Correlation of CO_2 Solubility in [Bmim][$C(CN)_3$] Ionic Liquid Utilizing a Modified form of SRK EoS

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Abstract
A modified form of the well-known SRK EoS (mSRK EoS), was employed to correlate CO_2 solubility in ionic liquid 1-butyl-3-methylimidazolium tricyanomethane ([Bmim][$C(CN)_3$]). This EoS was developed by Shiflett and Yokozeki (Fluid Phase Equilibria 294, 105–113 (2010)) to model the IL-containing systems. There exist four adjustable parameters for pure components in addition to five binary interaction coefficients in this model. In the present work, the "Modified Lydersen-Joback-Reid" method was also implemented to estimate the physical properties of [Bmim][$C(CN)_3$].
The results show the excellent performance of the model to correlate CO_2 solubility in [Bmim][$C(CN)_3$] so that the overall AAD% equal to 1.86 obtained.

Keywords: [Bmim][$C(CN)_3$], Ionic Liquid, CO_2 solubility, mSRK EoS, VLE

Introduction
An increased scope is to develop new absorbents with high CO_2 cyclic capacity, low reaction heat and low water content for improving the energy efficiency. It is estimated that 2% energy efficiency can be improved by saving 1 GJ/t CO_2 regeneration energy [1]. An almost new category of such solvents, known as Room Temperature Ionic Liquids (RTILs), are consisting of an organic cation and an inorganic or organic anion so that depending on their application, different cations and anions can be utilized [2]. A key factor in the appraisal of ILs for potential application in gas sweetening systems, is knowing about the solubility of gases at different temperatures and pressures [3]. Therefore, it is definitely worth developing predictive methods for estimating the properties of such systems over a varied range of conditions. For the sake of the associating nature of the present components, phase behavior of these systems is too far from ideality [4].
Afsharpour [5] implemented the RETM, and SRK-CPA EoS to model H2S solubility in [C_2mim][Ace], and [C_6mim][Ace] ILs. The results show AADs% below 2 for pure ILs. Also, average deviations equal to 12.44 and 4.75 for the [hmim][Ace] and [emim][Ace] were obtained, respectively. Furthermore, Afsharpour and kheiri [6-9], modeled the CO_2 and H_2S and their mixtures absorption in ILs [Omim][Tf_2N], [C_4mim][$MeSO_4$], [C_8mim][PF_6] and [C_2mim][PF_6] employing SRK-CPA EoS with AADs% below 20 for all the ILs.

Ji et al. [10] used electrolyte version of PC-SAFT EoS to investigate the density and CH_4 and CO_2 solubilities in imidazolium-based ILs applying different modeling strategies. The ion-based strategy including a Debye–Hückel Helmholtz energy term to represent the ionic interactions was followed. A fitting error of 0.14% on average was obtained in this work.
The solubility of CO_2, CO, O_2, and CHF_3 in imidazolium-based ILs was represented with truncated Perturbed-Chain Polar SAFT (tPC-PSAFT) EoS by Karakatsani et al. [11]. Their reults show that in all cases, the agreement between tPC-PSAFT correlation and experimental data for mixtures is very good. Modeling of CO_2 solubility in BF_4^-, PF_6^-, and Tf_2N-imidazoliumbased ILs as well as H_2 and Xe in Tf_2N-imidazolium-based ILs using soft-SAFT EoS were studied by Andreu and Vega [12,13].
Yokozeki and Schiflett [14], developed a ternary equation of state (EoS) model for the CO_2/H_2S/[bmim][PF_6] system in order to understand the separation of these gases using room-temperature ionic liquids (RTILs). The presentrd model is based on a generic RK (Redlich-Kwong) EOS, with empirical interaction parameters for each binary system.
In this work, 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.
This communication presents the simulation results for CO_2 solubility in 1-butyl-3-methylimidazolium tricyanomethane ([Bmim][$C(CN)_3$]) ionic liquid using a modified form of the SRK EoS.

Modified SRK Equation of States (mSRK EoS)
A modified form of the generalized Redlich-Kwong EoS for ILs presented by Yokozeki and Schiflett [14] was employed to correlate the solubility data. This model could be presented as below:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \tag{1}$$

$$a = \sum_{i,j=1}^{N} \sqrt{a_i a_j}\, f_{ij}(T)\left(1-k_{ij}\right)x_i x_j;\ a_i(T) = 0.427480\frac{R^2 T_{c_i}^2}{P_{c_i}}\alpha_i(T) \tag{2}$$

$$b = \frac{1}{2}\sum_{i,j=1}^{N}\left(b_i + b_j\right)\left(1-k_{ij}\right)\left(1-m_{ij}\right)x_i x_j;\ b_i = 0.08664\frac{RT_{c_i}}{P_{c_i}} \tag{3}$$

in which

$$\alpha(T) = \sum_{k=0}^{<3}\beta_k\left(\frac{T_c}{T} - \frac{T}{T_c}\right)^k \tag{4}$$

$$f_{ij}(T) = 1 + \frac{\tau_{ij}}{T} \tag{5}$$

$$k_{ij} = \frac{l_{ij}l_{ji}\left(x_i + x_j\right)}{l_{ji}x_i + l_{ij}x_j} \tag{6}$$

wherein the coefficients β_i, τ_{ij}, l_{ij}, l_{ji}, and m_{ij} are the adjustable parameters of the model. β_i are related to the pure components while others are utilized as binary interaction coefficients. βi parameters for H_2S have been reported in [14]. Moreover, for ILs, β_0 is considered equal to one and β_1 will be adjusted together with the other binary interaction coefficients. More details about the model can be found in [14].

Results and discussion

Critical Properties Estimation

To estimate the ionic liquid critical properties, we applied the "Modified Lydersen-Joback-Reid" method extended by Valderrama and Robles [15]. Following the model, boiling point, critical temperature, critical pressure, and acentric factor can be determined through the following relations, respectively.

$$T_b = 198.2 + \sum n\Delta T_{bM} \tag{7}$$

$$T_c = \frac{T_b}{A_M + B_M \sum n\Delta T_M - \left(\sum n\Delta T_M\right)^2} \tag{8}$$

$$P_c = \frac{M}{\left[C_M + \sum n\Delta P_M\right]^2} \tag{9}$$

$$\omega = \frac{(T_b - 43)(T_c - 43)}{(T_c - T_b)(0.7T_c - 43)} \log\left[\frac{P_c}{P_b}\right] - \frac{(T_b - 43)}{(T_c - T_b)} \log\left[\frac{P_c}{P_b}\right] + \log\left[\frac{P_c}{P_b}\right] - 1 \tag{10}$$

In which ΔT_{bM}, ΔT_M, and ΔP_M are the parameters of the method which are presented in [15]. Moreover, $A_M = 0.5703$, $B_M = 1.0121$, $C_M = 0.2573$.
The estimated physical properties for [Bmim][$C(CN)_3$], have been reported in Table 1.

Table 1. Estimated physical properties for [Bmim][$C(CN)_3$].

Property	T_c (K)	T_b(K)	P_c (bar)	ω
[Bmim][$C(CN)_3$]	1184.98	915.06	21.136	0.9266

The pure components parameters

The pure parameters (β_0 to β_3) of CO_2 were extracted from the literature [14] and have been reported in Table 2. Moreover, parameter β_1 of the ILs is obtained through fitting the solubility data to the model and in the next section will discussed.

Table 2. Pure component parameters for the mSRK EoS.

Component	β_0	B_1	B_2	B_3	Ref.
[Bmim][$C(CN)_3$]	1.00000	1.08840	0.00000	0.00000	[This Work]
CO_2	1.00049	0.43866	-0.10498	0.06250	[14]

Binary systems

CO_2 solubility data in [Bmim][$C(CN)_3$] was taken from literature [16]. The ranges of tempreature and pressures of the utilized experimental data are between 288- 335 K and 0.01-10 MPa, respectively.
The parameters of binary interaction, k_{ij}s, for binary CO_2 + [Bmim][$C(CN)_3$] system, can be obtained through minimizing an objective function as equation (11):

$$OF = \frac{100}{N}\sum_{i}^{N}\frac{\left|\rho_i^{exp} - \rho_i^{calc}\right|}{\rho_i^{exp}} \quad (11)$$

In this way, binary parameters found as scaler values according to the **Table 3**.

Table 3. The binary interaction parameters and AAD% for solubility of CO_2 in [Bmim][C(CN)$_3$].

Binary System	Parameters					
	β_1	τ_{ij}	m_{ij}	l_{ij}	l_{ji}	AAD%
[Bmim][C(CN)$_3$] + CO_2	1.0884	0.0001	0.0694	-0.0744	34.2278	**1.86**

The overall AAD % for the IL+ CO_2 systems was calculated equal to 1.86. Moreover, **Figure 1** illustrates the experimental and calculated results at different temperatures. As one it can be deduced from the AAD% value and the figure, there exist a good agreement between experimental data and calculated results.

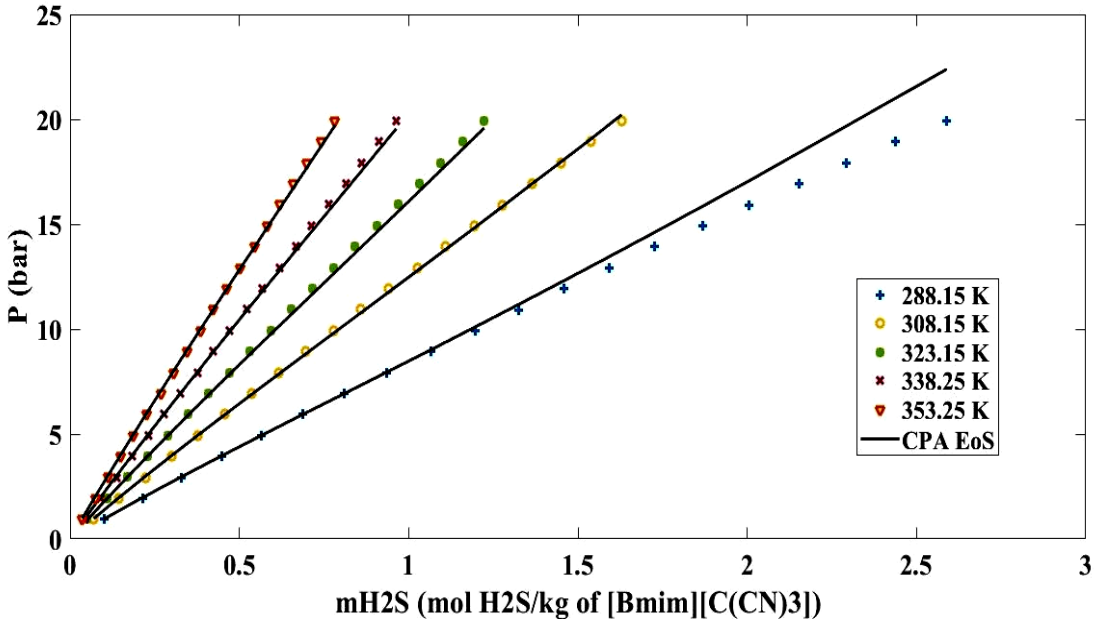

Figure 1. The experimental and calculated pressure versus CO_2 liquid mole fractions in ionic liquid [Bmim][C(CN)$_3$] at different temperatures.

Conclusions

Because of the non-ideal behavior of the ionic liquids, a simple equation of state will not be able to correlate such systems with acceptable deviations. Therefore, some new EoSs are needed to arrive at reasonable results. In this way, CO_2 solubility in ionic liquids [Bmim][C(CN)$_3$] was thermodynamically modeled utilizing the mSRK EoS. This modification has been applied to elevate the model applicability in non-ideal systems. In fact, the main reason to choose the mSRK is that the model combines accuracy and simplicity with respect to the more complex variants EoSs. Besides, the "Modified Lydersen-Joback-Reid" method was implemented to estimate the physical properties of [Bmim][C(CN)$_3$]. The overall AAD % in the binary system including CO_2+ [Bmim][C(CN)$_3$] is 1.86. As the results show, the show, very good accuracy to correlate CO_2 solubility in [Bmim][C(CN)$_3$] was achieved.

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