

RESEARCH PAPER

## A modified UNIFAC model in predicting the solubility of CO<sub>2</sub> and H<sub>2</sub>S in imidazolium-based ionic liquids

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### ARTICLE INFO

Article History:

Received 22 November 2019

Revised 16 February 2020

Accepted 27 February 2020

Keywords:

ionic liquids

acid gases

free-volume

UNIFAC model

### ABSTRACT

In this work, a modified UNIFAC model was proposed to investigate the solubility of acid gases, i.e., CO<sub>2</sub> and H<sub>2</sub>S in nine imidazolium-based ionic liquids (ILs). The influence of effective parameters including temperature, the nature of anions and cations of the ILs, and the length of alkyl chain on the solubility of acid gases in the ILs were studied. The interaction parameters between the new functional subgroups of the fragmented ILs such as [IM], [BF<sub>4</sub>], [PF<sub>6</sub>], [Tf<sub>2</sub>N], CH<sub>3</sub> and CH<sub>2</sub> with CO<sub>2</sub> and H<sub>2</sub>S molecules were reported using the original UNIFAC model. In the proposed model, the segment fraction in the Flory-Huggins term of the UNIFAC combinatorial part was modified considering the free-volume differences between the ionic liquid and the acid gas molecules. While the free-volume parameter represents the free-volume percent ratio of ionic liquid to that of the acid gas, it was regressed for each system using the extensive VLE experimental data from literature. It was verified that the free-volume parameter can be a linear function of the molecular weight of the ionic liquids and, thus, only the values for the molecular weight of the ionic liquids are required to estimate the free-volume parameters. The modeling results were compared with those of the original UNIFAC model. The results showed that the proposed model accurately correlated the VLE experimental data for the systems containing ILs in the presence of CO<sub>2</sub> and/or H<sub>2</sub>S at pressures up to 150 bar.

**How to cite this article:** Sedghkardar M.H., Taghikhani V., Ghotbi C., Shariati A., A modified UNIFAC model in predicting the solubility of CO<sub>2</sub> and H<sub>2</sub>S in imidazolium-based ionic liquids. *Journal of Oil, Gas and Petrochemical Technology*, 2020; 7(1): 1-13. DOI: 10.22034/JOGPT.2020.113091.

### 1. Introduction

Acid gases composed of CO<sub>2</sub> and H<sub>2</sub>S are commonly available in natural gas as impurities and, thus, the removal of these impurities is important in the natural gas processing and petroleum refining. H<sub>2</sub>S is toxic and corrosive and thus it can poison the catalysts used in the natural gas refining and processing. In addition, carbon dioxide (CO<sub>2</sub>) is the most abundant greenhouse gas arising from the anthropogenic activities, and its emissions must be reduced to prevent the excessive global warming and climate change.

Moreover, it can reduce the heating value of the natural gas and has known to have the greenhouse effect [1-2].

Although there are different methods of CO<sub>2</sub> removal such as adsorption using calcium-based adsorbents, and membrane separation, the absorption into liquid solvents is the most used method for removing the acid gas from the natural gas in the gas sweetening process [3-6]. Amine scrubbing is currently commercially used for the gas sweetening process. The contamination of natural gas stream due to its volatility and, therefore, the energy

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cost for the regeneration are major drawbacks in the sweetening process with alkanolamines [1].

For over a decade, ILs have been considered as promising alternative chemicals for the amine solutions due to their negligible vapor pressure, chemical stability, and non-flammability [1]. Moreover, it is feasible to choose a suitable IL for a specific process by combining various cations and anions [2]. While alkanolamine solutions can chemically absorb acid gases during the acid gas removal process, the ionic liquids can selectively and physically absorb the acid gas molecules at different conditions. Hence, for the gas sweetening processes, ionic liquids can be used when there is a high concentration of the acid gases in the feed stream. As a result, for the application of ILs in the gas separation processes such as gas sweetening process, the knowledge about the solubility of acid gases in ILs is indispensable. Shariati and Peters [7] and Jalili et. al [8] showed the phase behavior of CO<sub>2</sub> and H<sub>2</sub>S with various imidazolium-based ILs, respectively.

Aki et al. [9] indicated that the interaction of CO<sub>2</sub> with the anions significantly affects the CO<sub>2</sub> solubility in the ILs. They discovered that the CO<sub>2</sub> highly dissolves in ILs with anions containing fluoroalkyl (CF<sub>3</sub>) due to the CO<sub>2</sub>-philic nature of the fluoroalkyl groups. Therefore, they suggested that this behavior is due to the CO<sub>2</sub>-philic nature of the fluoroalkyl groups. Furthermore, using ATR-IR spectroscopy for CO<sub>2</sub> with [bmim][BF<sub>4</sub>] and [bmim][PF<sub>6</sub>], Kazarian et al. [10] suggested that the interaction of CO<sub>2</sub> with the fluorinated anions in ILs is another factor that causes the higher solubility of CO<sub>2</sub> in ILs.

In order to choose the most desirable IL among the variety of ILs they may be formed, and also to save time and cost of the experimental measurement, it is desirable to develop a predictive thermodynamic model for calculating the gas solubilities in ILs. So far, different thermodynamic models have been proposed in the literature for VLE calculation of CO<sub>2</sub> solubility in ILs [11-14]. However, in this work, a modified UNIFAC model was proposed by introducing the free-volume parameter, which represents the ratio of the inaccessible free-volume around ionic liquid molecules to that of the acid gases. The proposed model along with the Peng Robinson (PR) EOS was applied to calculate the phase behavior of the systems including imidazolium based ILs in the presence of acid gases. The effects of anions and cation alkyl chain length on the solubility of acid gases in ILs were also studied.

## 2. Model and parameters

In this work, the VLE for the binary systems, consisting of ionic liquids and CO<sub>2</sub> or H<sub>2</sub>S at high pressure were calculated using the gamma-phi approach. Due to the negligibility of vapor pressure of ionic liquids, it is suggested that the vapor phase consists of pure CO<sub>2</sub> or H<sub>2</sub>S. The PR EOS was used to estimate the fugacity coefficient of the acid gases. Moreover, the activity coefficient of the liquid phase was calculated using the UNIFAC model [15]. In an IL and acid gas mixture, the ionic liquid molecules can be more packed than the acid gas molecules. Then, the free-volume effects should be considered since the original UNIFAC model has been used for the mixture of normal fluid mixtures with the small free-volume effects.

In this study, a modified segment fraction for the Flory-Huggins (F-H) term of the UNIFAC combinatorial part was proposed. The new expression for the segment fraction considers the free-volume differences between ILs and the acid gases. The benefit of the new proposed model over the previously proposed free volume based model such as the UNIFAC-FV [16] and the Entropic-FV [17] models is that in contrast to the foregoing ones, the proposed model does not need the values for the molar volumes of ionic liquids and acid gases.

### 2.1. The UNIFAC model

The basic idea of UNIFAC is that the non-ideality of a complex mixture can be modeled on the basis of smaller group of atoms within the molecules (functional subgroups). The groups contribute in a fixed way to the non-ideal property, independent of the nature of other groups that may be present. Furthermore, the way it contributes to the deviation from the ideal behaviors is made up of two parts: first, a contribution due to the difference in the size and shape between existing groups or combinatorial part and the second term is a contribution due to the energetic interactions between the groups which is considered as residual part [15].

Therefore, the activity coefficient of the UNIFAC model is expressed as:

$$\ln \gamma_i^{UNIFAC} = \ln \gamma_i^C + \ln \gamma_i^R \quad (1)$$

where the superscripts C and R stand for the combinatorial and residual. The combinatorial in equation (1) is given by following,

$$\ln \gamma_i^{Comb} = \frac{\ln(\varphi_i)}{x_i} + 1 - \frac{\varphi_i}{x_i} - \frac{zq}{2} \left[ \frac{\ln(\vartheta_i)}{\vartheta_i} + 1 - \frac{\varphi_i}{\vartheta_i} \right] \quad (2)$$

where

$$r_i = \sum_{k=1}^n v_k^i R_k \quad (3)$$

$$q_i = \sum_{k=1}^n v_k^i Q_k \quad (4)$$

$$\varphi_i = \frac{r_i x_i}{\sum_{i=1}^n r_i x_i} \quad (5)$$

$$\theta_i = \frac{q_i x_i}{\sum_{i=1}^n q_i x_i} \quad (6)$$

where in equation (2) Z is the coordination number and was set to be 10. The  $R_k$  and  $Q_k$  were calculated based on the van der waals (vdw) group volume and surface area as follows [18]:

$$R_k = \frac{V_{wk}}{15.17} \quad (7)$$

$$Q_k = \frac{A_{wk}}{2.5 \times 10^9} \quad (8)$$

The residual part was obtained using the equation (9):

$$\ln \gamma_i^R = \sum_k v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \quad (9)$$

Where  $\Gamma_k$  is the group residual activity coefficient,  $\Gamma_k^{(i)}$  is the group k residual activity in a reference solution containing only component i, and  $v_k^i$  is the number of k group in component i. The group interaction parameter  $\Psi_{nm}$  between n and m groups is calculated as shown in the following equation:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right) \quad (10)$$

Where  $a_{nm}$  is the adjustable group interaction parameter between groups n and m.

## 2.2 The modified UNIFAC model

In the modified proposed model, the volume fraction in the originian UNIFAC was substituted by the free-volume fraction in the F-H term to consider the free-volume effects. Also, the Staverman-Guggenheim term was used to account for the molecular shape differences between the ionic liquids and acid gases as:

$$\ln \gamma_i^{Comb} = \frac{\ln(\varphi_i^{fv})}{x_i} + 1 - \frac{\varphi_i^{fv}}{x_i} \quad (11)$$

$$- \frac{zq}{2} \left[ \frac{\ln(\varphi_i)}{\theta_i} + 1 - \frac{\varphi_i}{\theta_i} \right]$$

With

$$\varphi_i^{fv} = \frac{x_i v_i^{fv}}{\sum_i x_i v_i^{fv}} \quad (12)$$

according to Entropic-FV model [17], component i free-volume is calculated as follows:

$$v_i^{fv} = v_i - v_i^{vdw} \quad (13)$$

Hence, the free-volume fraction can be written as:

$$\varphi_1^{fv} = \frac{x_1 \left( \frac{v_1 - v_1^{vdw}}{v_1^{vdw}} \right) v_1^{vdw}}{x_1 \left( \frac{v_1 - v_1^{vdw}}{v_1^{vdw}} \right) v_1^{vdw} + x_2 \left( \frac{v_2 - v_2^{vdw}}{v_2^{vdw}} \right) v_2^{vdw}} \quad (14)$$

where the subscripts 1 and 2 stand for the acid gas and IL, respectively. Rearranging the above equation leads to the following equation:

$$\varphi_1^{fv} = \frac{x_1 v_1^{vdw}}{x_1 v_1^{vdw} + x_2 \left( \frac{v_2 - v_2^{vdw}}{v_2^{vdw}} \right) v_2^{vdw}} \quad (15)$$

where the free-volume percent is defined as:

$$\%FV = \frac{v - v^{vdw}}{v} \times 100 \quad (16)$$

according to equations (15) and (16);

$$\varphi_1^{fv} = \frac{x_1 v_1^{vdw}}{x_1 v_1^{vdw} + x_2 \left( \frac{\%FV_{IL}}{\%FV_{gas}} \right) v_2^{vdw}} \quad (17)$$

as a result, the new adjustable parameter in the proposed model can be written as:

$$\alpha = \frac{\%FV_{IL}}{\%FV_{gas}} \quad (18)$$

Therefore, the free-volume parameter in the proposed model represents the free-volume percent ratio of ionic liquid to that of acid gas.

It should be stated that according to Bondi's relation the parameter  $r_v$  is proportional to the vdw volume, thus, the vdw in equation (17) can be replaced with the parameter  $r_i$  as:

$$\varphi_1^{fv} = \frac{x_1 r_1}{x_1 r_1 + \alpha x_2 r_2} \quad (19)$$

The values for the free-volume parameters,  $\alpha$ , for each system can be regressed using the VLE experimental data.

## 2.3. Ionic liquid Functional group

To calculate the VLE phase behavior of the

systems containing imidazolium-based ILs using group contribution models, four new functional subgroups were introduced upon the fragmentation of IL molecules. The fragmented IL molecules consist of [IM], [BF<sub>4</sub>], [PF<sub>6</sub>] and [Tf<sub>2</sub>N] as given in Figure 1. In order to use the UNIFAC based

models, the values for the vdws properties and the group interaction parameters for these new subgroups should be specified. In this work, the VLE data available in the literature for the systems studied were used to obtain the parameters for these subgroup interactions.

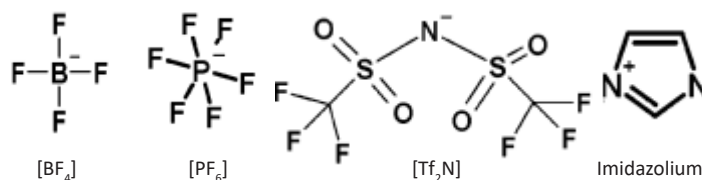


Figure 1. Four new main groups for original UNIFAC and Mod. UNIFAC

Table 1 gives the  $R_k$  and  $Q_k$  parameters of the subgroups obtained using the method introduced by

Bondi [18]. Parameters  $r_i$  and  $q_i$  of a component are estimated as the sum of  $R_k$  and  $Q_k$  parameters.

Table 1. Group Volume ( $R_k$ ) and Surface Area ( $Q_k$ ) Parameters for UNIFAC model

Group	$R_k$	$Q_k$	Ref.
CH <sub>3</sub>	0.9011	0.848	[22]
CH <sub>2</sub>	0.6744	0.540	[22]
Imidazolium	2.0260	0.868	[2]
Tf <sub>2</sub> N	5.7740	4.932	[2]
PF <sub>6</sub>	3.5134	3.852	[23]
BF <sub>4</sub>	2.1429	1.967	[23]
CO <sub>2</sub>	1.2900	1.124	[22]
H <sub>2</sub> S	1.1723	1.070	[22]

Table 2 presents the number of subgroups in the fragmented ionic liquids. The subgroup interactions with CO<sub>2</sub> and H<sub>2</sub>S molecules were obtained using the experimental VLE data with the

Simplex-Nelder-Mead optimization method [19] through the following objective function:

$$OF = \sum_{i=1}^{NP} \frac{|P_i^{exp} - P_i^{calc}|}{P_i^{exp}} \quad (20)$$

Table 2. ILs Fragmentation for UNIFAC model

	CH <sub>3</sub>	CH <sub>2</sub>	Imidazolium	Anion
[emim][Tf <sub>2</sub> N]	2	1	1	1 Tf <sub>2</sub> N
[bmim][Tf <sub>2</sub> N]	2	3	1	1 Tf <sub>2</sub> N
[hmim][Tf <sub>2</sub> N]	2	5	1	1 Tf <sub>2</sub> N
[emim][PF <sub>6</sub> ]	2	1	1	1 PF <sub>6</sub>
[hmim][PF <sub>6</sub> ]	2	5	1	1 PF <sub>6</sub>
[bmim][PF <sub>6</sub> ]	2	3	1	1 PF <sub>6</sub>
[hmim][BF <sub>4</sub> ]	2	5	1	1 BF <sub>4</sub>
[bmim][BF <sub>4</sub> ]	2	3	1	1 BF <sub>4</sub>
[omim][BF <sub>4</sub> ]	2	7	1	1 BF <sub>4</sub>

### 3. Results and discussion

Table 3 gives the values for the interaction parameters between the subgroups in the systems containing ionic liquids, CO<sub>2</sub> and H<sub>2</sub>S. It should be stated that these parameters were obtained for

the original UNIFAC model using the extensive VLE data available in the literature. Thus, these regressed values were directly used in the proposed modified UNIFAC model.

Table 3. The group interaction parameters for both UNIFAC and Mod. UNIFAC models

a <sub>ij</sub>	CH <sub>2</sub>	Tf <sub>2</sub> N	PF <sub>6</sub>	BF <sub>4</sub>	[IM] <sup>a</sup>	CO <sub>2</sub>	H <sub>2</sub> S
CH <sub>2</sub>	0	-1869.06	922.84	1481.24	1176.33	627.35	20647.56
Tf <sub>2</sub> N	151.93	0			1535.75	354.75	1031.05
PF <sub>6</sub>	2093.07		0		2119.77	43249.83	314.94
BF <sub>4</sub>	-5.79			0	223.03	141.10	1368.28
[IM] <sup>a</sup>	927.40	-1315.26	30735.70	-1044.54	0	195.46	58.84
CO <sub>2</sub>	-183.02	-1269.32	459.97	-44.61	72.08	0	
H <sub>2</sub> S	-105.27	-2031.63	9.90	-1016.09	382.20		0

<sup>a</sup> Imidazolium

Tables 4 and 5 present the range of temperature, pressure and acid gases concentrations for the studied binary systems. These tables also give the regressed free-volume parameters introduced in

the proposed model for each system within the range of the reported experimental data. The free-volume parameter is the only adjustable parameter introduced in the proposed model.

Table 4. Details on the Phase Equilibrium Data, the adjusted values of free-volume parameter (α) and the absolute average deviation (%AAD)

Range of Data			Free-volume		%AAD <sup>a</sup>		
CO <sub>2</sub> /	T (K)	P (MPa)	X <sub>CO<sub>2</sub></sub>	α	UNIFAC	This work	Ref.
[emim][Tf <sub>2</sub> N]	312.10-351.60	0.625-12.305	0.120-0.593	0.839	4.14	1.73	[24]
[bmim][Tf <sub>2</sub> N]	313.30	1.290-3.950	0.310-0.554	0.814	2.38	2.31	[25]
[emim][PF <sub>6</sub> ]	332.90-352.60	1.490-14.840	0.104-0.449	0.923	2.76	2.24	[5]
[bmim][PF <sub>6</sub> ]	313.30	0.780-6.887	0.100-0.501	0.901	1.89	2.23	[4]
[hmim][PF <sub>6</sub> ]	313.40	0.700-8.330	0.098-0.599	0.879	4.45	3.56	[6]
[bmim][BF <sub>4</sub> ]	303.19-333.15	0.740-14.440	0.102-0.482	0.951	1.68	1.36	[26]
[hmim][BF <sub>4</sub> ]	313.30	0.766-10.460	0.103-0.602	0.928	3.94	1.9	[27]
[omim][BF <sub>4</sub> ]	313.30	0.621-7.920	0.100-0.602	0.905	2.07	0.74	[28]

$$^a \text{AAD}\% = 100 * \frac{1}{NP} \sum_{i=1}^{NP} \frac{|P_i^{exp} - P_i^{calc}|}{|P_i^{exp}|}$$

Table 5. Details of the Phase Equilibrium Data, the adjusted values of free-volume parameter (α) and the absolute average deviation (%AAD) between the experimental and the predicted data using UNIFAC and the proposed model in this work for H<sub>2</sub>S/IL systems

Range of Data			Free-volume		%AAD <sup>a</sup>		
H <sub>2</sub> S/	T (K)	P (MPa)	X <sub>CO<sub>2</sub></sub>	α	UNIFAC	This work	Ref.
[bmim][Tf <sub>2</sub> N]	303.15-343.15	0.0944-0.916	0.070-0.364	0.789	2.04	1.16	[8]
[hmim][PF <sub>6</sub> ]	303.15-343.15	0.161-0.845	0.041-0.464	0.772	3.50	2.87	[7]
[bmim][PF <sub>6</sub> ]	303.15-343.15	0.123-1.011	0.044-0.358	0.882	1.49	1.21	[8]
[hmim][PF <sub>6</sub> ]	303.15-343.15	0.199-1.070	0.055-0.441	0.861	2.31	1.67	[7]
[bmim][BF <sub>4</sub> ]	303.15-343.15	0.061-0.813	0.038-0.354	0.939	2.54	2.57	[8]
[hmim][BF <sub>4</sub> ]	303.15-343.15	0.196-1.100	0.144-0.499	0.911	1.81	1.22	[7]

$$^a \text{AAD}\% = 100 * \frac{1}{NP} \sum_{i=1}^{NP} \frac{|P_i^{exp} - P_i^{calc}|}{|P_i^{exp}|}$$

Figures 2 and 3 show the variation of the free-volume parameter with the molecular weight of ILs in the presence of acid gases. As can be seen from these figures for both CO<sub>2</sub>/IL and H<sub>2</sub>S/IL systems the free-volume parameter can linearly change with the ionic liquid molecular weights. Table 6 presents the molecular weight of the studied ionic liquids. Equations (21) and (22) can be used

to express such linear relationships between the free-volume parameters and the ionic liquid molecular weights for the systems containing CO<sub>2</sub> and H<sub>2</sub>S respectively.

$$\alpha = -6.7489 \times 10^{-4}(Mw) + 1.0970 \quad (21)$$

$$\alpha = -7.3711 \times 10^{-4}(Mw) + 1.0977 \quad (22)$$

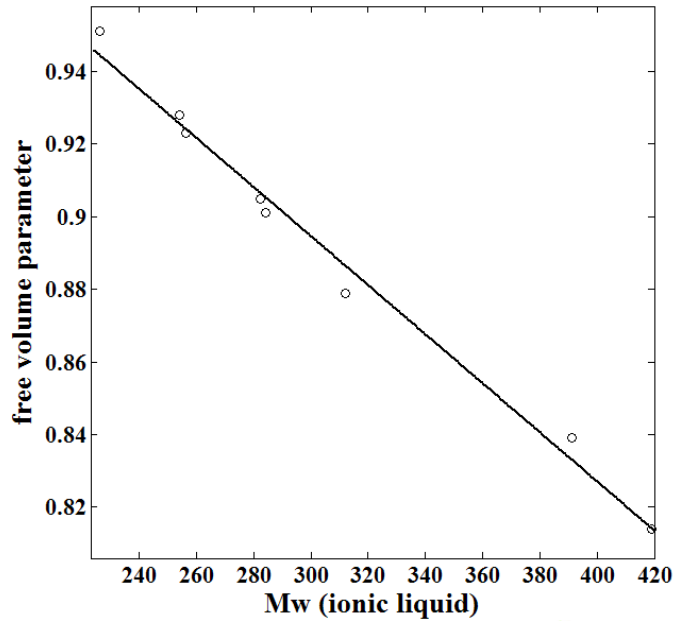


Figure 2. Linear relation between the molecular weight of ILs and free-volume parameter ( $\alpha$ ); o, optimized free-volume parameter for CO<sub>2</sub>/IL systems

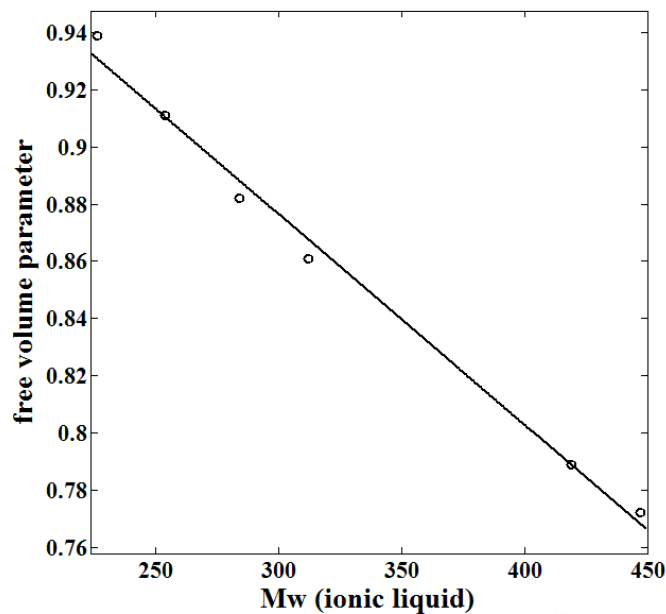


Figure 3. Linear relation between the molecular weight of ILs and free-volume parameter ( $\alpha$ ); o, optimized free-volume parameter for H<sub>2</sub>S/IL systems

Table 6. Molecular weight of ILs in this study

[Tf <sub>2</sub> N] <sup>-</sup>	Mw (gr mol <sup>-1</sup> )	[PF <sub>6</sub> ] <sup>-</sup>	Mw (gr mol <sup>-1</sup> )	[BF <sub>4</sub> ] <sup>-</sup>	Mw (gr mol <sup>-1</sup> )
[emim] <sup>+</sup>	391.2	[emim] <sup>+</sup>	256.2	[bmim] <sup>+</sup>	226.0
[bmim] <sup>+</sup>	419.2	[bmim] <sup>+</sup>	284.2	[hmim] <sup>+</sup>	254.0
[hmim] <sup>+</sup>	447.3	[hmim] <sup>+</sup>	312.2	[omim] <sup>+</sup>	282.1

Figure 4 shows that upon increasing the system pressure, the solubility of acid gases in the IL can increase. Also, it can be observed that the H<sub>2</sub>S solubility is significantly higher than that of CO<sub>2</sub> in the IL. According to Pomelli et al. [20] the acidic nature of hydrogen sulfide can lead to a strong

energetic interaction between the hydrogen atoms on the hydrogen sulfide molecules and the fluorine atoms on the anion part of the ionic liquid molecules. Such strong attraction forces can cause the higher solubility.

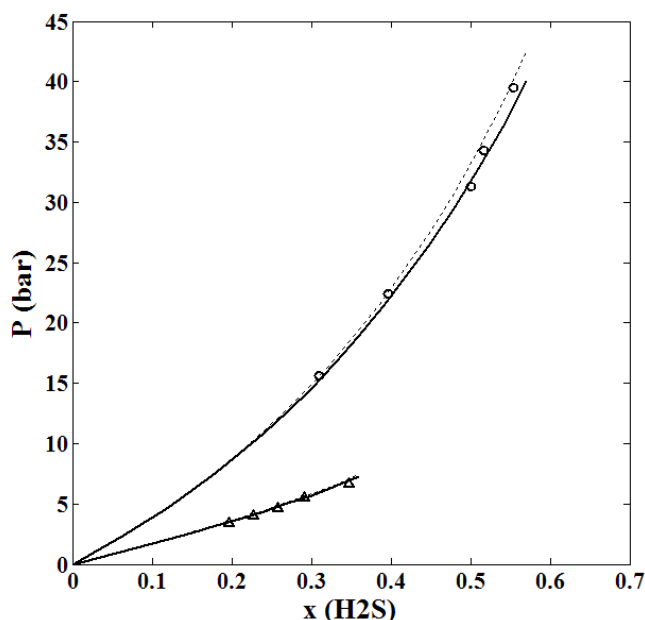


Figure 4. Comparison between the solubility of CO<sub>2</sub> and H<sub>2</sub>S in [bmim][Tf<sub>2</sub>N] at 313.15 K, CO<sub>2</sub>; Δ, H<sub>2</sub>S— Mod. UNIFAC; ----, original UNIFAC.

Figure 5 compares the P-x diagram for the binary systems of CO<sub>2</sub> in the studied [bmim] cation based ILs at 313.3 K. According to this figure, the solubility of CO<sub>2</sub> increases in [bmim] cation-based ionic liquids in the order of [BF<sub>4</sub>]<sup>-</sup> < [PF<sub>6</sub>]<sup>-</sup> < [Tf<sub>2</sub>N]<sup>-</sup>. As Figure 5 shows, there is a good agreement between the results obtained from the UNIFAC based models and the experimental data.

Figures 6 and 7 show the H<sub>2</sub>S solubility of [bmim] and [hmim] cation based ILs at 313.15 K. As it can be observed from these figures, the results are not in the same order, for [bmim] based ionic liquids. The solubility can increase in the order of: [PF<sub>6</sub>]<sup>-</sup> < [BF<sub>4</sub>]<sup>-</sup> < [Tf<sub>2</sub>N]<sup>-</sup>. However, for [hmim] based ionic liquids, H<sub>2</sub>S solubility is in the

sequence of [BF<sub>4</sub>]<sup>-</sup> > [Tf<sub>2</sub>N]<sup>-</sup> > [PF<sub>6</sub>]<sup>-</sup>. These figures also compare the results obtained from the original as well as the modified UNIFAC models in correlating the experimental data for the solubility of H<sub>2</sub>S in those mentioned ionic liquids. As can be seen, the modified UNIFAC model can correlate with the experimental data better than the original one.

According to Figure 8, CO<sub>2</sub> solubility improves by increasing the alkyl chain length within the whole range of pressure. Blanchard et. Al [21], explained that increasing the length of alkyl chain causes greater free space in the ionic liquids which allows more CO<sub>2</sub> molecules to dissolve into the ionic liquids. While the free space within the ionic liquids is saturated by CO<sub>2</sub>, no more CO<sub>2</sub> molecules

can dissolve into the ionic liquids even under the higher pressures. Also, the modified UNIFAC model can predict the VLE experimental data at higher pressures.

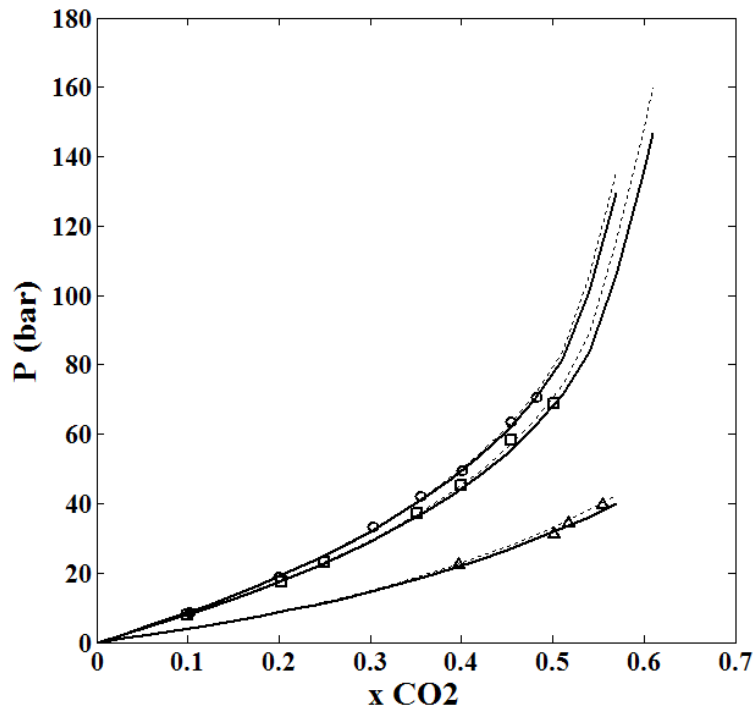


Figure 5. Effect of anion on the solubility of CO<sub>2</sub> in ILs at 313.3 K with experimental data, Δ, [bmim][Tf<sub>2</sub>N]; □, [bmim][PF<sub>6</sub>]; ○, [bmim][BF<sub>4</sub>]; —, Mod. UNIFAC; ----, UNIFAC.

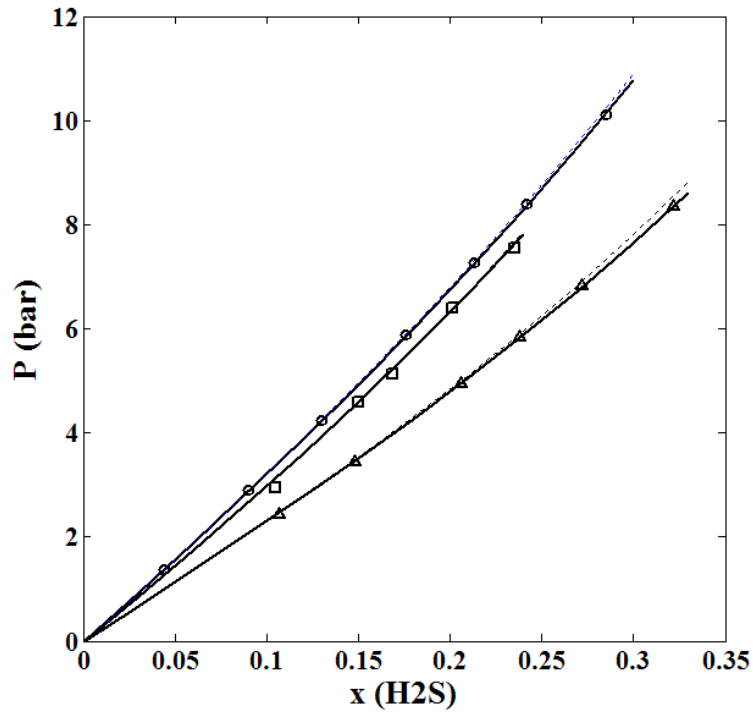


Figure 6. Effect of anion on the solubility of H<sub>2</sub>S in ILs at 313.15 K with experimental data, Δ, [bmim][Tf<sub>2</sub>N]; □, [bmim][BF<sub>4</sub>]; ○, [bmim][PF<sub>6</sub>]; —, Mod. UNIFAC; ----, original UNIFAC.



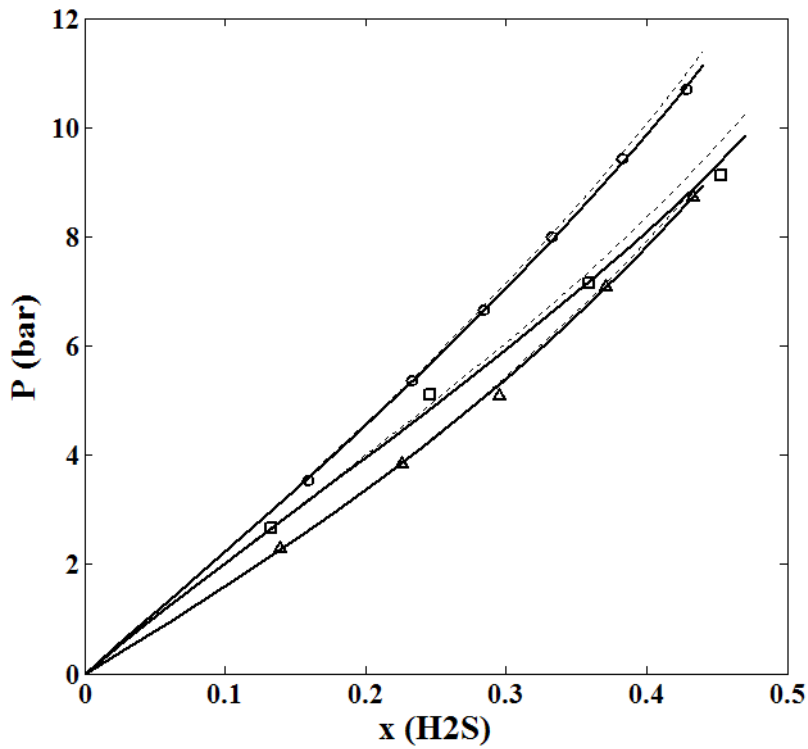


Figure 7. Effect of anion on the solubility of  $H_2S$  in ILs at 313.15 K with experimental data,  $\Delta$ , [hmim][ $BF_4$ ];  $\square$ , [hmim][ $Tf_2N$ ];  $\circ$ , [hmim][ $PF_6$ ]; —, Mod. UNIFAC; ----, UNIFAC.

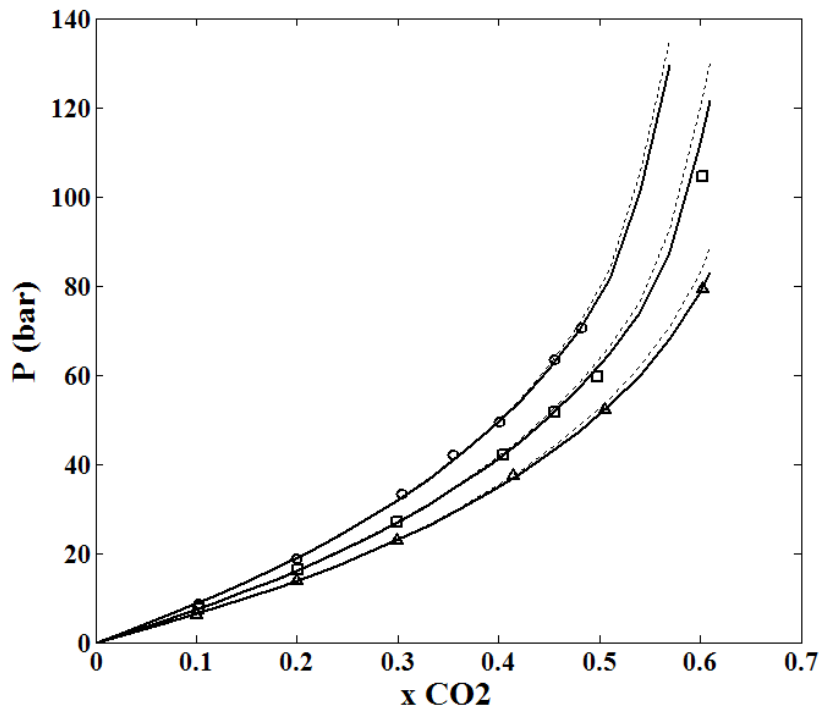


Figure 8. Effect of alkyl chain length on the cation and the solubility of  $CO_2$  in ILs at 313.3 K, With the experimental Data  $\Delta$ , [omim][ $BF_4$ ];  $\square$ , [hmim][ $BF_4$ ];  $\circ$ , [bmim][ $BF_4$ ]; —, Mod. UNIFAC; ----, UNIFAC.

The effect of temperature on the solubility of CO<sub>2</sub> and H<sub>2</sub>S in [emim][Tf<sub>2</sub>N] and [bmim][Tf<sub>2</sub>N] was investigated through Figures 9 and 10, respectively. As expected, the solubilities of CO<sub>2</sub> and H<sub>2</sub>S would improve along with the pressure enhancement and temperature reduction. The results at each

temperature and pressure were compared with those obtained from the original as well as the proposed models. As it can be seen, at lower temperatures and pressures both models can accurately correlate with the experimental data.

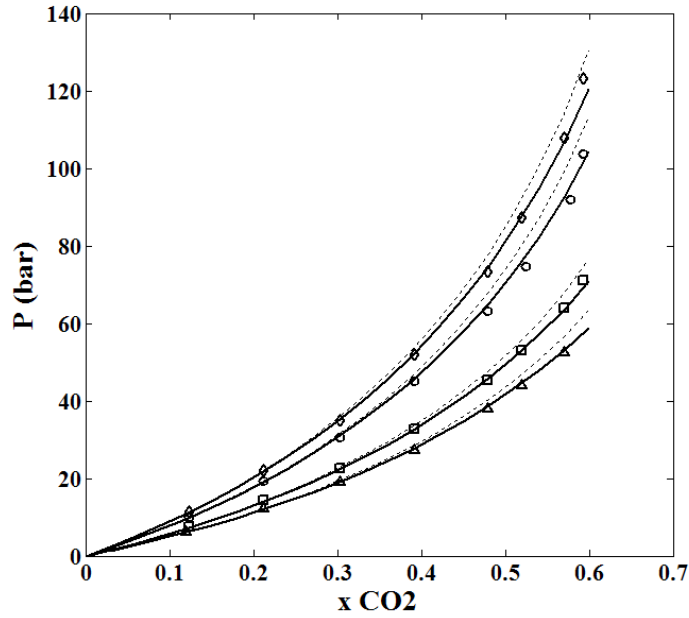


Figure 9. Effect of temperature on the solubility of CO<sub>2</sub> in [emim][Tf<sub>2</sub>N], with experimental data,  $\diamond$ , 351.6 K;  $\circ$ , 341.76 K;  $\square$ , 322.1 K;  $\Delta$ , 312.1 K; —, Mod. UNIFAC; ----, UNIFAC.

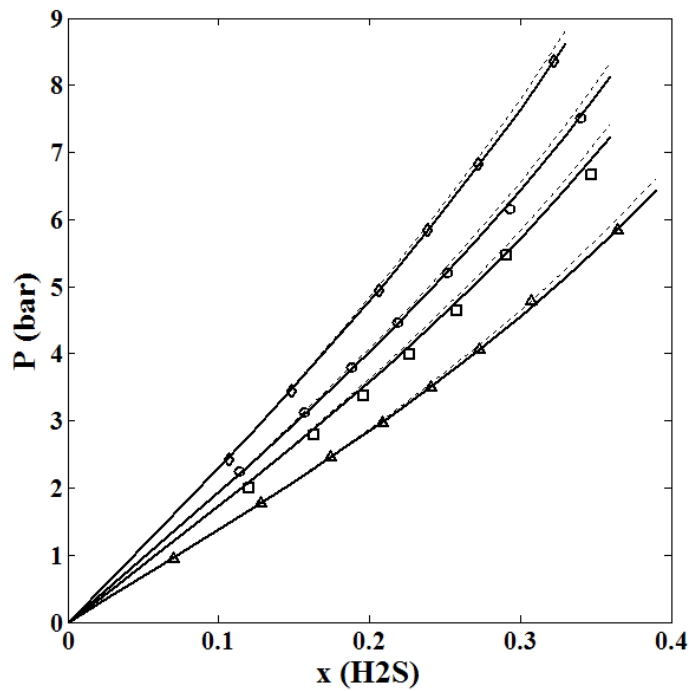


Figure 10. Effect of temperature on the solubility of H<sub>2</sub>S in [bmim][Tf<sub>2</sub>N], with experimental data,  $\diamond$ , 333.15 K;  $\circ$ , 323.15 K;  $\square$ , 313.15 K;  $\Delta$ , 303.15 K; —, Mod. UNIFAC; ----, UNIFAC.

#### 4. Conclusion

In this study, a modified UNIFAC model was proposed to investigate the solubility of acid gases in the imidazolium-based ILs. The effects of temperature, nature of anions and the alkyl chain length of cations on the solubility of acid gases in ILs were also investigated. The interaction parameters between the new functional subgroups of the fragmented ionic liquids with CO<sub>2</sub> and H<sub>2</sub>S molecules were reported using the original UNIFAC model. These regressed values were directly used in the proposed model. The proposed model was the modification of the UNIFAC model considering the free-volume effect. The free-volume parameter in the modified UNIFAC model represents the free-volume percent ratio of the ionic liquid to that of the acid gas. The parameter was regressed for each system using the extensive VLE experimental data available in the literature. It was shown that the free-volume parameter can change linearly with the molecular weight of ILs. The results obtained from the proposed model showed a good agreement with the VLE experimental data for the all studied binary systems. In addition, the results confirmed that the nature of anions in despite of cations significantly affect the solubility of acid gases in ILs. The solubility of CO<sub>2</sub> and H<sub>2</sub>S reduced by increasing the temperature. Also, in the case of CO<sub>2</sub>, it was shown that the solubility is higher in the ionic liquids with [Tf<sub>2</sub>N] anion which contains fluoroalkyl groups. In addition, a longer alkyl groups leads to the higher solubility of CO<sub>2</sub> in the ILs. To study the effect of anion group in the case of H<sub>2</sub>S, it was observed that while the solubility of H<sub>2</sub>S for [bmim] base ILs can change in the order of [PF<sub>6</sub>] < [BF<sub>4</sub>] < [Tf<sub>2</sub>N], for [hmim] based ILs, H<sub>2</sub>S solubility changes in the sequence of [PF<sub>6</sub>] < [Tf<sub>2</sub>N] < [BF<sub>4</sub>].

#### Nomenclature

##### List of Symbols

$a$	Activity
$a_{mn}$	UNIFAC group interaction parameter between groups m and n
$A_{wk}$	Van der Waals group surface area (cm <sup>2</sup> mol <sup>-1</sup> )
$f$	Fugacity
$f_i$	Fugacity of component i
$H_i$	Henry's constant of i
$m$	Molality (mol Kg <sup>-1</sup> )
$NP$	Number of experimental data points

$Q_k$	Surface parameter of group k
$q$	Surface area parameter
$R$	Reference state fugacity
$R_k$	Volume parameter of group k
$r$	Volume Parameter
$T$	Temperature (K)
$v$	Molar Volume
$x$	Mole fraction
$X_k$	Group mole fraction of k
$z$	Coordination number

#### Greek letters

$\alpha$	Free-volume Parameter
$\varphi$	Volume/Segment fraction
$\Gamma_k$	Residual activity coefficient of group k
$\Gamma_k^{(i)}$	Residual activity coefficient of group k in pure I component
$\gamma$	Mole based activity coefficient
$\theta$	Surface area fraction
$\psi_{mn}$	UNIFAC interaction parameter between groups m and n

#### Subscripts

1	Acid gas
2	IL
$i, j$	Component

#### Superscripts

$vdW$	Van der Waals
$l$	Liquid phase
$v$	Vapor phase
$Res$	Residual
$Comb$	Combinatorial
$fv$	Free-volume
$exp$	Experimental
$calc$	Calculated
$\infty$	Infinite

#### Abbreviations

AAD	Average absolute deviation
%FV	Free-volume percent
Mw	Molecular weight
VLE	Vapor-liquid equilibria
IL	Ionic liquid

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## بررسی حلالیت $H_2S$ و $CO_2$ در مایعات یونی بر پایه امیدازول با استفاده از مدل اصلاح شده UNIFAC

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### مشخصات مقاله

تاریخچه مقاله:

دریافت ۱ آذر ۱۳۹۸

دریافت پس از اصلاح ۲۷ بهمن ۱۳۹۸

پذیرش نهایی ۸ اسفند ۱۳۹۸

کلمات کلیدی:

مایعات یونی

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### چکیده

در این تحقیق، حلالیت گازهای اسیدی شامل  $CO_2$  و  $H_2S$  در ۹ مایع یونی بر پایه امیدازول توسط یک مدل ضریب فعالیت اصلاح شده UNI-FAC، مورد بررسی قرار گرفته است. تأثیر پارامترهای مؤثری از جمله دما، ماهیت آنیونها و کاتیونهای مایعات یونی و طول زنجیر آلکیلی بر حلالیت گازهای اسیدی در مایعات یونی مورد مطالعه قرار گرفته است. پارامترهای بر هم کنش زیرگروه های عاملی جدید موجود در مایعات یونی از جمله  $[IM]$ ،  $[BF_4]$ ،  $[PF_6]$ ،  $[Tf_2N]$ ،  $CH_3$  و  $CH_2$  با  $CO_2$  و  $H_2S$  با استفاده از مدل کلاسیک UNIFAC گزارش داده شده است. در مدل پیشنهادی، کسر حجمی موجود در عبارت ترکیبی فلوری-هاگینز مدل UNIFAC جهت در نظر گرفتن اختلاف حجم آزاد مایعات یونی و گازهای اسیدی اصلاح شده است. پارامتر حجم آزاد بیان کننده نسبت درصد حجم آزاد مولکول مایع یونی به درصد حجم آزاد مولکول گاز اسیدی می باشد. در این تحقیق، رابطه ای خطی با متغیر وزن مولکولی مایع یونی برای بدست آوردن پارامتر حجم آزاد ارائه شده است. نتایج حاصل از مدل سازی، نشان دهنده ی سازگاری بهتر مدل ارائه شده نسبت به مدل کلاسیک UNIFAC با داده های آزمایشگاهی تعادلی بخار-مایع ترکیباتی شامل مایعات یونی در حضور گازهای اسیدی تا فشار ۱۵۰ بار می باشد.

### نحوه استناد به این مقاله:

Sedghkardar M.H., Taghikhani V., Ghotbi C., Shariati A., A modified UNIFAC model in predicting the solubility of  $CO_2$  and  $H_2S$  in imidazolium-based ionic liquids. *Journal of Oil, Gas and Petrochemical Technology*, 2020; 7(1): 1-13. DOI: 10.22034/JOGPT.2020.113091.