in a broad temperature and pressure range. These parameters *k_{ij}* were used only between the gas and IL-anion and were applied as temperature-independent values. Only for two systems (CO + [C₆mim][Tf₂N] and O₂ + [C₆mim][Tf₂N]), temperature-dependent *k_{ij}* values were required in order to represent quantitatively the gas solubility at different temperatures.

List of symbols

<i>a</i>	dimensionless Helmholtz energy
ARD	average relative deviation
[BF ₄] [−]	tetrafluoroborate anion
[C _n mim] ⁺	1-alkyl-3-methylimidazolium cation
calc	calculation results
exp	experimental data
<i>k_B</i>	Boltzmann constant
<i>k_{ij}</i>	binary parameter between two components <i>i</i> and <i>j</i>
<i>m</i> ^{seg}	segment number
<i>M</i>	molecular weight
<i>N</i>	association sites per molecule
NP	number of experimental data points
<i>P</i>	pressure, bar
[PF ₆] [−]	hexafluorophosphate anion
<i>q</i>	charge of an ion
<i>T</i>	temperature
[Tf ₂ N] [−]	bis(trifluoromethylsulfonyl) imide anion
<i>u/k_B</i>	van der Waals-interaction (dispersion) energy parameter between two segments
<i>v</i>	molar volume
VLE	vapor–liquid equilibrium
<i>x</i>	mole fraction in the liquid phase

Greek letters

χ	abbreviation for an expression in Eq. (2)
ε	dielectric constant of a medium
ε ^{AiBi} / <i>k_B</i>	association-energy parameter
φ _{<i>i</i>}	fugacity coefficients
κ ^{AiBi}	association-volume parameter
κ	inverse Debye screening length
σ	segment diameter

Acknowledgements

X.J. thanks the Swedish Research Council and the Alexander von Humboldt foundation for financial support. X.J. also thanks Prof.

Maurer at Kaiserslautern University for his valuable comments and discussions.

References

- [1] M. Halmann, A. Steinfeld, *Energy* 31 (2006) 3171–3185.
- [2] R.A. Gawel, *Chem. Papers* 66 (2012) 1010–1018.
- [3] <http://www.gizmag.com/ionic-liquid-co2-emissions-control/11105/>
- [4] M.J. Muldoon, S. Aki, J.L. Anderson, J.K. Dixon, J.F. Brennecke, *J. Phys. Chem. B* 111 (2007) 9001–9009.
- [5] H. Sakhaeinia, A.H. Jalili, V. Taghikhani, A.A. Safekordia, *J. Chem. Eng. Data* 55 (2010) 5839–5845.
- [6] X. Ji, C. Held, G. Sadowski, *Fluid Phase Equilib.* 335 (2012) 64–73.
- [7] J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma, G. Maurer, *J. Chem. Eng. Data* 51 (2006) 1364–1367.
- [8] S.R.S. Raeissi, L.J. Florusse, C.J. Peters, *J. Chem. Eng. Data* 56 (2011) 1105–1107.
- [9] J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma, G. Maurer, *J. Chem. Eng. Data* 51 (2006) 11–14.
- [10] J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma, G. Maurer, *J. Chem. Eng. Data* 54 (2009) 966–971.
- [11] J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma, G. Maurer, *Fluid Phase Equilib.* 228 (2005) 207–211.
- [12] J. Kumelan, Á. Pérez-Salado Kamps, I. Urukova, D. Tuma, G. Maurer, *J. Chem. Thermodyn.* 37 (2005) 595–602.
- [13] A.H. Jalili, M. Rahmati-Rostami, C. Ghotbi, M. Hosseini-Jenab, A.N. Ahmadi, *J. Chem. Eng. Data* 54 (2009) 1844–1849.
- [14] M. Rahmati-Rostami, C. Ghotbi, M. Hosseini-Jenab, A.N. Ahmadi, A.H. Jalili, *J. Chem. Thermodyn.* 41 (2009) 1052–1055.
- [15] A.H. Jalili, M. Safavi, C. Ghotbi, A. Mehdizadeh, M. Hosseini-Jenab, V. Taghikhani, *J. Phys. Chem. B* 116 (2012) 2758–2774.
- [16] L.F. Vega, O. Vilaseca, F. Llovel, J.S. Andreu, *Fluid Phase Equilib.* 294 (2010) 15–30.
- [17] E.K. Karakatsani, L.G. Economou, M.C. Kroon, C.J. Peters, G.J. Witkamp, *J. Phys. Chem. C* 111 (2007) 15487–15492.
- [18] M.C. Kroon, E.K. Karakatsani, I.G. Economou, G.J. Witkamp, C.J. Peters, *J. Phys. Chem. B* 110 (2006) 9262–9269.
- [19] Y.S. Chen, F. Mutelet, J.N. Jaubert, *J. Phys. Chem. B* 116 (2012) 14375–14388.
- [20] J.S. Andreu, L.F. Vega, *J. Phys. Chem. C* 111 (2007) 16028–16034.
- [21] J.S. Andreu, L.F. Vega, *J. Phys. Chem. B* 112 (2008) 15398–15406.
- [22] F. Llovel, R.M. Marcos, N. MacDowell, L.F. Vega, *J. Phys. Chem. B* 116 (2012) 7709–7718.
- [23] X. Ji, H. Adidharma, *Chem. Eng. Sci.* 64 (2009) 1985–1992.
- [24] X. Ji, H. Adidharma, *Fluid Phase Equilib.* 293 (2010) 141–150.
- [25] X. Ji, H. Adidharma, *Fluid Phase Equilib.* 315 (2012) 53–63.
- [26] S.S. Ashrafmansouri, S. Raeissi, *J. Supercrit. Fluids* 63 (2012) 81–91.
- [27] J. Gross, G. Sadowski, *Ind. Eng. Chem. Res.* 40 (2001) 1244–1260.
- [28] J. Gross, J. Vrabec, *AIChE J.* 52 (2006) 1194–1204.
- [29] M. Kleiner, J. Gross, *AIChE J.* 52 (2006) 1951–1961.
- [30] J. Vrabec, J. Gross, *J. Phys. Chem. B* 112 (2008) 51–60.
- [31] L.F. Cameretti, G. Sadowski, J.M. Mollerup, *Ind. Eng. Chem. Res.* 44 (2005) 3355–3362.
- [32] A. Carneiro, C. Held, O. Rodriguez, E. Macedo, G. Sadowski, *J. Phys. Chem. B* (2013) 9980–9995.
- [33] A. Nann, J. Mündges, C. Held, S.P. Verevkin, G. Sadowski, *J. Phys. Chem. B* 117 (2013) 3173–3185.
- [34] H. Passos, I. Khan, M.B. Oliveira, P.J. Carvalho, L.M.N.B.F. Santos, C. Held, G. Sadowski, M.G. Freire, J.A.P. Coutinho, *J. Phys. Chem. B* (2013) (submitted for publication).
- [35] C. Held, L.F. Cameretti, G. Sadowski, *Ind. Eng. Chem. Res.* 50 (2011) 131–141.
- [36] V. Vins, V. Vacek, *J. Chem. Eng. Data* 54 (2009) 2395–2403.
- [37] X.H. Tang, J. Gross, *Fluid Phase Equilib.* 293 (2010) 11–21.
- [38] <http://www.fiz-chemie.de/infoterm/html/molpages/03/25/mol32542.html>
- [39] J. Jacquemin, P. Husson, V. Majer, M.F.C. Gomes, *J. Solution Chem.* 36 (2007) 967–979.
- [40] M.F.C. Gomes, *J. Chem. Eng. Data* 52 (2007) 472–475.
- [41] J. Jacquemin, P. Husson, V. Majer, M.F.C. Gomes, *Fluid Phase Equilib.* 240 (2006) 87–95.
- [42] J. Jacquemin, M.F.C. Gomes, P. Husson, V. Majer, *J. Chem. Thermodyn.* 38 (2006) 490–502.
- [43] J.L. Anthony, E.J. Maginn, J.F. Brennecke, *J. Phys. Chem. B* 106 (2002) 7315–7320.
- [44] J.L. Anthony, J.L. Anderson, E.J. Maginn, J.F. Brennecke, *J. Phys. Chem. B* 109 (2005) 6366–6374.
- [45] J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma, G. Maurer, *Ind. Eng. Chem. Res.* 46 (2007) 8236–8240.
- [46] J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma, G. Maurer, *J. Chem. Thermodyn.* 38 (2006) 1396–1401.
- [47] C. Vogelpohl, C. Brandenbusch, G. Sadowski, *J. Supercrit. Fluids* (2013) (submitted for publication).
- [48] C. Le Thi, S. Tamouza, J.P. Passarello, P. Tobaly, J.C. de Hemptinne, *Ind. Eng. Chem. Res.* 45 (2006) 6803–6810.