Thermodynamic modeling of CO_2 solubility in ionic liquid ([C_n-mim] [Tf_2N]; n=2, 4, 6, 8) with using Wong-Sandler mixing rule, Peng-Rabinson equation of state (EOS) and differential evolution (DE) method

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Abstract−Environmental and safety regulations are creating increasing interest in ionic liquids which have been used as alternative solvents for a wide range of industrial applications. Knowing the phase equilibrium of these materials is very important. In this study, the solubility of CO_2 in ionic liquid 1-alkyl-3 methylimidazolium bis (trifluoromethyl-sulfonyl) imide ([C_n-mim][Tf_2N]; n=2, 4, 6, 8) was probed with the Peng-Robinson (PR) equation of state (EOS) and Wong-Sandler mixing rule and van Laar model for excess Gibbs free energy. The differential evolution (DE) optimization method was applied to optimize the binary interaction parameter and activity coefficients. Moreover, binary interaction parameters and activity coefficients were presented as mathematical correlations that for various materials have depended on temperature. Our results showed that average absolute derivations of our proposed model were less than other existing models, and by using the aforesaid method better prediction could be achieved.

Key words: Phase Behavior, Carbon Dioxide, 1-Alkyl-3-methylimidazolium Bis (trifluoromethylsolfonyl) Imide, Wong-Sandler Mixing Rule, DE Optimization Method

INTRODUCTION

Ionic liquids (ILs) are usually defined as organic salts composed of large asymmetric organic cations and organic or inorganic anions with melting point at or below 100 °C. They tend to have extremely low vapor pressure, a broad liquid range of over 300 °C, and density greater than that of water, good thermal stability, low melting point, high ionic conductivity and large electrochemical window [1]. They are also good solvents for many organic and inorganic compounds. The chemical structure of [C_n-mim] [Tf_2N] is shown in Fig. 1.

The tunable property of ILs through an endless combination of cations and anions allows the design of solvents for the development of more efficient processes and products. Low melting point of ionic liquids is due to the asymmetry of the cation, whereas many of the physical properties of ionic liquids such as their miscibility with conventional solvents and hygroscopicity are considered to be determined by the nature of the anion. Ionic liquids have recently

gained great attention in a variety of chemical processes. A potential application of ionic liquids is for gas and liquid separation process. To select an efficient ionic liquid for use as a gas separation medium, it is necessary to know the solubility of the gas in ionic liquid phase. Thus, phase equilibrium properties of carbon dioxide in ILs are required [2-6]. These properties must be either experimentally obtained or semi-empirically correlated. One of the most common methods used for the correlation and prediction of phase equilibrium in mixture is use of equation of state (EOS). Common and industrial important equations of state are the cubic equations derived from van der Waals equation of state (VdW). Among the many cubic EOS of VdW types nowadays available, the model proposed by Peng and Robinson [7] is widely used because of its simplicity and flexibility [8]. Brennecke et al. reported that using supercritical fluid can help in extracting a desired solute from an ionic liquid [9,10]. Anthony et al. studied the solubility of some gases in [bmim] [PF_6] at different temperatures of 283, 298 and 323 K by means of gravimetric microbalance [11]. Shariati et al. and Kroon et al. studied the high pressure phase behavior of binary mixtures consisting of carbon dioxide and imadazolium- based ionic liquids (1-alkyl-3-methylimidazolium tetrafluoroborate and 1-alkyl-3-methylimidazolium hexafluorophosphate) over a wide range of solute concentrations and at pressure up to about 100 MPa [12-15]. Oh and Lee probed phase equilibrium carbon dioxide in ionic liquid 1-butyl-3-methyl-imidazolium bis (trifluoromethylsulfonyl) amide ([bmim][Tf_2N]) at high pressure up to about 30 MPa and in range of temperature between 298.15 °K to 343.15 °K [16]. Carvalho et al. using Peng-Robinson EOS and Wong-Sandler mixing rule investigated the phase behavior of the binary system of carbon dioxide (CO_2)+ 1-ethyl-3-methyl-imidazolium bis (trifluoromethylsulfonyl) imide ([C_2-mim][Tf_2N]) and CO_2+1-methyl-3-pentyl-imidazolium bis (trif-
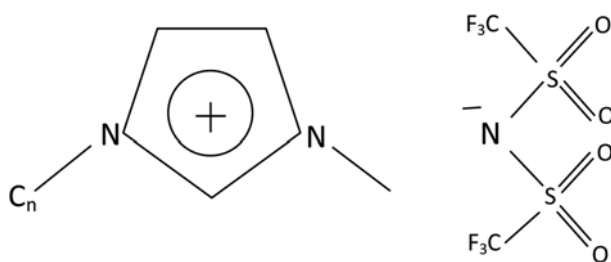

Fig. 1. Chemical structure of [C_n-mim][Tf_2N].

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luoromethylsulfonyl) imide ([C_5-mim][Tf_2N]) at temperatures up to 363 °K and pressures up 50 MPa [17]. Shin et al. reported solubility carbon dioxide (CO_2) in ionic liquids 1-alky l-3-methylimidazolium bis (trifluoromethanesulfonate) imide ([C_n-mim][TfO]; =2, 4, 6, 8) at pressure up to about 40 MPa and at temperatures between 303.85 and 344.55 °K with using the Peng-Robinson equation of state and Van der Waals (VdW) mixing rule [18]. Lachwa et al. studied liquid-liquid equilibria 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, ([C_6 mim][Tf_2N]) and alkan-1-ols $C_nH_{2n+1}OH$ with n=4, 5, 6 and 8 at a nominal pressure of 0.1 MPa up to 50 MPa [19] and finally Peters et al. probed the phase behavior CO_2 and imidazolium-base ionic liquids ([C_n-mim][PF_6]) and ([C_n-mim][BF_4]) at pressure up to about 100 MPa [20]. Shiflett and Yakozeki developed a ternary equation of state model for the CO_2/H_2S/[bmim][PF_6] system because of the separation of these gases by using of ionic liquids at room temperature. It is shown that present ionic liquid can affect the gaseous selectivity [21]. Carvalho et al. proved the solubility of CO_2 in phosphonium-based ionic liquids. A thermodynamic model based on the Peng-Robinson equation of state with Wong-Sandler mixing rule, using the UNIQUAC model for the activity coefficient [22]. Ren et al., studied (vapor+liquid) equilibrium, (vapor+liquid+liquid) equilibrium and (liquid+liquid) equilibrium of n-alkyl-3-imidazolium bis (trifluoromethylsulfonyl) amide ionic liquid with CO_2 at temperatures of (298.15, 323.15, 343.15) K and pressure up to 25 MPa. The Peng-Robinson equation of state with van der Waals 2-parameter mixing rule with estimated IL critical properties were used to model and correlate the experimental data [23]. Kim et al. studied solubilities of carbon dioxide in ionic liquids, [bmim][PF_6], [C_6mim][PF_6], [emim][BF_4], [emim][Tf_2N] and [C_6mim] [Tf_2N] at 298.15 K and up to 1 MPa. A group contribution form of a non-random lattice-fluid model was applied to predict solubilities in pure ionic liquids [24]. In this work, we predicted solubility of CO_2 in four imidazolium based ionic liquids with the [Tf_2N] anion by using the Peng-Robinson equation of state with the adjustable parameters in its mixing rules and the experimental data found in the open literature for the binary system studied. In summary, the thermodynamic model included the Peng-Robinson equation of state, the Wong-Sandler mixing rule and the van-Laar model for excess Gibbs free energy (G^E) in the mixing rules, model designated as PR/WS/VL in all of the paper.

THERMODYNAMIC MODELING

For a gas (1)+ionic liquid (2) system, the ionic liquid is taken to be non-volatile and only pure gas exists in the gas phase. The condition for the phase equilibrium is satisfied when the fugacities of the gas component have equal values in both phases at a constant temperature and pressure:

$$f_1^{gas} = \hat{f}_1^{IL} \qquad (1)$$

where f_1^{gas} is the gas fugacity in pure gas phase and $\hat{f}_1^{IL}$ is the fugacity of gas in ionic liquid phase. The relationship of fugacity with temperature and pressure can be expressed by an equation of state. So far, the ordinary form of cubic equations of state has been used to investigate phase equilibria of discrete components successfully. In this paper, the PR EOS has been modified in order to predict the phase behavior of a semicontinuous system.

1. The PR EOS

Following equations demonstrate the original form of the PR EOS [25]:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \qquad (2)$$

where P is the pressure, T is the temperature, v is the molar volume, R is the universal gas constant. Wong and Sandler derived general form mixing rules first by combining the quadratic dependence of the second virial coefficient on composition and relation between the second virial coefficient and the parameters in a cubic EOS. The second equation in their mixing rules was derived by taking the limit of the excess Helmholtz free energy for a cubic EOS mixture at infinite pressure. Helmholtz free energy is less pressure dependent, and can be approximated by excess Gibbs energy at low pressure where most experimental data are collected [26]. The mixture parameters in ionic liquid phase are calculated from the Wong-Sandler mixing rule [27]:

$$b = \frac{\sum_i^N \sum_j^N x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \sum_i^N \frac{x_i a_i}{b_i RT} - \frac{A_\infty^E(x)}{\Omega RT}} \qquad (3)$$

where

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2}[b_i + b_j] - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}) \qquad (4)$$

$$a = b \left[\sum_i^N \frac{a_i x_i}{b_i} + \frac{A_\infty^E(x)}{\Omega} \right] \qquad (5)$$

In these equations, $\Omega = -0.62323$ for the PR equation, and $A_\infty^E(x)$ is calculated using an appropriate model and assuming that $A_\infty^E(x) \approx A_0^E(x) \approx G_0^E(x)$ being, $G_0^E(x) = g^E$, the excess Gibbs free energy at low pressure [28]. The combining rule for $(b-(a/RT))_{ij}$ includes one adjustable parameter k_{ij} and it was assumed that binary interaction parameter is dependent on temperature.

The van Laar model for the excess Gibbs free energy g^E included in the Wong-Sandler was used. This model contains two empirical parameters for a binary mixture. Therefore, for a binary mixture the Wong-Sandler mixing rule includes one adjustable binary interaction parameter k_{12} for $(b-(a/RT))_{ij}$, besides the two parameters included in the g^E model. These three adjustable parameters for each of the mixtures have been determined using experimental phase equilibrium data at constant temperature, available in the literature for the mixtures studied. The van Laar model has been presented in the literature using different expressions for the parameters of the models. The expressions used in this work for binary mixtures are presented in the form as follows:

$$\frac{g^E}{RT} = \frac{(A_{12}/RT)x_1 x_2}{x_1(A_{12}/A_{21}) + x_2} \qquad (6)$$

The expression for the fugacity of gas component in gas and ionic liquid phases with PR EOS and Wong-Sandler mixing rule is: [29]

$$\ln(\phi_i^G) = \frac{\partial Nb/\partial N_i}{b}(Z-1) - \ln\left(Z - \frac{bP}{RT} \right)$$

$$+\frac{a}{2\sqrt{2}bRT}\left[\frac{\frac{1}{N}(\partial N^2 a/\partial N_i)}{a}-\frac{\partial Nb/\partial N_i}{b}\right]\ln\left[\frac{Z+(1-\sqrt{2})\frac{bP}{RT}}{Z+(1+\sqrt{2})\frac{bP}{RT}}\right] \quad (7)$$

The partial derivatives in the above expression are

$$\frac{\partial Nb}{\partial N_i}=\frac{1}{1-D}\left(2\sum_j x_j\left(b-\frac{a}{RT}\right)_{ij}\right)$$

$$-\frac{\sum_i\sum_j x_i x_j\left(b-\frac{a}{RT}\right)}{(1-D)^2}\left(1-\left(\frac{a_i}{b_i RT}+\frac{\ln(\gamma_i)}{\Omega}\right)\right) \quad (8)$$

$$\frac{1}{N}\left(\frac{\partial N^2 a}{\partial N_i}\right)=RTD\left(\frac{\partial Nb}{\partial N_i}\right)+RTb\left(\frac{a_i}{b_i RT}+\frac{\ln(\gamma_i)}{\Omega}\right) \quad (9)$$

$$D=\frac{G^E}{\Omega RT}+x_i\frac{a_i}{b_i RT} \quad (10)$$

Information about the critical properties and acentric factor is needed to utilize the PR-EOS. Those properties are readily available for CO_2, but they are not available for the ionic liquids. Therefore, those properties for the ionic liquids need to be estimated. In this work, we used Joback's method [30], a group contribution method, to estimate the critical temperature and pressure (T_c and P_c) for the ionic liquids. The group identities and Joback's values for contributions to the critical properties are available in the reference [30].

The acentric factors of the ionic liquids were estimated by the Ambrose-Walton corresponding-states method [30]. The normal boiling temperatures, critical properties and acentric factors of the ionic liquids are listed in Table 1.

For a CO_2+ionic liquid system, at a given temperature and CO_2 mole fraction (x_1), we calculated equilibrium pressures or bubble pressures (P), which satisfied the equilibrium relation (Eq. (1)). The volumetric properties of gas and ionic liquid phases, which were necessary to calculate the fugacities of gas in gas and ionic liquid phases, were obtained by solving the PR-EOS (Eq. (2)). A nonlinear least square method was used to solve this problem. The same calculations were repeated at different CO_2 mole fractions, and finally a $P-x_1$ diagram was completed.

Before performing the equilibrium calculations described above by using the PR/WS/VL, the adjustable parameters, binary interaction parameter and activity coefficients (k_{12} and A_{12}, A_{21}), were determined first for each system. The experimentally obtained $P-x_1$ data at a given temperature for a CO_2+ionic liquid system were correlated with the PR-EOS, and then a set of optimum values of the k_{12} and A_{12}, A_{21} parameters were found by minimizing the following objective function:

$$OF=\sum_i^N\left|\frac{P_i^{exp}-P_i^{calc}}{P_i^{exp}}\right| \quad (11)$$

Table 1. Critical properties and acentric factor of ionic liquids estimated from the method of Joback

Ionic liquids	T_c (K)	P_c (MPa)	ω
[C_2-mim][Tf_2N]	788.05	3.31	1.225
[C_4-mim][Tf_2N]	831.39	2.69	1.289
[C_6-mim][Tf_2N]	876.24	2.22	1.327
[C_8-mim][Tf_2N]	923.02	1.87	1.331

where P_i^{exp} is the experimental value of pressure and P_i^{calc} is the pressure calculated by the PR-EOS at the experimental value of CO_2 mole fraction, and N is the number of data points. The differential evolution (DE) optimization method, which solves a nonlinear least-squares problem, was used.

THE DE OPTIMIZATION METHOD [31,32]

1. Computational Steps

The DE method, an exceptionally simple, heuristic and robust evolution strategy, which is significantly fast in numerical optimization [33], was applied to find the true global optimum values of the presented model parameters. Check whether the parameters of the trial vector are within the bounds. If an individual of this trial vector is outside of the bounds, then this parameter is assigned a value randomly within the associated bounds.

2. Strategies

Different DE strategies are used to make it capable of dealing with different kinds of problems. So far, ten schemes of strategies have been presented [34]. A strategy that is successful in one problem may not work well in another specified one. Selection of the best strategy could be determined by trial and error [33]. The strategies can vary based on the vector to be perturbed, number of difference vectors considered for perturbation, and finally the type of crossover used.

RESULTS AND DISCUSSION

The experimental results found in the literature for solubility of CO_2 in the ionic liquids [C_n-mim][Tf_2N] (n=2, 4, 6, 8) show that CO_2 gives very high solubility in ionic liquids at lower pressures, while the equilibrium pressure increases very steeply at higher concentrations of CO_2. The solubility of CO_2 in the ionic liquids decreases with an increase in temperature. In general, a system in which a large amount of CO_2 dissolves in the liquid phase at low pressure tends to give a simple two phase envelope with a mixture critical temperature at moderate pressure.

The PR-EOS using the WS mixing rule was used to describe the experimental data of the solubility of CO_2 in [C_n-mim][Tf_2N]. In this work binary interaction parameter and activity coefficient are considered as temperature dependent with regard to the correlations below:

$$k_{ij}=n_1 T^2+n_2 T+n_3 \quad (12)$$

$$A_{12}=n_1 T^2+n_2 T+n_3 \quad (13)$$

$$A_{21}=n_1 T^2+n_2 T+n_3 \quad (14)$$

The binary interaction parameter and activity coefficients (n_1, n_2, n_3) for [C_n-mim][Tf_2N] (n=2, 4, 6, 8) were optimized using the $P-x_1$ data for each system. Table 2 summarizes the binary interaction parameter and activity coefficients for each system. The modeling results are summarized in Table 3. The average absolute deviations in percentage (AAD%) between the calculated and experimental equilibrium pressures which is defined as below, were calculated for each system and temperature.
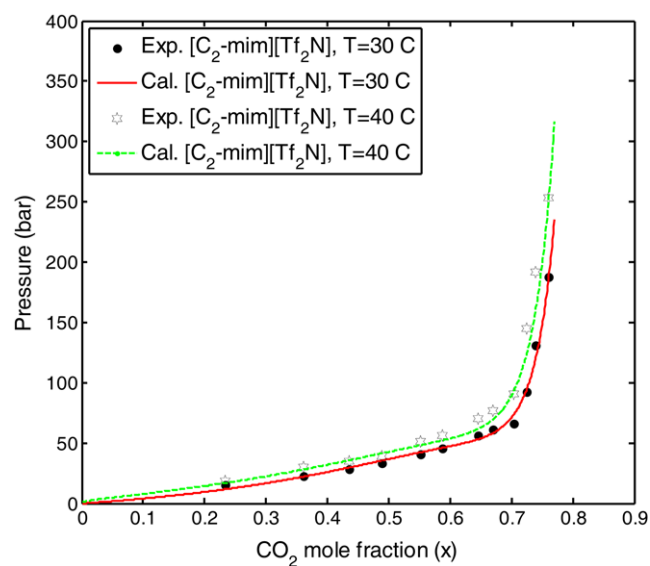
$$ADD\,(\%)=(1/N)\left(\sum_i^N\left|\frac{P_i^{exp}-P_i^{calc}}{P_i^{exp}}\right|\times 100\right) \quad (15)$$

Table 2. Adjustable parameters for k_{ij}, A_{12} and A_{21} of the PR-EoS optimized for the CO_2+[C_n-mim][Tf₂N] (n=2, 4, 6, 8) systems
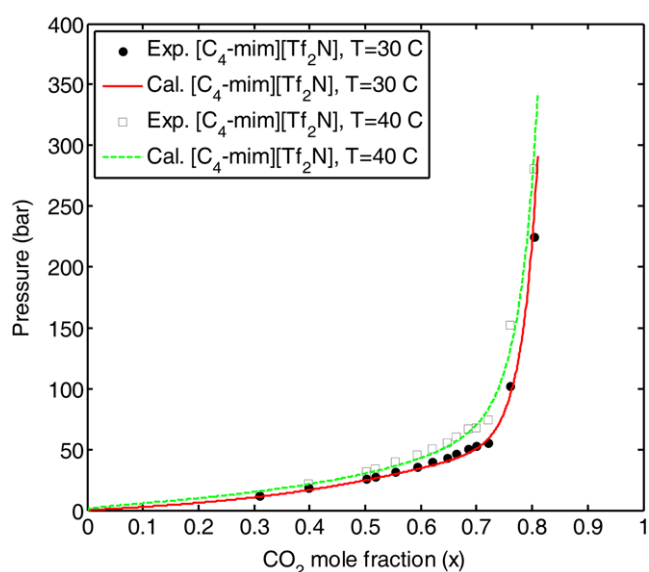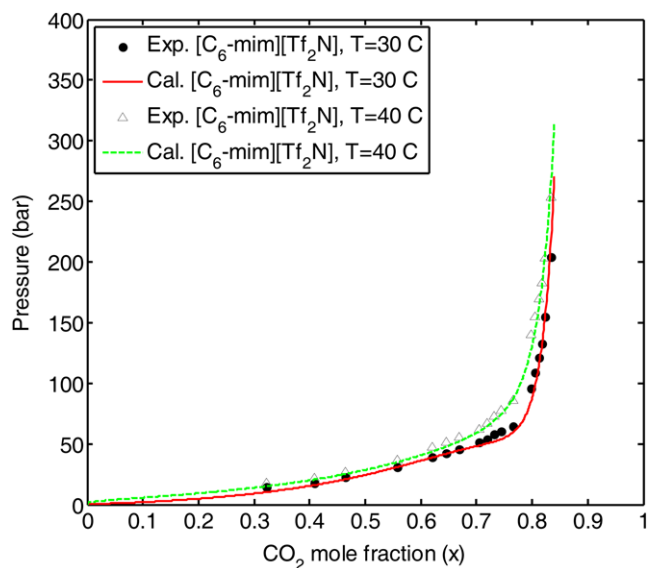
Ionic liquids	Parameter	Coefficient		
		n_1	n_2	n_3
[C_2-mim][Tf₂N]	K_{12}[a]	$(-2.5813)10^{-4}$	$(1.5740)10^{-1}$	-23.501
	A_{12}	$(1.3654)10^{-4}$	$(-8.940)10^{-2}$	16.01
	A_{21}	$(8.9826)10^{-3}$	-5.5603	861.58
[C_4-mim][Tf₂N]	K_{12}	$(4.9511)10^{-4}$	$(-3.1570)10^{-1}$	50.712
	A_{12}	$(-7.226)10^{-3}$	4.644	-742.91
	A_{21}	$(-1.0825)10^{-2}$	6.8434	-1078.9
[C_6-mim][Tf₂N]	K_{12}	$(-7.3443)10^{-5}$	$(4.6700)10^{-2}$	-7.3103
	A_{12}	$(1.9956)10^{-3}$	-1.226	189.62
	A_{21}	$(-1.5684)10^{-2}$	9.8994	-1556.2
[C_8-mim][Tf₂N]	K_{12}	$(-8.3941)10^{-4}$	$(5.3480)10^{-1}$	-84.91
	A_{12}	$(1.1896)10^{-3}$	$(-7.74)10^{-1}$	118.33
	A_{21}	$(1.0595)10^{-2}$	-6.5724	1020.2

[a]$K_{12}=K_{21}$

Table 3. Deviations between experimental and calculated values in equilibrium pressures

Ionic liquids	AAD%		
	30 °C	40 °C	Average
[C_2-mim][Tf₂N]	4.5000	4.1031	4.3015
[C_4-mim][Tf₂N]	5.4092	3.9100	4.6596
[C_6-mim][Tf₂N]	5.8032	4.8110	5.3071
[C_8-mim][Tf₂N]	4.7980	4.9773	4.8876

Fig. 2. P−x diagrams of the CO_2+[C_2-mim][Tf₂N] mixtures at temperature of 30° and 40 °C. The linear are the calculations by the PR- EOS model.

Fig. 3. P−x diagrams of the CO_2+[C_4-mim][Tf₂N] mixtures at temperature of 30° and 40 °C. The linear are the calculations by the PR-EOS model.

Fig. 4. P−x diagrams of the CO_2+[C_6-mim][Tf₂N] mixtures at temperature of 30° and 40 °C. The linear are the calculations by the PR- EOS model.

To better show the capability of the proposed correlations for the parameters of the PR/WS/VL model, the solubility of CO_2 in the ILs [C_n-mim][Tf₂N] (n=2, 4, 6, 8) over a wide pressure range was calculated with the PR-EOS accompanied with the WS mixing rule and results are compared to available experimental data. Graphical results for the binary systems studied but for different temperatures are shown in Figs. 2 to 5. It can be concluded that the PR EOS with using WS mixing rule can satisfactorily model the high-pressure solubility of CO_2 in [C_n-mim][Tf₂N] over a wide range of pressure up to the supercritical region of CO_2. The solubilities of CO_2 in [C_n-mim][Tf₂N] were nearly the same at lower pressure, while they differed greatly at elevated pressure. In the high pressure range, the CO_2 solubility increased as the length of the 1-alkyl chain of [C_n-mim][Tf₂N] increased.

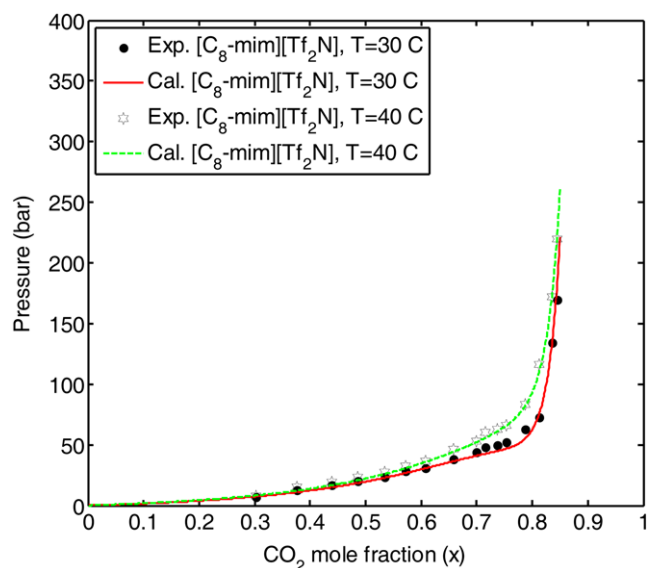As seen in the Figs. 2 to 5, good agreement between calculated

Fig. 5. P–x diagrams of the CO₂+[C₈-mim][Tf₂N] mixtures at temperature of 30° and 40 °C. The linear are the calculations by the PR- EOS model.

Table 4. Comparison of errors of different models for solubilities of CO₂ in ionic liquids [Cₙ-mim][Tf₂N] (n=2, 4, 6, 8)

Models	Ionic liquids	AAD%		
		30 °C	40 °C	Average
PR/WS/VL	[C₂-mim][Tf₂N]	4.5000	4.1031	4.3015
	[C₄-mim][Tf₂N]	5.4092	3.9100	4.6596
	[C₆-mim][Tf₂N]	5.8032	4.8110	5.3071
	[C₈-mim][Tf₂N]	4.7980	4.9773	4.8876
PR/VdW[a]	[C₂-mim][Tf₂N]	12.0000	13.5000	12.7500
	[C₄-mim][Tf₂N]	11.7000	11.0000	11.3500
	[C₆-mim][Tf₂N]	9.7000	9.6000	9.6500
	[C₈-mim][Tf₂N]	10.6000	9.9000	10.2500

[a]Experimental data in ref. [35]

values and experimental data is found.

In this paper, we compared AAD% of results obtained from the proposed model with that of another model which used quadratic mixing rules [2]. As shown in Table 4, the PR/WS/VL model allows a good description of the experimental data compared to the proposed model with different mixing rule by Shin et al. [35], because the average absolute deviations of the proposed model were less than other existing model.

CONCLUSIONS

A thermodynamic consistency test based on the Peng-Robinson EoS with the Wong-Sandler/van Laar mixing rule was applied to the available data in the literature for the binary systems studied showing that they are thermodynamically consistent. As demonstrated in the prior section, the model was capable of satisfactorily modeling the high-pressure solubility of CO_2 in [C_n-mim] [Tf₂N] over a wide range of pressure up to the supercritical region of CO_2. The solubility of CO_2 in [C_n-mim] [Tf₂N] decreased with an increase

in temperature; also, variation of the length of the 1-alkyl chain in the cation of [C_n-mim] [Tf₂N] was found to have a large effect on the CO_2 solubility.

On the other hand, the accuracy of PR/WS/VL model was greater than that reported in the literature for similar types of mixtures, as presented in Table 4.

NOMENCLATURE

a   : EOS attractive term [bar cm⁶/kmol²]
b   : EOS repulsive term [cm³/mol]
$\hat{f}$: mixture fugacity
G^E : excess gibbs free energy
R   : the universal constant
T   : temperature
υ : molar volume [cm³/mol]
Z   : compressibility factor

Greek Letters
Ω : constant parameter=−0.62323
γ : activity coefficient

REFERENCES

1. K. N. Marsh, A. Deev, A. C.-T. Wu, E. Tran and A. Klamt, *Korean J. Chem. Eng.*, **19**, 357 (2002).
2. E. K. Shin, B. C. Lee and J. S. Lim, *J. Supercrit. Fluids*, **45**, 282 (2008).
3. J. S. Andreu and L. F. Vega, *J. Phys. Chem. B*, **112**, 15398 (2008).
4. P. J. Carvalho, V. H. Álvarez and J. J. B. Machado, *J. Supercrit. Fluids*, **48**, 99 (2009).
5. D. J. Oh and B. C. Lee, *Korean J. Chem. Eng.*, **23**(5), 800 (2006).
6. S. Raeissi and C. J. Peters, *J. Chem. Eng. Data*, **54**, 382 (2009).
7. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, **15**(1), 59 (1976).
8. J. O. Valderrama, *Ind. Eng. Chem. Res.*, **42**(7), 1603 (2003).
9. L. A. Blanchard and J. F. Brenneche, *Ind. Eng. Chem. Res.*, **40**, 287 (2001).
10. L. A. Blanchard, D. Hancu, E. J. Beckman and J. F. Brennecke, *Nature*, **399**, 28 (1999).
11. J. L. Anthony, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, **106**, 7315 (2002).
12. A. Shariati and C. Peters, *J. Supercrit. Fluids*, **25**, 109 (2003).
13. A. Shariati and C. J. Peters, *J. Supercrit. Fluids*, **34**, 173 (2005).
14. M. Costantini, V. A. Toussaint; A. Shariati, C. J. Peters and I. Kikic, *J. Chem. Eng. Data*, **50**, 52 (2005).
15. M. Kroon, A. Shariati, M. Costantini, J. van Spronsen, G.-J. Witkamp, R. A. Sheldon and C. Peters, *J. Chem. Eng. Data*, **50**, 173 (2005).
16. D.-J. Oh and B.-C. Lee, *Korean J. Chem. Eng.*, **23**(5), 800 (2006).
17. P. J. Carvalho, V. H. Alvarez, J. J. B. Machado, J. Pauly, J.-L. Daridon, I. M. Marrucho, M. Aznar and J. A. P. Coutinho, *J. Supercrit. Fluids*, **48**, 99 (2009).
18. E.-K. Shin and B.-C. Lee, *J. Chem. Eng. Data*, **53**, 2728 (2008).
19. Joanna Lachwa, Pedro Morgado, Jose M. S. S. Esperanca, Henrique J. R. Guedes, Jose N. Canongia Lopes and Luis Paulo N. Rebelo, *J. Chem. Eng. Data*, **51**, 2215 (2006).

20. A. Shariati, K. Gutkowski and C. J. Peters, *AIChE J.*, **51**, 1532 (2005).
21. Mark B. Shiflett and A. Yokozeki, *Fluid Phase Equilibria*, **294**, 105 (2010).
22. Pedro J. Carvalho, Victor H. Alvarez, Isabel M. Marrucho, Martin Aznar and Joao A. P. Coutinho, *J. Supercrit. Fluids*, **52**, 258 (2010).
23. Wei Ren, Brent Sensenich and Aaron M. Scurto, *J. Chem. Thermodynamics*, **42**, 305 (2010).
24. Y. S. Kim, W. Y. Choi, J. H. Jang, K.-P. Yoo and C. S. Lee, *Fluid Phase Equilibria*, **228-229**, 439 (2005).
25. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fund.*, **15**, 59 (1976).
26. Wei-Yin Chen and Jiangping Liu, Mathcad Modules for Supercritical Fluid Extraction Based on Mixing Rules Appendix A- Mixing Rules (2007).
27. S. Dahl and M. L. Michelsen, *AIChE J.*, **36**, 1829 (1990).
28. H. Orbey and S. I. Sandler, Cambridge University Press, Cambridge, England (1998).
29. J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 3rd Ed., Prentice-Hall, NJ (1999).
30. B. E. Poling, J. M. Prausnitz and J. P. O'Connell, The Properties of Gases and Liquids, 5th Ed., McGraw-Hill, NY (2001).
31. A. Eslamimanesh and F. Esmaeilzadeh, *Fluid Phase Equilibria*, **291**, 141 (2010).
32. A. Eslamimanesh, A. Shariati Presented at VIII Iberoamerican conference on Phase Equilibria and Fluid Properties for process design (Equifase), Praia da Rocha, Portugal, Oct. (2009).
33. R. Storn, *J. Global Optim.*, **11**, 341 (1997).
34. K. Price and R. Storn, Home page of differential evolution as on April 25. URL: http://www.ICSI.Berkeley.edu/storn/code.html.
35. E.-K. Shin, B.-C. Lee and J. S. Lim, *J. Supercrit. Fluids*, **45**, 282 (2008).