



Modeling H₂S and CO₂ solubility in ionic liquids using the CPA equation of state through a new approach



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ABSTRACT

In this communication, the solubility of two single gases, hydrogen sulfide and carbon dioxide, in the fourteen ionic liquids ([emim][eFAP], [emim][EtSO₄], [emim][OTf], [emim][Tf₂N], [bmim][BF₄], [bmim][PF₆], [hmim][PF₆], [hmim][Tf₂N], [omim][PF₆], [omim][Tf₂N], [HOemim][BF₄], [HOemim][OTf], [HOemim][PF₆] and [HOemim][Tf₂N]) are modeled using the CPA EoS through a new approach. First, the critical temperature of ionic liquids was estimated using modified Lydersen-Joback-Reid method. Then, Using the CPA EoS, the pure parameters of ionic liquids were obtained through optimization on both of H₂S and CO₂ solubility data in ionic liquids as well as experimental liquid density data of ionic liquids. In next step, the interaction parameters between the ionic liquids and H₂S as well as the ionic liquids and CO₂ were calculated. Using the obtained pure parameters of the ionic liquids and the interaction parameters, the vapor-liquid equilibrium data were tested for thermodynamic consistency. Also, the proposed systems were modeled by the SRK EoS and the obtained results were compared by the obtained ones by the CPA EoS. For all the studied systems, the percent average absolute deviation (AAD %) was lower than 10% that shows good agreement between the experimental and calculated values.

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1. Introduction

Recently researchers have focused on ionic liquids and have published many papers regarding investigation of ionic liquids' properties and their applications in different fields. Ionic liquids are low melting point components that contain bulky organic cations and polyatomic organic or inorganic anions. Low vapor pressure and high thermal stability are their other specifications which made them applicable for a variety of industrial applications such as electrochemical applications [1], as solvents for synthesis and catalysis [2], as media for clean liquid-liquid extraction [3] and CO₂ capture [4].

Hydrogen sulfide and carbon dioxide are the main acid gas impurities of natural gas that should be separated in gas sweetening process. The main method of acid gas removing is using aqueous solutions of alkanolamines such as mono-ethanolamine, di-ethanolamine, methyldiethanolamine, tri-ethanolamine and di-glycolamine [5]. Using alkanolamines has some disadvantages like alkanolamines vaporization or degradation. Not only ionic

liquids can cover these problems, but also they show higher absorption in comparison with alkanolamines [6].

To simulate and control process of gas solubility in ionic liquids, thermodynamic modeling is necessary to determine phase behavior of such systems. In the past years, a variety of thermodynamic models have been used to correlate and predict physical properties and phase behavior of systems containing ionic liquids. Some of these solubility studies are summarized in Table 1.

In the present study, the solubility of two single gases H₂S and CO₂ in fourteen ionic liquids ([emim][eFAP], [emim][EtSO₄], [emim][OTf], [emim][Tf₂N], [bmim][BF₄], [bmim][PF₆], [hmim][PF₆], [hmim][Tf₂N], [omim][PF₆], [omim][Tf₂N], [HOemim][BF₄], [HOemim][OTf], [HOemim][PF₆] and [HOemim][Tf₂N]) are modeled using the CPA and the SRK equations of state. The first step was calculating the critical temperature of the ionic liquids using modified Lydersen-Joback-Reid [27–29]. Then, the pure parameters of the CPA EoS for the ionic liquids were calculated by fitting of the model on the experimental solubility data of H₂S and CO₂ in the ionic liquids and also experimental liquid density data of the ionic liquids. In the next step, the interaction parameters between the gases and the ionic liquids were obtained. Also, the consistency of the proposed experimental solubility data was investigated by

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Table 1
Proposed equations of state for modeling systems containing ionic liquid.

EoS	Experimental points	Ionic liquid	Ref.
PR	CO ₂ Solubility	[emim][Tf ₂ N], [bmim][Tf ₂ N], [hmim][Tf ₂ N], [omim][Tf ₂ N]	[7]
	CO ₂ & CHF ₃ Solubility	[emim][PF ₆]	[8]
	Propionaldehyde & Valeraldehyde Solubility	[emim][EtSO ₄]	[9]
	Tetrafluoroethane Solubility	[hmim][Tf ₂ N]	[10]
RK	CO ₂ Solubility	[bmim][BF ₄], [bmim][PF ₆]	[11]
	Ammonia Solubility	[bmim][BF ₄], [bmim][PF ₆], [hmim][Cl], [emim][Tf ₂ N]	[12]
	Ammonia Solubility	[emim][Ac], [emim][SCN], [emim][EtSO ₄], [DMEA][Ac]	[13]
	CO ₂ Solubility	[bmim][Ac]	[14]
Lattice Fluid	CO ₂ Solubility	[bmim][PF ₆], [hmim][PF ₆], [emim][BF ₄], [hmim][BF ₄], [emim][Tf ₂ N], [hmim][Tf ₂ N]	[15]
	CO ₂ & C ₃ H ₆ Solubility	[hmim][Tf ₂ N]	[16]
	Aromatic Compounds Solubility	[bmim][PF ₆]	[17]
	Aromatic Compounds Solubility	[bmim][BF ₄], [bmim][Cl], [bmim][PF ₆], [bmim][Tf ₂ N]	[18]
SAFT Types	H ₂ S Solubility	[bmim][PF ₆], [hmim][PF ₆], [bmim][BF ₄], [hmim][BF ₄], [bmim][NTf ₂], [hmim][NTf ₂]	[19]
	CO ₂ Solubility	[emim][BF ₄], [bmim][BF ₄], [hmim][BF ₄], [omim][BF ₄], [emim][PF ₆], [bmim][PF ₆], [hmim][PF ₆], [omim][PF ₆]	[20]
	CO, O ₂ & CHF ₃ Solubility	[bmim][PF ₆]	[21]
	CO ₂ Solubility	[bmim][BF ₄], [hmim][BF ₄], [omim][BF ₄]	[22]
CPA	CO ₂ Solubility	[emim][Tf ₂ N] and [bmim][Tf ₂ N]	[23]
	CO ₂ Solubility	[bmim][Tf ₂ N], [dmim][Tf ₂ N], [Pyrr _{4,1}][Tf ₂ N], [N _{4,1,1,1}][Tf ₂ N], [N _{1,8,8,8}][Tf ₂ N], [N _{6,6,6,14}][Tf ₂ N]	[24]
	CHF ₃ , CH ₂ F ₂ & CH ₃ F Solubility	[bmim][Tf ₂ N], [P _{6,6,6,14}][Tf ₂ N], [m-2-HEA][Pr], [m-2-HEA][P]	[25]
	CHF ₃ , CH ₂ F ₂ & CH ₃ F Solubility	[P _{6,6,6,14}][Cl], [P _{4,4,4,1}][C ₁ SO ₄], [P _{4,4,4,2}][Et ₂ PO ₄]	[26]

using the presented method by Valderrama et al. that is designed for binary mixtures containing ionic liquid [30]. Finally, the obtained results by the CPA EoS were compared with the obtained ones by the SRK EoS [31]. Critical temperature, critical pressure and acentric factor of ionic liquids were estimated by Lydersen-Joback-Reid method and are presented in Table 2.

2. Thermodynamic framework

2.1. CPA EoS

The CPA EoS has been widely used by researchers for modeling associating systems. It combines the SRK EoS with Wertheim's theory. Physical interactions are taken into account by the SRK term and hydrogen bonding interactions are proposed by Wertheim's theory.

$$\tilde{a}_{CPA}^{res} = \tilde{a}_{SRK}^{res} + \tilde{a}_{Assoc}^{res} \quad (1)$$

where $\tilde{a} = A/nRT$ and A, n, R and T are Helmholtz free energy, total number of moles, the gas constant and temperature [32–34].

Table 2
Critical properties of the ionic liquids calculated by the Lydersen-Joback-Reid method.

IL	M (mol/gr)	T _c (K)	P _c (bar)	ω
[emim][eFAP]	556.18	759.7	10.0	0.8743
[emim][EtSO ₄]	236.29	1067.5	40.5	0.3744
[emim][OTf]	260.23	992.3	35.8	0.3255
[emim][Tf ₂ N]	391.30	1249.3	32.7	0.2157
[bmim][BF ₄]	226.03	643.2	20.4	0.8877
[bmim][PF ₆]	284.19	719.4	17.3	0.7917
[hmim][PF ₆]	312.24	764.9	15.5	0.8697
[hmim][Tf ₂ N]	447.41	1292.8	23.9	0.3893
[omim][PF ₆]	340.29	810.8	14.0	0.9385
[omim][Tf ₂ N]	475.48	1317.8	21.0	0.4811
[HOemim][BF ₄]	213.97	691.9	24.7	1.1643
[HOemim][OTf]	276.23	1059.1	36.7	0.6526
[HOemim][PF ₆]	272.13	766.6	20.2	1.0368
[HOemim][Tf ₂ N]	407.30	1297.0	33.1	0.5171

2.2. VLE calculation

In this work, the pure parameters of ionic liquids are obtained through fitting on the reported solubility data of two component systems. In the calculations, the presence of ionic liquid in vapor phase is ignored and vapor phase is considered as pure gas. The variables in the calculations were vapor and liquid densities.

Equilibrium criteria for H₂S-IL system is given as follows:

$$\begin{cases} \mu_{H_2S}^v = \mu_{H_2S}^l \\ P^v = P^l \end{cases} \quad (2)$$

and for CO₂-IL system:

$$\begin{cases} \mu_{CO_2}^v = \mu_{CO_2}^l \\ P^v = P^l \end{cases} \quad (3)$$

For solving each set of equation, Newton-Raphson method was used as follow:

$$Y_{n+1} = Y_n - \Omega J^{-1} G \quad (4)$$

In above relation, Y, G, J and Ω are the variables vector, the equations vector, the Jacobin matrix and the damping factor, respectively. For all cases by setting Ω to 0.1, it is possible to solve each set of equation [5].

2.3. Consistency test

The consistency method presented by Valderrama et al. was proposed for assessing the experimental data [30]. The method is originated from the Gibbs-Duhem equation and contains two terms; experimental term (A_p) and modeling term (A_φ) that are calculated by the following relations:

$$A_p = \int \frac{1}{P x_2} dP \quad (5)$$

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