

Modeling the Solubility of Acid Gases in Ionic Liquids Using PC-SAFT Equation of State

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Abstract: In this work, the PC-SAFT equation of state (EoS) has been used to model the solubility of acid gases (CO₂ and H₂S) in two imidazolium-based ionic liquids (ILs) ([C₈-mim][PF₆] and [C₈-mim][Tf₂N]). Parameters of pure ILs were estimated using experimental densities. Two strategies were considered to model densities of pure ILs. In strategy 1, ILs were modeled as nonassociating compounds and in strategy 2 ILs were considered as self-associating molecules and both association sites were assigned to each ILs. According to the results, the associating contribution should be taken into account in order to accurately correlate the properties of ILs. The solubility of CO₂ and H₂S in ionic liquids was then studied. In order to describe the experimental gas solubilities quantitatively, binary interaction parameters between the ILs and the gases were applied, which were allowed to depend linearly on temperature. After fitting a binary interaction parameter k_{ij} on experimental VLE data, the model was able to describe accurately the solubility of acid gases in these two ionic liquids. Using second strategy, an average deviation of less than 2.2% and 3.2% in the calculation of the mole fraction of CO₂ and H₂S in ILs (x_2) were obtained, respectively.

Keywords: Acid Gas, Ionic Liquid, Solubility, PC-SAFT

1. Introduction

The global use of natural gas is growing rapidly due to its favorable characteristics and its environmental advantages in comparison with other fossil fuels such as oil and coal. This trend is expected to increase in the next few decades with the progressive replacement of fuel oil and coal by this relatively environment-friendly source of energy. However, this development will depend on the progress of gas processing technologies to give access to reserves which are not exploitable now.

Natural gas extracted from some wells contains significant amounts of sulfur and carbon dioxide hydrogen sulfide and other sulfur compounds (such as mercaptans). The composition of acid gases in natural gas varies widely depending on the gas field. Acid gas

impurities, i.e. CO₂ and H₂S are detrimental to natural gas properties. For instance, in cryogenic conversion of natural gas to LNG, CO₂ transforms to solid state, hence, hinders the transportation of liquid in the pipes or the corrosive H₂S reduces service time of the transportation pipes. In addition H₂S is hazardous for human beings and CO₂ has no heating value. As a result the concentration of acid gas impurities in natural gas must be reduced to a specified level before further processing. Processes in which remove acid gases are commonly referred as sweetening processes because they result in products that no longer have acid (Kohl & Nielsen, 1997; Sakhaeinia, Jalili, Taghikhani, & Safekordi, 2010).

The conventional acid gas removal technologies can be classified as: chemical absorption,

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physical absorption, hybrid process and membrane separation process. In chemical absorption process, acid gases components react chemically with the solvent and formed dissolved chemical compounds. The solvent is regenerated in a stripper column by application of heat. Heat breaks the chemical bounds between acid gases and solvent and drives out the acid gases from the solution. The conventional chemical absorption process is amine process where alkanolamines is used as a solvent. In physical absorption process, acid gases are being absorbed physically and without chemical reaction in an organic solvent. Acid gases are absorbed in the solvent due to their high solubility. Since solubility rises with increasing of pressure and decreasing of temperature, physical absorption is mostly effective at high pressures and low temperatures. Therefore, compared to amine process, usually physical absorption capital and operating costs is higher in comparison to a process using high pressure equipment and refrigerating units to achieve high pressure and low temperature as operational conditions. In addition, physical solvent is used for bulk removal of acid gases whereas application of chemical solvent is to achieve very low acid gas concentration. It should be noted that the choice between a physical and an amine based solvent has to be taken based on analysis of each case. Sometimes a physical solvent has lower operating and capital costs. However nowadays chemical absorption with amines dominates the market. In a hybrid process a physical and chemical solvent are applied simultaneously to benefit from the advantages of both processes. Membrane separation systems are mainly used for bulk removal of CO₂. This process is commonly applied at conditions with large flows or high CO₂ contents (Camper, Bara, Gin, & Noble, 2008; Karadas, Atilhan, & Aparicio, 2010; Kohl & Nielsen, 1997).

In the gas processing industry absorption by chemical solvents has been used commercially for the removal of acid gas impurities from natural gas. The currently preferred chemical solvent technology for acid gas removal is chemical absorption of acid gases by amine-based absorbents. The solvents for such processes are chosen assuming that the absorption step can be reversed by changing the conditions of temperature and pressure. Absorption takes place at high pressure and low temperature, giving high loadings of absorbed component in the solvent. The solvent is then sent to a regenerator, which operates at high temperature and low pressure, causing desorption of the absorbed components and

regenerating the solvent. Heat is added to the regenerator to provide the heat of reaction, the sensible heat change of the solvent, and to generate a vapor flow for stripping by partially reboiling the solvent (Sakhaeini et al., 2010).

However, the acid gas separation in general consumes a lot of energy, and exploring low-cost gas separation technologies is still a hot research topic. Recent research reveals that ionic liquids are promising liquid absorbents for gas separation. This is mainly due to the extremely low vapor pressure of pure ionic liquids (e.g., ca. 10^{-10} Pa at 298 K for [C₄mim][PF₆] (Bier & Dietrich, 2010) compared to 3 kPa at 298 K for H₂O ("NIST Scientific and Technical Databases, Thermophysical Properties of Fluid Systems," 2014)) 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 gas separation purposes (Muldoon, Aki, Anderson, Dixon, & Brennecke, 2007).

Ionic liquids (ILs) also known as liquid salts and liquid electrolytes are a class of salts with a melting temperature below 100 °C and are composed entirely of ions. The low melting points of ILs are due to the high degree of asymmetry between their organic cation and inorganic or organic anion. At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice (Wasserscheid & Welton, 2008).

Due to their specific properties, ILs have received great attention by the scientific community and have found their way into a wide variety of industrial applications. One of the foreseeable industrial applications in the field of natural gas processing is the replacement of traditional organic solvents such as alkanolamine solutions widely used for the absorption of H₂S from sour gases, by suitable ILs.

Although experimental measurements are broadly available and can already provide some insights into the understanding of gas solubility in ILs (Jalili et al., 2012; Ji, Held, & Sadowski, 2012; Raeissi, Florusse, & Peters, 2011; Rahmati-Rostami, Ghotbi, Hosseini-Jenab, Ahmadi, & Jalili, 2009; Safavi, Ghotbi, Taghikhani, Jalili, & Mehdizadeh, 2013), 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 model estimations should agree at least qualitatively with experimental observations. In addition,

thermodynamic modeling gives insight into fundamental factors which control the gas solubility and selectivity, and it is required to perform the process simulation, design and optimization. During the past years, several thermodynamic models have been reported to represent phase behavior of mixtures containing ILs (Vega, Vilaseca, Llovel, & Andreu, 2010), and among different models Statistical Associating Fluid Theory (SAFT)-based approaches have been attracted much attention due to several advantages such as their physical background. Their main advantage over the traditional cubic EoS is that they take into account the structure of the molecule, similarly to group contribution models. Several variations of SAFT models have been developed to represent the gas solubility in imidazolium-based ILs, for example, truncated Perturbed-Chain Polar SAFT (tPC-PSAFT) (Karakatsani, Economou, Kroon, Peters, & Witkamp, 2007), PC-SAFT (Chen, Mutelet, & Jaubert, 2012), soft-SAFT (Llovel, Marcos, MacDowell, & Vega, 2012), heterosegmented SAFT (Ji & Adidharma, 2010), SAFT- γ (Ashrafmansouri & Raeissi, 2012) as well as ePC-SAFT (Ji et al., 2012). Most of them require binary fitting parameters, which are usually adjusted to gas-solubility data in order to represent gas solubilities quantitatively.

In this work, the PC-SAFT EoS was chosen to model both the pure components and the binary systems of acid gases and ILs ($\{\text{CO}_2 + \text{IL}\}$ and $\{\text{H}_2\text{S} + \text{IL}\}$). This model has been applied for the calculation of pure ILs densities and mole fractions of CO_2 and H_2S in different ILs at various temperatures and pressures. The ILs of interest in this work are imidazolium-based and contain one of the anions $[\text{PF}_6]^-$ and $[\text{TF}_2\text{N}]^-$.

2. Theory

2.1. The PC-SAFT Model

The perturbed-chain statistical associating fluid theory (PC-SAFT) EoS, which is similar to other SAFT type equations of state, was developed in 2001 by Gross and Sadowski (Gross & Sadowski, 2001). They applied a perturbation theory for chain molecules and used a hard-chain reference fluid, for comparison with other classical SAFT equations of state that used a hard-sphere reference, meaning that molecules are assumed to be chains of freely jointed spherical segment and the dispersion term accounts for attractions between spherical segments not attractions between hard chains. The PC-SAFT equation can be expressed in terms of the

reduced residual Helmholtz energy, which is made up of the following contributions:

$$\tilde{a} \equiv \frac{A}{NkT} = \tilde{a}^{id} + \tilde{a}^{hc} + \tilde{a}^{disp} + \tilde{a}^{assoc} \quad (1)$$

The hard-sphere chain contribution accounting for the repulsion of the chain-like molecules is made up by the hard-sphere and the chain formation contributions:

$$\begin{aligned} \tilde{a}^{hc} &= \bar{m}\tilde{a}^{hs} + \tilde{a}^{chain} \\ &= \bar{m}\tilde{a}^{hs} - \sum_i x_i(m_i - 1)\ln g_{ij}^{hs} \end{aligned} \quad (2)$$

where $\bar{m}$ is the average number of segments per chain:

$$\bar{m} = \sum_{i=1}^{NC} x_i m_i \quad (3)$$

The hard-sphere term is given by the mixture version of the Carnahan-Starling (Gross & Sadowski, 2001) EoS for hard-spheres:

$$\begin{aligned} \tilde{a}^{hs} &= \frac{6}{\pi\rho_s} \left[\frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_3^3}{\zeta_3(1-\zeta_3)^2} \right. \\ &\quad \left. + \left(\frac{\zeta_3^3}{2} - \xi_0 \right) \ln \left(1 - \frac{\zeta_3}{\zeta_3} \right) \right] \end{aligned} \quad (4)$$

where ζ_n are the partial volume fractions defined by:

$$\zeta_n = \frac{\pi}{6} \rho \sum_{i=1}^n x_i m_i d_i^n \quad n \in \{0, 1, 2, 3\} \quad (5)$$

$\rho = N_{AV}/V_m$ is the number density. N_{AV} is the Avogadro's number and V_m is the molar volume. d_i is the Chen and Kreglewski (Gross & Sadowski, 2001) temperature-dependent segment diameter of component i :

$$d_i = \sigma_i \left[1 - 0.12 \exp \left(-\frac{3\epsilon_i}{kT} \right) \right] \quad (6)$$

The chain term in Equation 2 depends also on the radial distribution function at contact, which is given by:

$$\begin{aligned} g_{ij}^{hs} &= \frac{1}{1-\zeta_3} + \left(\frac{d_i d_j}{d_i + d_j} \right) \frac{3\zeta_2}{1-\zeta_3} \\ &\quad + \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2\zeta_2^2}{(1-\zeta_3)^3} \end{aligned} \quad (7)$$

The radial distribution function denotes the probability density for finding a hard-sphere belonging to a j -molecule at a distance d from a hard sphere belonging to an i -molecule.

In PC-SAFT, the dispersion term is written for chains of segments based on second order perturbation theory (Gross & Sadowski, 2001), i.e. the attractive part of the chain interactions

is calculated from a first and a second order perturbation, according to Barker and Henderson. Basically, these are calculated by integrating the intermolecular interactions over the entire mixture volume, which leads to:

$$\tilde{a}^{disp} = -2\pi\rho I_1(\eta, \bar{m})\bar{m}^2\epsilon\sigma^3 - \pi\rho\bar{m}C_1 I_2(\eta, \bar{m})\bar{m}^2\epsilon^2\sigma^3 \quad (8)$$

$\eta = \zeta_3$ is the packing fraction. The required integrals are approximated by power-series in density, where the coefficients of the power series are functions of the chain length:

$$I_1 = \sum_{i=0}^6 a_i(\bar{m})\eta^i \quad (9)$$

$$I_2 = \sum_{i=0}^6 b_i(\bar{m})\eta^i \quad (10)$$

The coefficients $a_i(\bar{m})$ and $b_i(\bar{m})$ are dependent on segment number according to the following equations:

$$a_i(\bar{m}) = a_{0i} + \frac{\bar{m}-1}{\bar{m}}a_{1i} + \frac{\bar{m}-1}{\bar{m}} \times \frac{\bar{m}-2}{\bar{m}}a_{2i}$$

$$b_i(\bar{m}) = b_{0i} + \frac{\bar{m}-1}{\bar{m}}b_{1i} + \frac{\bar{m}-1}{\bar{m}} \times \frac{\bar{m}-2}{\bar{m}}b_{2i}$$

and

$$\frac{\bar{m}^2\epsilon^y\sigma^3}{\sum_{i=1}^{NC}\sum_{j=1}^{NC}x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT}\right)^y \sigma_{ij}^3} \quad y \in \{1,2\} \quad (11)$$

The cross-parameters are obtained from the combining rules:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (12)$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}(1 - k_{ij}) \quad (13)$$

where one binary interaction parameter, k_{ij} , is introduced to correct the segment-segment interactions of unlike chains. The association contribution is only included for systems containing components capable of self-associating and cross-associating (e.g. alcohols and acids). The association contribution is:

$$\tilde{a}^{assoc} = \sum_i x_i \left[\sum_{A_i} \left(\ln X^{A_i} - \frac{1}{2} X^{A_i} \right) + \frac{1}{2} M_i \right] \quad (14)$$

where X^{A_i} is the mole fraction of molecules i not bonded at site A , M_i is the number of association sites on each molecule and $\sum_{A_i}$ represents a sum over all associating sites on each molecule. The parameter X^{A_i} is given by:

$$X^{A_i} = \left(1 + N_{AV} \sum_j \rho_j \sum_{B_j} X^{B_j} \Delta^{A_i B_j} \right)^{-1} \quad (15)$$

where ρ_j is the molar density of component j , and $\Delta^{A_i B_j}$ is a measure of the association strength between site A on molecule i and site B on molecule j . This parameter is a function of the association volume $\kappa^{A_i B_j}$, the association energy $\epsilon^{A_i B_j}$, and the radial distribution function as follows:

$$\Delta^{A_i B_j} = g_{ij}^{hs} \left[\exp\left(\frac{\epsilon^{A_i B_j}}{kT}\right) - 1 \right] (\sigma_{ij}^3 \kappa^{A_i B_j}) \quad (16)$$

PC-SAFT models a pure substance i with a maximum of five parameters: the segment number $m_{seg,i}$, the segment diameter σ_i , the van der Waals-interaction (dispersion) energy parameter between two segments ϵ_i/k in which k is the Boltzmann constant. For molecules with association interactions, N association sites per molecule are characterized by the association-energy parameter $\epsilon^{A_i B_j}/k$ and the association-volume parameter $\kappa^{A_i B_j}$. Generally, these parameters are determined by fitting to liquid-density and/or vapor-pressure data of a pure component. In case of ILs that are hardly volatile, only density data was used for the parameter fitting in this work.

2.2. Gas Solubility in ILs

Solubility measurements of acid gases (CO_2 and H_2S) in ionic liquids was based on the pressure drop method that has been used in most experimental studies in literature and described in previous publications (Jalili et al., 2012; Rahmati-Rostami et al., 2009; Safavi et al., 2013; Sakhaeinia et al., 2010). Here the ionic liquid is brought into contact with a gas in a small chamber with a defined volume at a constant temperature. When thermodynamic equilibrium is attained, the pressure above the liquid solution is constant and directly related to the solubility of the gas in the liquid. The quantity of solute present in the liquid solution is calculated by the difference between two PVT measurements: first on introduction of the gas from a container of known volume into the equilibrium cell containing the IL and secondly after reaching thermodynamic equilibrium. The most accurate PVT data presented by National Institute of Standards and Technology (NIST) for pure compounds (NIST Scientific and Technical Databases) was used to calculate compressibility factors of H_2S and CO_2 gases, which were needed for solubility calculations. A detailed description of the experimental apparatus, procedure and experimental data can be obtained from our previous publications (Jalili et al., 2012; Safavi et al., 2013).

The $\varphi - \varphi$ approach is applied to describe the equilibrium condition between the vapor and liquid phases. As the vapor pressure of ILs is extremely low at temperatures up to 450 K, it was assumed that the IL will not vaporize into the gas-rich phase. Thus the iso-fugacity condition for vapor-liquid equilibrium for ionic liquid (1) and the dissolved gas (2) at fixed temperature and pressure can be written as:

$$\varphi_2^v = x_2^l \varphi_2^l \quad (17)$$

where x_2 and φ_2^l are the mole fraction and fugacity coefficient of the gas in liquid phase,

respectively, and ϕ_2^v is the fugacity coefficient of the pure gas at the same temperature and pressure in the gas phase.

2.3. Calculation procedure

Equations of state are often constructed in terms of the Helmholtz free energy (A). Helmholtz free energy is a function taking system temperature, volume and composition as its natural independent variables. Experimental data of thermodynamic properties are usually measured and reported as functions of system temperature, pressure and composition. All thermodynamic properties of a system can be derived from Helmholtz free energy by standard differentiation with respect to its independent variables.

Computation of the thermodynamic properties from Helmholtz free energy is accomplished by

first calculating the volume V of a single liquid phase in the system from the pressure equation at given temperature, pressure and composition (T, P, n), as that of experimental data. The pressure equation is given by:

$$P = f(T, V, n) \quad (18)$$

$$= - \left(\frac{\partial A(T, V, n)}{\partial V} \right)$$

Any equation root-finding algorithm (root solver routine) such as bisection method or Newton-Raphson method can do the job. Secondly substitute the volume V into different derivatives of Helmholtz free energy to calculate other thermodynamic properties. The algorithm is presented below (Figure 1). Vector and matrix variables are expressed in bold font in the algorithm.

Algorithm

```
Function [fug_coef, fug_coef_derivatives, thermo_properties]=EOS(T, P, n, parameters)
Call function [parameters]=EOS_parameter_initialization(T, P, n, parameters)
Call function [V]=volume_solver(T, P, n, parameters)
Call function [fug_coef, fug_coef_derivatives, thermo_properties] = fugacity_calculator(T, V, P, n, parameters)
End function EOS
Function [V]=volume_solver(T, P, n, parameters)
function='Pressure_equation'
set starting value V0
Call [V, output_information]=Newton_Raphson(function, V0, [T, P, n, parameters], inputsetting)
End function volume_solver
Function [f, dfdV]=Pressure_equation (T, V, P, n, parameters)

$$f = P - \left( \frac{\partial A(T, V, n)}{\partial V} \right)$$


$$dfdV = - \left( \frac{\partial^2 A(T, V, n)}{\partial V^2} \right)$$

End function Pressure_equation
```

Figure 1. Algorithm used for computation of the thermodynamic properties.

All model equations and calculation subroutines required for determining properties of pure substances and mixtures and for solving phase equilibrium problems were implemented. Specific subroutines for the calculation pressure (P), molecular packing fraction (η), critical point of pure substances, residual Helmholtz free energy ($\bar{a}$), fugacity coefficient in logarithmic form ($\ln \phi_i$) and vapor pressure were used.

In order to determine packing fraction (η) for a given pressure considering the iterative procedure is required. Calculation of η is based on the use of Newton's method for minimizing the following equation:

$$F_{obj} = 1 - \frac{P_{calc}}{P_{specified}} \quad (19)$$

F_{obj} is the objective function, P_{calc} is the pressure calculated by the equation of state and $P_{specified}$ is given pressure. Figure 2 shows the iterative procedure for the calculation of η based on Newton's method. The values of 1×10^{-8} for vapor phase and 0.5 for liquid phase were used as a initial estimation of η . In Figure 2 only the procedure for determining a single root is presented. The determination of the remaining roots, where necessary, is performed by repeating the procedure using a new initialization value for the variable η , according to the phase to be determined.

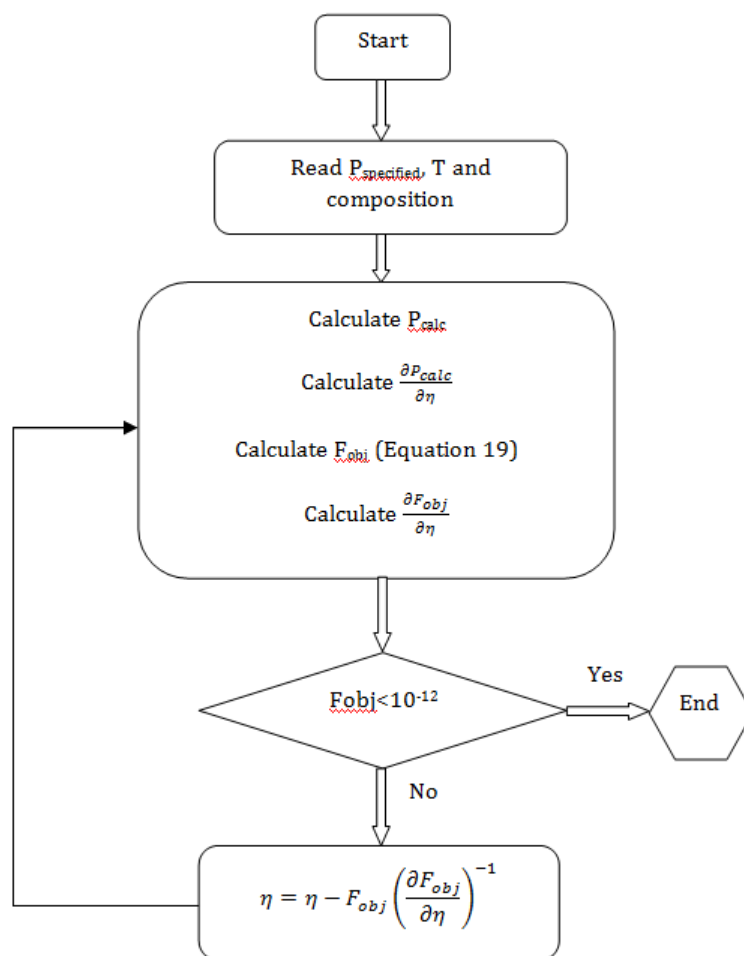


Figure 2. Calculation procedure for determining η by Newton's method.

2.4. Molecular Model for Pure Components

Before applying the models to binary mixtures, it is necessary to obtain the molecular parameters of the pure compounds. CO₂ was modeled as a nonassociating substance. Thus the CO₂ molecule was represented by three molecular parameters: m : the segment number; σ : the segment diameter; ϵ/k : the segment energy parameter. The values of the model parameters for CO₂ were taken from the literature (Gross & Sadowski, 2001).

Two associating sites were considered for H₂S and the values of parameters were taken from the article by Tang and Gross (Tang & Gross, 2010) (see Table 1).

In this work, two strategies were considered to model densities of pure ILs. In strategy 1, ILs

were modeled without any specific interactions other than hard-chain and dispersion forces. In this case, the three pure-component parameters (m , σ , ϵ/k) were obtained by fitting pure-component data. In strategy 2, ILs were considered as self-associating molecules and two association sites were assigned to each ILs. The association interaction was allowed between two different sites of two IL molecules. In order to keep a minimum number of fitting parameters, the associating parameters (ϵ^{AiBj} and k^{AiBj}) assumed to be constant for the both considered ILs ($\epsilon^{AiBj}/k = 5000$ K and $k^{AiBj} = 0.1$) (Ji et al., 2012). These two sets of parameters were compared to determine whether the associating contribution of ILs should be taken into account.

Table 1. PC-SAFT parameters for CO₂ and H₂S used in this work.

	Mw	m	$\sigma(\text{\AA})$	ϵ/k (K)	k^{AiBj}	ϵ^{AB}/k (K)
CO ₂	44.0	2.785	2.073	169.21	-	-
H ₂ S	34.08	1.649	3.055	229.84	0.001	536.6

3. Results and Discussion

3.1. ILs Parameters

The molecular parameters of PC-SAFT for pure ILs were determined, using the available experimental densities data (Gardas et al., 2007; Taguchi, 2009), to minimize the following objective function (OF):

$$OF = \frac{1}{N} \sum_{i=1}^N \left(\frac{\rho_i^{cal} - \rho_i^{exp}}{\rho_i^{exp}} \right)^2 \quad (18)$$

which takes into account the deviations between calculated and experimental liquid densities. N is the number of experimental data. The results for the molecular parameters for two strategies and the absolute relative deviations ARD (%) in the density are provided in Table 2. ARD (%) is defined as:

$$ARD = \frac{100}{N} \sum_{i=1}^N \frac{|\rho_i^{cal} - \rho_i^{exp}|}{\rho_i^{exp}} \quad (19)$$

The trend of deviations for each family of ILs is shown in Figure 3. According to the results, there is a good improvement by considering ILs as self-associating Compounds. Therefore, the associating contribution should be taken into account in order to accurately correlate the properties of ILs.

Then, the PC-SAFT equation was evaluated in the representation of the thermodynamic properties of pure ILs such as temperature-dependent density. The resulting density-temperature diagrams are shown in Figure 4. We can thus conclude that the density is well represented by the PC-SAFT equation of state.

Table 2. Optimized PC-SAFT model parameters for pure ILs.

	Mw	m	$\sigma(\text{\AA})$	ε/k (K)	κ^{AiBj}	ε_{AB}/k (K)	ARD%
[C ₈ -mim][PF ₆]	340.29	4.936	4.489	527.228	-	-	0.116
		5.239	4.381	440.646	0.1	5000	0.040
[C ₈ -mim][Tf ₂ N]	475.48	7.277	4.281	428.321	-	-	0.102
		9.829	3.831	334.191	0.1	5000	0.050

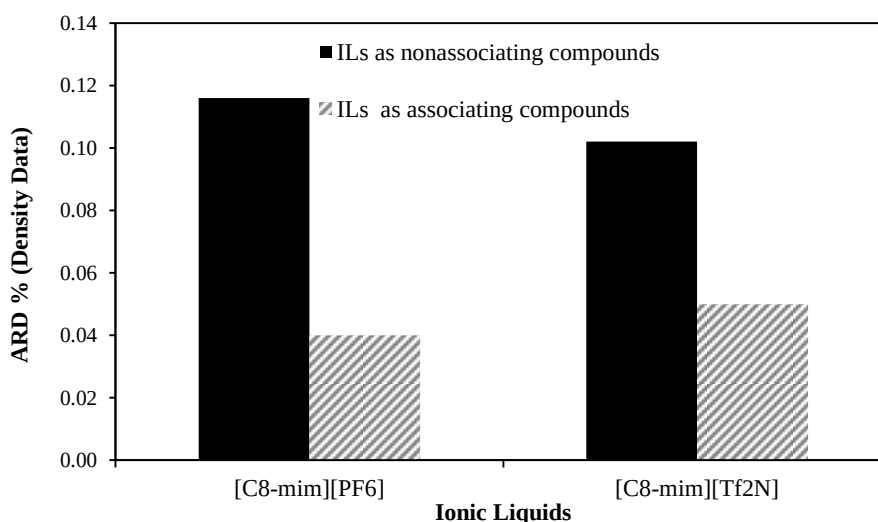


Figure 3. Absolute relative deviations of density for the studied ionic liquids.

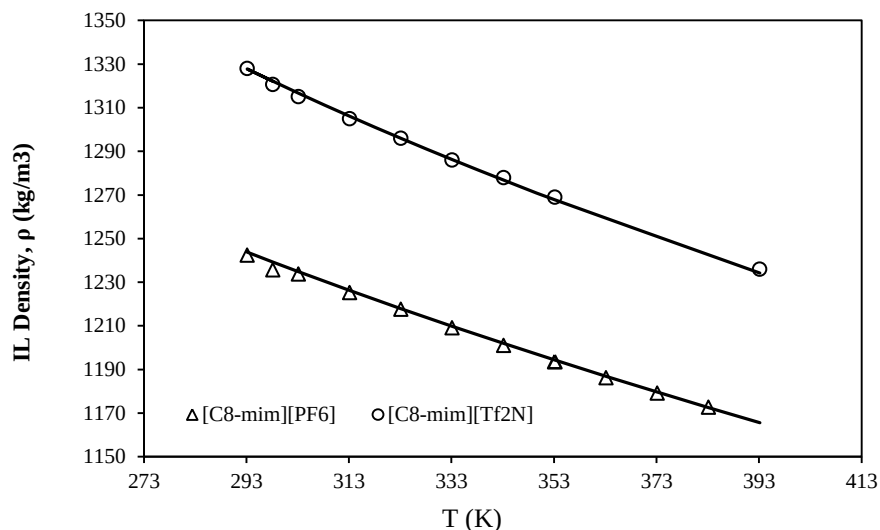


Figure 4. Density vs. temperature diagrams for ILs considered as associating compounds based on calculations using the PC-SAFT model. Symbols are experimental data.

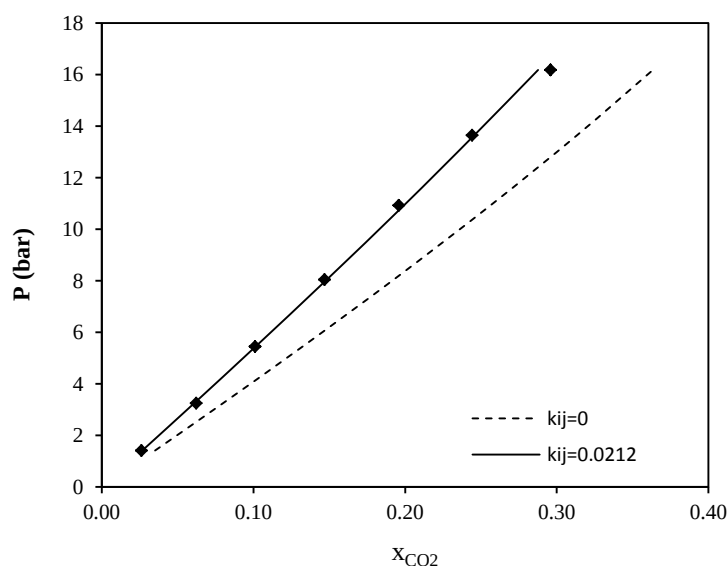


Figure 5. Effect of interaction parameter: Symbols represent experimental solubility data of CO₂ in [C₈-mim][PF₆] at T=323.15 K. Dash line, $k_{ij} = 0$; solid line, k_{ij} fitted with experimental data.

3.2. Binary Mixtures

We studied the solubility of CO₂ and H₂S in two ionic liquids [C₈-mim][Tf₂N] and [C₈-mim][PF₆] using the PC-SAFT model. The use of the PC-SAFT EoS for mixtures requires knowledge of the binary interaction parameter k_{ij} . This parameter is generally fitted on experimental VLE data. It was demonstrated that better results are obtained when the interaction parameter is temperature-dependent and different from 0 (or 1) (Chen et al., 2012; Ji et al., 2012). As an example, results for {[C₈-mim][PF₆] + CO₂} at T = 323 K with k_{ij} constant ($k_{ij} = 0$) and k_{ij} fitted by VLE data are shown in Figure 5. A large difference was found for $k_{ij} = 0$ as compared to the experimental data.

Therefore, in this work, the k_{ij} parameters of various binary mixtures containing ILs and acid gases were determined to minimize the deviations between calculated and experimental VLE data. A flash algorithm (Figure 6) was used to perform VLE calculations [for a selected binary system and a given T and P, we have found the compositions of the liquid (x) and gas (y) phases in equilibrium].

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parameter is generally fitted on experimental VLE data. It was demonstrated that better results are obtained when the interaction parameter is temperature-dependent and different from 0 (or 1) (Chen et al., 2012; Ji et al., 2012). As an example, results for $\{[C_8\text{-mim}][PF_6] + CO_2\}$ at $T = 323\text{ K}$ with k_{ij} constant ($k_{ij} = 0$) and k_{ij} fitted by VLE data are shown in Figure 5. A large difference was found for $k_{ij} = 0$ as compared to the experimental data. Therefore, in this work, the k_{ij} parameters of various binary mixtures containing ILs and acid gases were determined to minimize the deviations between calculated and experimental VLE data. A flash algorithm (Figure 6) was used to perform VLE calculations [for a selected binary system and a

given T and P , we have found the compositions of the liquid (x) and gas (y) phases in equilibrium].

Available experimental data (Jalili et al., 2012; Safavi et al., 2013) was used to optimize binary interaction parameters. For all binary mixtures, the obtained solubility isotherms calculated by PC-SAFT model compared with the experimental data are shown in Figures 7,8. It can be seen that the calculated values are in good agreement with the experimental data. The solubilities of hydrogen sulfide and carbon dioxide in $[C_8\text{-mim}][PF_6]$ and $[C_8\text{-mim}][Tf_2N]$ decreases by increasing the temperature and their solubility behaviour is typical of physical solvents as shown in Figures 7,8.

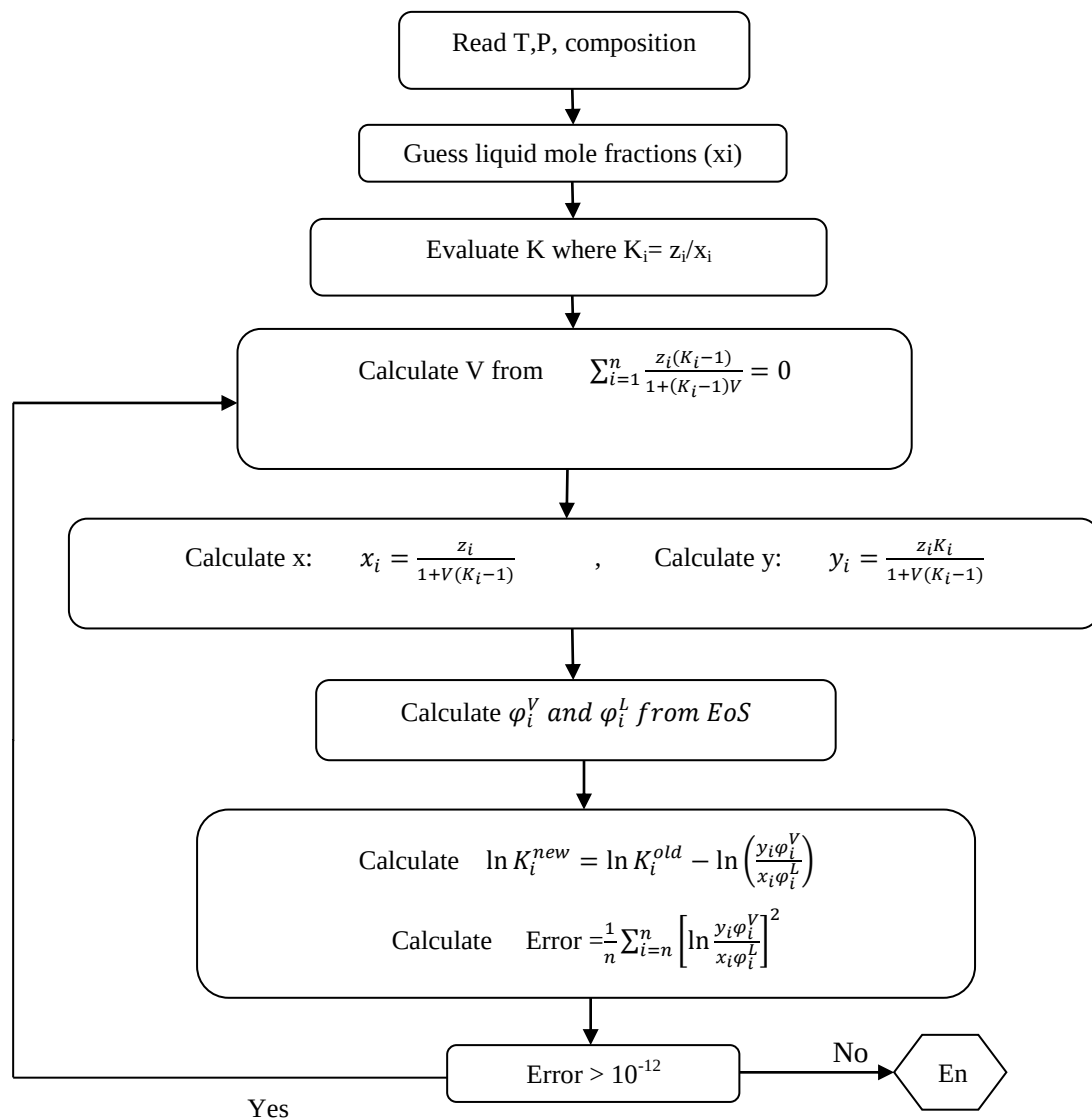


Figure 6. Calculation procedure in a typical TP flash algorithm.

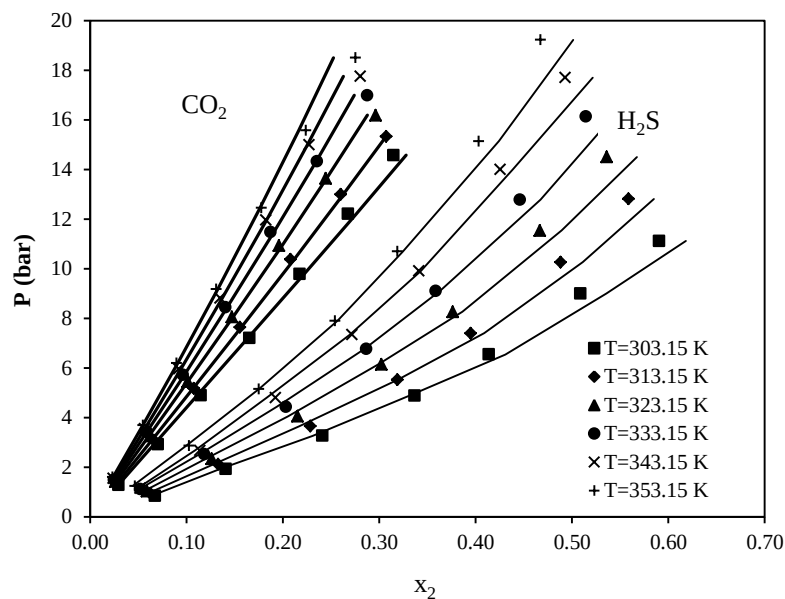


Figure 7. Comparison between experimental solubility data and those calculated by the PC-SAFT model for [C₈-mim][PF₆]. x_2 is the mole fraction of CO₂ / H₂S in ionic liquid.

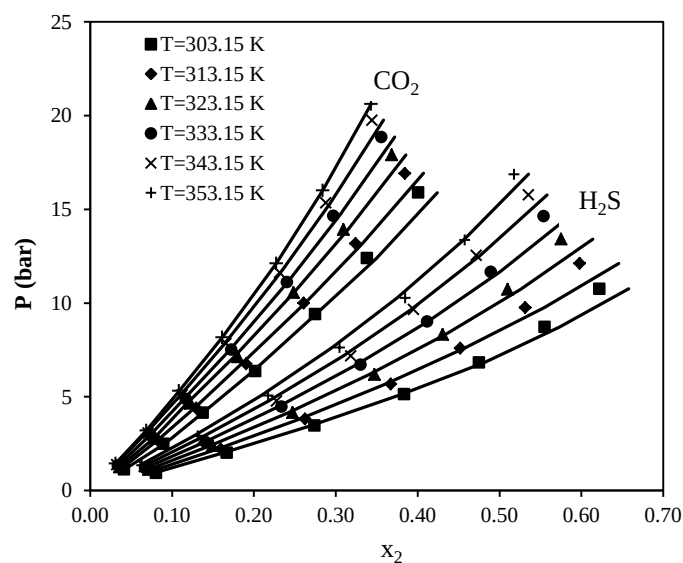


Figure 8. Comparison between experimental solubility data and those calculated by the PC-SAFT model for [C₈-mim][Tf₂N]. x_2 is the mole fraction of CO₂ / H₂S in ionic liquid.

In Table 3 values of the optimized binary interaction parameters at different temperatures, the average of relative deviations (ARD%) in the solubility calculations and average of ARD% for each binary system in all temperature range (303.15-353.15 K) are reported. The temperature-dependency of k_{ij} parameters are shown in Figure 9. As can be seen in Table 3, accurate results are obtained using PC-SAFT model and this model is capable of accurately modeling the solubility of CO₂ and H₂S in ILs. In all cases, good agreement between experimental VLE data with the calculated values obtained.

According to the results in Table 3 the PC-SAFT with temperature dependent k_{ij} values can reliably describe the solubility of CO₂ and H₂S in ILs for the considered systems with ARD values less than 10%. The ARD for [C₈-mim][PF₆]-H₂S is higher than for the other systems studied in this work.

Considering adjustable binary parameters k_{ij} between the gas and IL 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.

In our previous works (Jalili et al., 2012; Safavi et al., 2013) the obtained experimental solubility data were modelled by using two distinct correlation equations, i.e. the extended Henry's law combined with the Pitzer activity coefficient model for electrolytes (Rard, Platford, & Pitzer, 1991) and a generic Redlich-Kwong type EoS proposed by Shiflett and Yokozeki for gas/ionic liquid systems (Shiflett & Yokozeki, 2007). In Table 4 ARD% and MRD% of correlated mole fractions by using of the three models, Pitzer, RK and PC-SAFT, are compared with each other. Table 4 shows that the Pitzer's model correlates the solubility data of CO₂ and H₂S in ILs with a higher accuracy than the RK and PC-SAFT Eos.

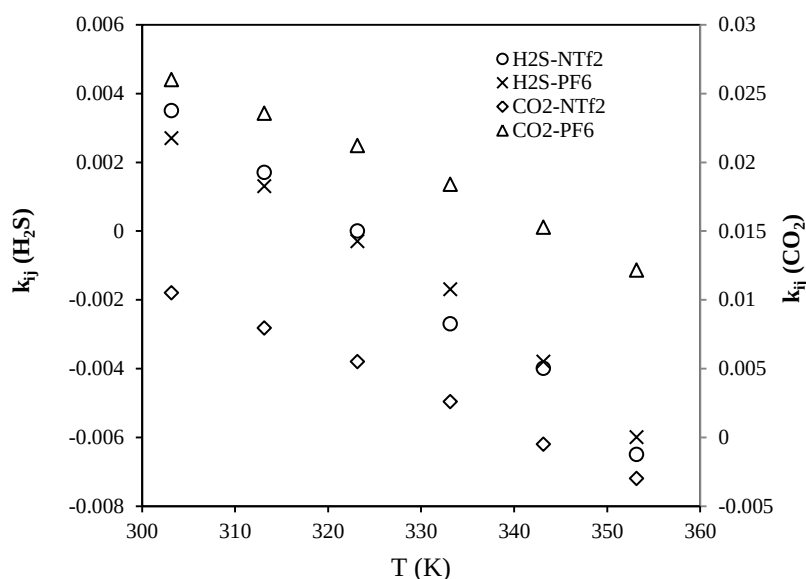


Figure 9. Temperature- k_{ij} for different ILs binary systems with H₂S and CO₂.

Table 3. k_{ij} Interaction parameters at different temperatures. MRD: Maximum Relative Deviation.

ILs	T (K)	CO ₂		H ₂ S	
		k_{ij}	ARD%	k_{ij}	ARD%
[C ₈ -mim][PF ₆]	303.15	0.0260	2.796	0.0027	4.219
	313.15	0.0236	1.067	0.0013	3.707
	323.15	0.0212	1.421	-0.0003	4.006
	333.15	0.0184	2.013	-0.0017	3.323
	343.15	0.0153	2.459	-0.0038	2.721
	353.15	0.0122	2.962	-0.006	3.088
	Average of ARD%		2.120		3.511
	MRD (%)		8.219		5.843
[C ₈ -mim][Tf ₂ N]	303.15	0.0105	1.844	0.0035	2.600
	313.15	0.0080	2.466	0.0017	3.388
	323.15	0.0061	1.986	0.0000	2.546
	333.15	0.0026	2.063	-0.0023	1.884
	343.15	-0.0005	2.239	-0.0040	3.048
	353.15	-0.0030	1.975	-0.0065	3.046
	Average of ARD%		2.096		2.752
	MRD (%)		5.879		7.920

Table 4. Comparison between average relative deviations (ARD%) and maximum relative deviations (MRD%) by Pitzer and RK models from previous works (Jalili et al., 2012; Safavi et al., 2013) and PC-SAFT model.

System	Pitzer model		RK EoS		PC-SAFT EoS	
	ARD%	MRD%	ARD%	MRD%	ARD%	MRD%
CO ₂ /[C ₈ -mim][PF ₆]	1.77	5.3	1.83	8.5	2.12	8.2
H ₂ S/[C ₈ -mim][PF ₆]	2.27	5.9	2.36	6.4	3.51	5.8
CO ₂ /[C ₈ -mim][Tf ₂ N]	0.76	3.2	3.1	7.9	2.09	5.9
H ₂ S/[C ₈ -mim][Tf ₂ N]	1.0	2.8	1.7	6.9	2.75	7.9

4. Conclusion

In this work, the solubilities of H₂S and CO₂ in selected ionic liquids ([C₈-mim][PF₆] and [C₈-mim][Tf₂N]) have been accurately modeled using equations of state based on the SAFT theory. The PC-SAFT parameters of pure ILs were estimated from component density data. The investigation shows that the model can predict qualitatively the solubility of CO₂ and H₂S in these ILs at temperatures from 303.15 to 353.15 K and pressures up to 20 bar. The PC-SAFT EoS was also used with success in the correlation of the experimental data. By applying temperature-dependent interaction parameters (k_{ij}) it was possible for the considered systems to predict the experimentally observed temperature-dependence of gas solubilities in ILs (decreasing solubility with increasing temperature). Temperature-dependent k_{ij}

values were required in order to represent quantitatively the gas solubility at different temperatures. We showed that PC-SAFT EoS is able to reproduce the solubility of CO₂ and H₂S in imidazolium-based ILs in a wide range of temperatures and pressures.

5. References

- Ashrafmansouri, S.-S., & Raeissi, S. (2012). Modeling gas solubility in ionic liquids with the SAFT- γ group contribution method. *The Journal of Supercritical Fluids*, 63, 81-91.
- Bier, M., & Dietrich, S. (2010). Vapour pressure of ionic liquids. *Molecular Physics*, 108(2), 211-214. doi: 10.1080/00268971003604609
- Camper, D., Bara, J. E., Gin, D. L., & Noble, R. D. (2008). Room-temperature ionic liquid-amine solutions: Tunable solvents for

- efficient and reversible capture of CO₂. *Industrial & Engineering Chemistry Research*, 47(21), 8496-8498.
- Chen, Y., Mutelet, F., & Jaubert, J.-N. (2012). Modeling the Solubility of Carbon Dioxide in Imidazolium-Based Ionic Liquids with the PC-SAFT Equation of State. *The Journal of Physical Chemistry B*, 116(49), 14375-14388. doi: citeulike-article-id:12274367
doi: 10.1021/jp309944t
- Gardas, R., Freire, M., Carvalho, P., Marrucho, I., Fonseca, I., Ferreira, A., & Coutinho, J. (2007). PpT Measurements of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data*, 52(5), 1881-1888. doi: citeulike-article-id:2553144
doi: 10.1021/je700205n
- Gross, J., & Sadowski, G. (2001). Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Industrial & Engineering Chemistry Research*, 40(4), 1244-1260.
- Jalili, A. H., Safavi, M., Ghotbi, C., Mehdizadeh, A., Hosseini-Jenab, M., & Taghikhani, V. (2012). Solubility of CO₂, H₂S, and their mixture in the ionic liquid 1-octyl-3-methylimidazolium bis (trifluoromethyl) sulfonylimide. *The Journal of Physical Chemistry B*, 116(9), 2758-2774.
- Ji, X., & Adidharma, H. (2010). Thermodynamic modeling of CO₂ solubility in ionic liquid with heterosegmented statistical associating fluid theory. *Fluid Phase Equilibria*, 293(2), 141-150.
- Ji, X., Held, C., & Sadowski, G. (2012). Modeling imidazolium-based ionic liquids with ePC-SAFT. *Fluid Phase Equilibria*, 335, 64-73.
- Karadas, F., Atilhan, M., & Aparicio, S. (2010). Review on the use of ionic liquids (ILs) as alternative fluids for CO₂ capture and natural gas sweetening. *Energy & Fuels*, 24(11), 5817-5828.
- Karakatsani, E. K., Economou, I. G., Kroon, M. C., Peters, C. J., & Witkamp, G.-J. (2007). tPC-PSAFT modeling of gas solubility in imidazolium-based ionic liquids. *The Journal of Physical Chemistry C*, 111(43), 15487-15492.
- Kohl, A., & Nielsen, R. (1997). Gas Purification, fifth e d: Gulf Publishing Company, Texas.
- Llovel, F., Marcos, R., MacDowell, N., & Vega, L. (2012). Modeling the absorption of weak electrolytes and acid gases with ionic liquids using the soft-SAFT approach. *The Journal of Physical Chemistry B*, 116(26), 7709-7718.
- Muldoon, M. J., Aki, S. N., Anderson, J. L., Dixon, J. K., & Brennecke, J. F. (2007). Improving carbon dioxide solubility in ionic liquids. *The Journal of Physical Chemistry B*, 111(30), 9001-9009.
- NIST Scientific and Technical Databases, Thermophysical Properties of Fluid Systems. (2014). 2014, from <http://webbook.nist.gov/chemistry/fluid/>
- Raeissi, S., Florusse, L., & Peters, C. (2011). Hydrogen solubilities in the IUPAC ionic liquid 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide. *Journal of Chemical & Engineering Data*, 56(4), 1105-1107.
- Rahmati-Rostami, M., Ghotbi, C., Hosseini-Jenab, M., Ahmadi, A. N., & Jalili, A. H. (2009). Solubility of H₂S in ionic liquids [hmim][PF₆], [hmim][BF₄], and [hmim][Tf₂N]. *The Journal of Chemical Thermodynamics*, 41(9), 1052-1055.
- Rard, J., Platford, R., & Pitzer, K. S. (1991). Activity Coefficients in Electrolyte Solutions. *CRC Press, Boca Raton, FL*, 209-277.
- Safavi, M., Ghotbi, C., Taghikhani, V., Jalili, A. H., & Mehdizadeh, A. (2013). Study of the solubility of CO₂, H₂S and their mixture in the ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate: Experimental and modelling. *The Journal of Chemical Thermodynamics*, 65, 220-232.
- Sakhaeina, H., Jalili, A. H., Taghikhani, V., & Safekordi, A. A. (2010). Solubility of H₂S in Ionic Liquids 1-Ethyl-3-methylimidazolium Hexafluorophosphate ([emim][PF₆]) and 1-Ethyl-3-methylimidazolium Bis (trifluoromethyl) sulfonylimide ([emim][Tf₂N]). *Journal of Chemical & Engineering Data*, 55(12), 5839-5845.
- Shiflett, M. B., & Yokozeki, A. (2007). Solubility of CO₂ in room temperature ionic liquid [hmim][Tf₂N]. *The Journal of Physical Chemistry B*, 111(8), 2070-2074.
- Taguchi, R. M., H.; Smith, R.L.J. (2009). High-Pressure Densities of [Cn-mim][PF₆] and [Cnmim][BF₄]. *Journal of Chemical and Engineering Data*, 54, 22-27.
- Tang, X., & Gross, J. (2010). Modeling the phase equilibria of hydrogen sulfide and carbon dioxide in mixture with hydrocarbons and water using the PCP-SAFT equation of state. *Fluid Phase Equilibria*, 293(1), 11-21.
- Vega, L. F., Vilaseca, O., Llovel, F., & Andreu, J. S. (2010). Modeling ionic liquids and the solubility of gases in them: Recent

advances and perspectives. *Fluid Phase Equilibria*, 294(1), 15-30.

Wasserscheid, P., & Welton, T. (2008). *Ionic liquids in synthesis* (Vol. 1): Wiley Online Library.