RESEARCH PAPER

A modified UNIFAC model in predicting the solubility of CO_2 and H_2S in imidazolium-based ionic liquids

Mohammad Hashem Sedghkerdar[1], Vahid Taghikhani[2], Cyrus Ghotbi[2], Alireza Shariati[3]*

[1] *Gas, Oil and Petrochemical Engineering Department, Persian Gulf University, Bushehr, Iran*

[2] *Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran*

[3] *School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran*

ARTICLE INFO

ABSTRACT

In this work, a modified UNIFAC model was proposed to investigate the solubility of acid gases, i.e., CO_2 and H_2S 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_4], [PF6], [Tf_2N], CH_3 and CH_2 with CO_2 and H_2S 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 verfied that the free-volume parameter can be a linear fuction 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_2 and/or H_2S at pressures up to 150 bar.

1. Introduction

Acid gases composed of CO_2 and H_2S 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_2S is toxic and corrosive and thus it can poison the catalysts used in the natural gas refining and processing. In addition, carbon dioxide (CO_2) 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].

Altough there are different methods of CO_2 removal such as adsorption using calcium-based adsorbents, and membrabe separation, the absorption into liquid solvents is the most used method for removing the acid gas form the natural gas in the gas sweetening process [3-6]. Amine scrubbing is currently commertially used for the gas sweetening pocess. The contamination of natural gas stream due to its volatility and, therefore, the energy

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 sweeting 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_2 and H_2S with various imidazolium-based ILs, respectively.

Aki et al. [9] indicated that the interaction of CO_2 with the anions significantly affects the CO_2 solubility in the ILs. They discovered that the CO_2 highly dissolves in ILs with anions containing fluoroalkyl (CF_3) due to the CO_2-philic nature of the fluoroalkyl groups. Therefore, they suggested that this behavior is due to the CO_2 -philic nature of the fluoroalkyl groups. Furthermore, using ATR-IR spectroscopy for CO_2 with [bmim][BF_4] and [bmim][PF_6], Kazarian et al. [10] suggested that the interaction of CO_2 with the fluorinated anions in ILs is another factor that causes the higher solubility of CO_2 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_2 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_2 or H_2S 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_2 or H_2S. 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:

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

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

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

where

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

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

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

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

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]:

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

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

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

$$ln\gamma_i^R = \sum_k v_k^i \left(ln\Gamma_k - ln\Gamma_k^i \right) \qquad (9)$$

Where Γ_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 Ψ_{nm} between n and m groups is calculated as shown in the following equation:

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

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:

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

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

With

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

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

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

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

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

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

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

where the free-volume percent is defined as:

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

according to equations (15) and (16);

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

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

$$\alpha = \frac{(\%FV)_{IL}}{(\%FV)_{gas}} \qquad (18)$$

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_i, is proportional to the vdw volume, thus, the vdw in equation (17) can be replaced with the parameter r_i as:

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

The values for the free-volume parameters, α, 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$_4$], [PF$_6$] and [Tf$_2$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.
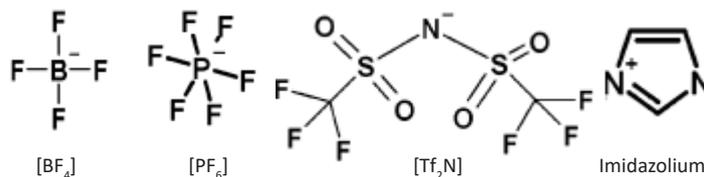

Figure 1. Four new main groups for original UNIFAC and Mod. UNIFAC

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$_3$	0.9011	0.848	[22]
CH$_2$	0.6744	0.540	[22]
Imidazolium	2.0260	0.868	[2]
Tf$_2$N	5.7740	4.932	[2]
PF$_6$	3.5134	3.852	[23]
BF$_4$	2.1429	1.967	[23]
CO$_2$	1.2900	1.124	[22]
H$_2$S	1.1723	1.070	[22]

Table 2 presents the number of subgroups in the fragmented ionic liquids. The subgroup interactions with CO$_2$ and H$_2$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$_3$	CH$_2$	Imidazolium	Anion
[emim][Tf$_2$N]	2	1	1	1 Tf$_2$N
[bmim][Tf$_2$N]	2	3	1	1 Tf$_2$N
[hmim][Tf$_2$N]	2	5	1	1 Tf$_2$N
[emim][PF$_6$]	2	1	1	1 PF$_6$
[hmim][PF$_6$]	2	5	1	1 PF$_6$
[bmim][PF$_6$]	2	3	1	1 PF$_6$
[hmim][BF$_4$]	2	5	1	1 BF$_4$
[bmim][BF$_4$]	2	3	1	1 BF$_4$
[omim][BF$_4$]	2	7	1	1 BF$_4$

3. Results and discussion

Table 3 gives the values for the interaction parameters between the subgroups in the systems containing ionic liquids, CO_2 and H_2S. 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_{ij}	CH_2	Tf_2N	PF_6	BF_4	[IM] [a]	CO_2	H_2S
CH_2	0	-1869.06	922.84	1481.24	1176.33	627.35	20647.56
Tf_2N	151.93	0			1535.75	354.75	1031.05
PF_6	2093.07		0		2119.77	43249.83	314.94
BF_4	-5.79			0	223.03	141.10	1368.28
[IM][a]	927.40	-1315.26	30735.70	-1044.54	0	195.46	58.84
CO_2	-183.02	-1269.32	459.97	-44.61	72.08	0	
H_2S	-105.27	-2031.63	9.90	-1016.09	382.20		0

[a] 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[a]		
CO_2/	T (K)	P (MPa)	X_{CO2}	α	UNIFAC	This work	Ref.
[emim][Tf_2N]	312.10-351.60	0.625-12.305	0.120-0.593	0.839	4.14	1.73	[24]
[bmim][Tf_2N]	313.30	1.290-3.950	0.310-0.554	0.814	2.38	2.31	[25
[emim][PF_6]	332.90-352.60	1.490-14.840	0.104-0.449	0.923	2.76	2.24	[5]
[bmim][PF_6]	313.30	0.780-6.887	0.100-0.501	0.901	1.89	2.23	[4]
[hmim][PF_6]	313.40	0.700-8.330	0.098-0.599	0.879	4.45	3.56	[6]
[bmim][BF_4]	303.19-333.15	0.740-14.440	0.102-0.482	0.951	1.68	1.36	[26]
[hmim][BF_4]	313.30	0.766-10.460	0.103-0.602	0.928	3.94	1.9	[27]
[omim][BF_4]	313.30	0.621-7.920	0.100-0.602	0.905	2.07	0.74	[28]

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

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_2S/IL systems

	Range of Data			Free-volume	%AAD[a]		
H_2S/	T (K)	P (MPa)	X_{CO2}	α	UNIFAC	This work	Ref.
[bmim][Tf_2N]	303.15-343.15	0.0944 -0.916	0.070-0.364	0.789	2.04	1.16	[8]
[hmim][PF_6]	303.15-343.15	0.161-0.845	0 .041-0.464	0.772	3.50	2.87	[7]
[bmim][PF_6]	303.15-343.15	0.123-1.011	0.044-0.358	0.882	1.49	1.21	[8]
[hmim][PF_6]	303.15-343.15	0.199-1.070	0.055-0.441	0.861	2.31	1.67	[7]
[bmim][BF_4]	303.15-343.15	0.061-0.813	0.038-0.354	0.939	2.54	2.57	[8]
[hmim][BF_4]	303.15-343.15	0.196-1.100	0.144-0.499	0.911	1.81	1.22	[7]

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

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_2/IL and H_2S/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_2 and H_2S respectively.

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

$$\alpha = -7.3711 * 10^{-4}(Mw) + 1.0977 \quad (22)$$
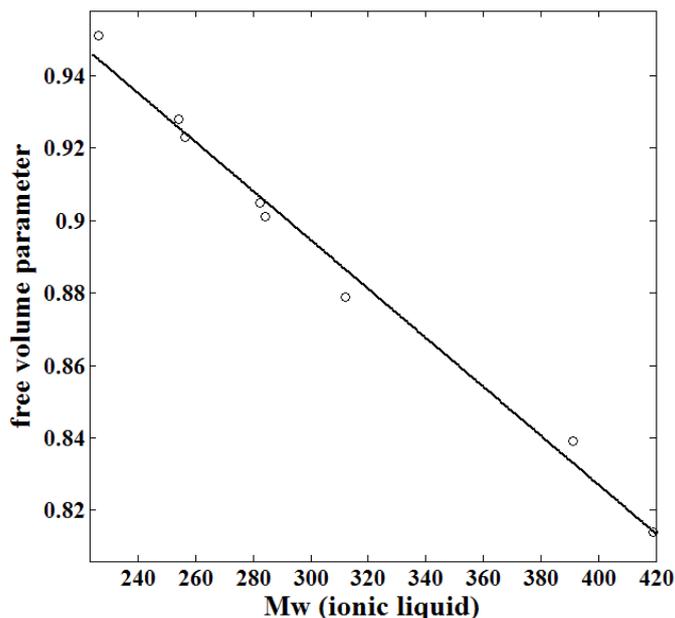
Figure 2. Linear relation between the molecular weight of ILs and free-volume parameter (α); o, optimized free-volume parameter for CO_2/IL systems
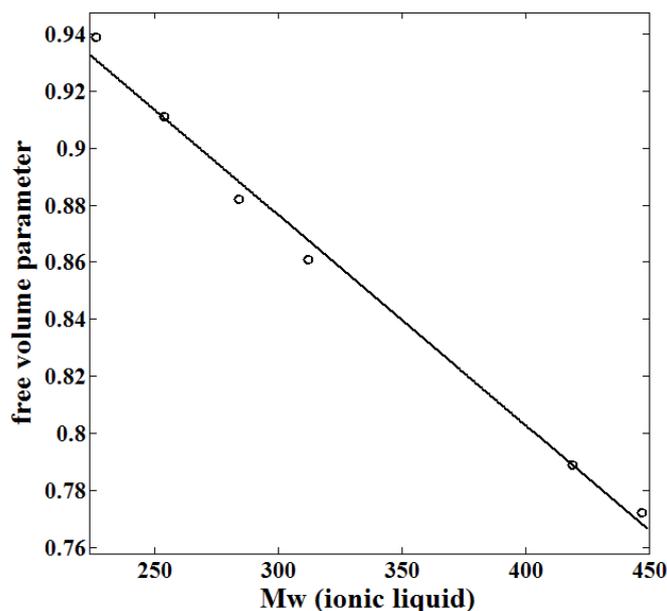

Figure 3. Linear relation between the molecular weight of ILs and free-volume parameter (α); o, optimized free-volume parameter for H_2S/IL systems

Table. 6. Molecular weight of ILs in this study

$[Tf_2N]^-$	Mw (gr mol^{-1})	$[PF_6]^-$	Mw (gr mol^{-1})	$[BF_4]^-$	Mw (gr mol^{-1})
$[emim]^+$	391.2	$[emim]^+$	256.2	$[bmim]^+$	226.0
$[bmim]^+$	419.2	$[bmim]^+$	284.2	$[hmim]^+$	254.0
$[hmim]^+$	447.3	$[hmim]^+$	312.2	$[omim]^+$	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_2S solubility is significantly higher than that of CO_2 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.
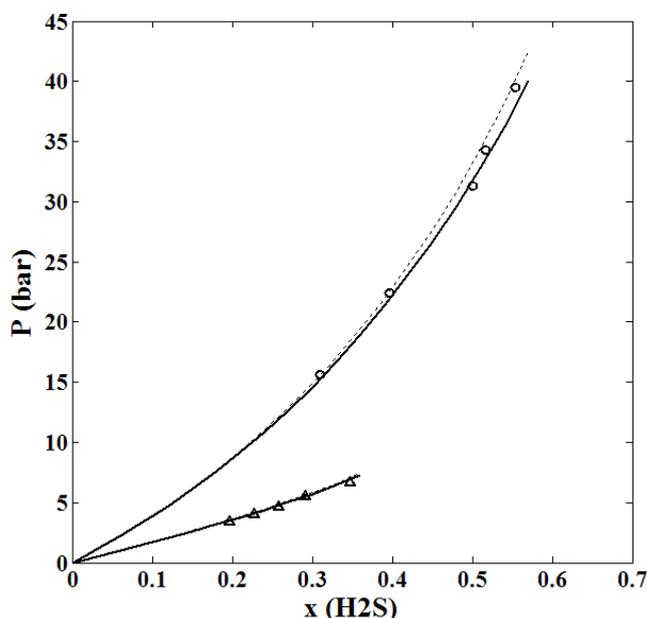

Figure 4. Comparison between the solubility of CO_2 and H_2S in [bmim][Tf$_2$N] at 313.15 K, CO_2; Δ, H_2S— Mod. UNIFAC; ----, original UNIFAC.

Figure 5 compares the P-x diagram for the binary systems of CO_2 in the studied [bmim] cation based ILs at 313.3 K. According to this figure, the solubility of CO_2 increases in [bmim] cation-based ionic liquids in the order of $[BF_4] < [PF_6] < [Tf_2N]$. 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_2S 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: $[PF_6] < [BF_4] < [Tf_2N]$. However, for [hmim] based ionic liquids, H_2S solubility is in the sequence of $[BF_4] > [Tf_2N] > [PF_6]$. 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_2S 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_2 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_2 molecules to dissolve into the ionic liquids. While the free space within the ionic liquids is saturated by CO_2, no more CO_2 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.
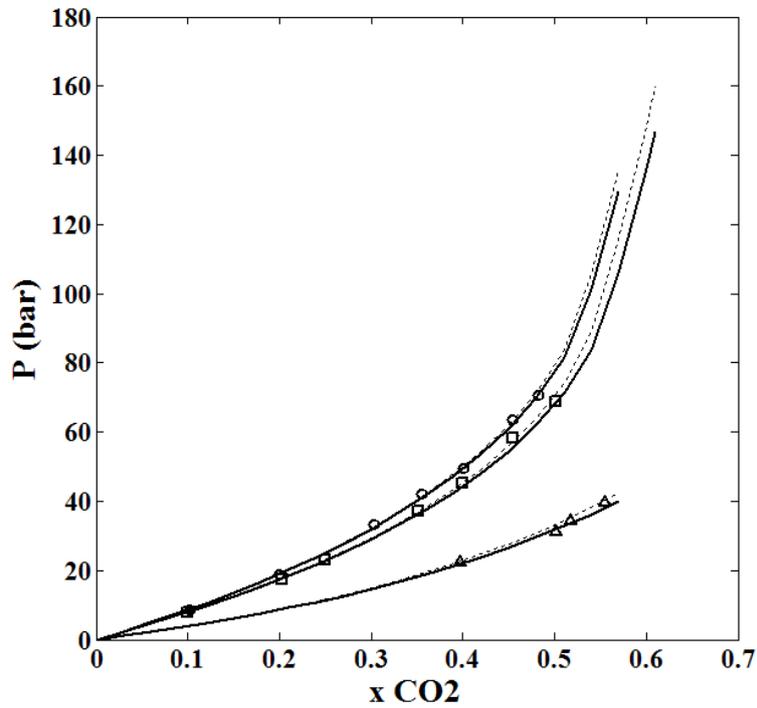

Figure 5. Effect of anion on the solubility of CO_2 in ILs at 313.3 K with experimental data, Δ, [bmim][Tf$_2$N]; □, [bmim][PF$_6$]; ○, [bmim][BF$_4$]; — Mod. UNIFAC; ----, UNIFAC.
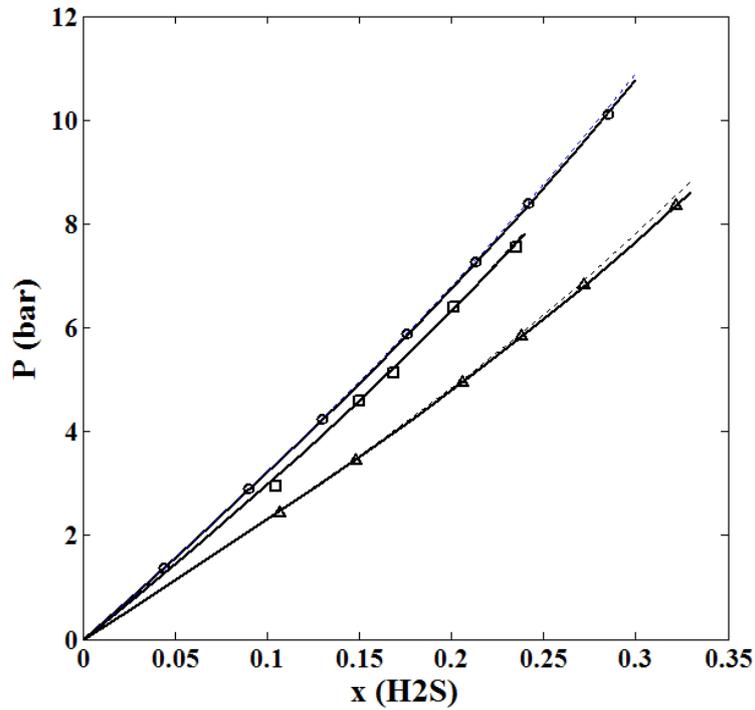

Figure 6. Effect of anion on the solubility of H_2S in ILs at 313.15 K with experimental data, Δ, [bmim][Tf$_2$N]; □, [bmim][BF$_4$]; ○, [bmim][PF$_6$]; —, Mod. UNIFAC; ----, original UNIFAC.
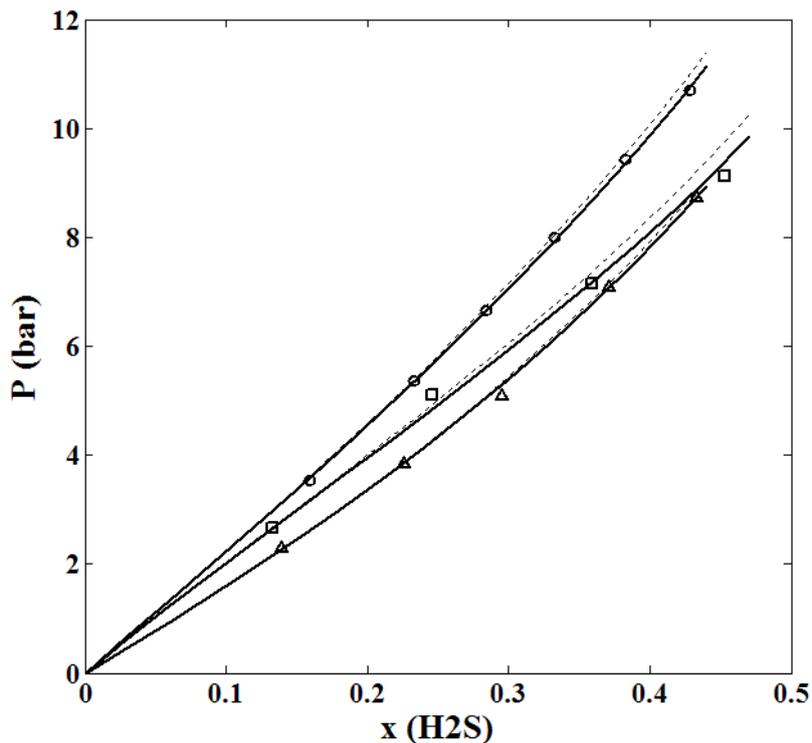
Figure 7. Effect of anion on the solubility of H$_2$S in ILs at 313.15 K with experimental data, Δ, [hmim][BF$_4$]; □, [hmim][Tf$_2$N]; ○, [hmim][PF$_6$]; —, Mod. UNIFAC; ----, UNIFAC.
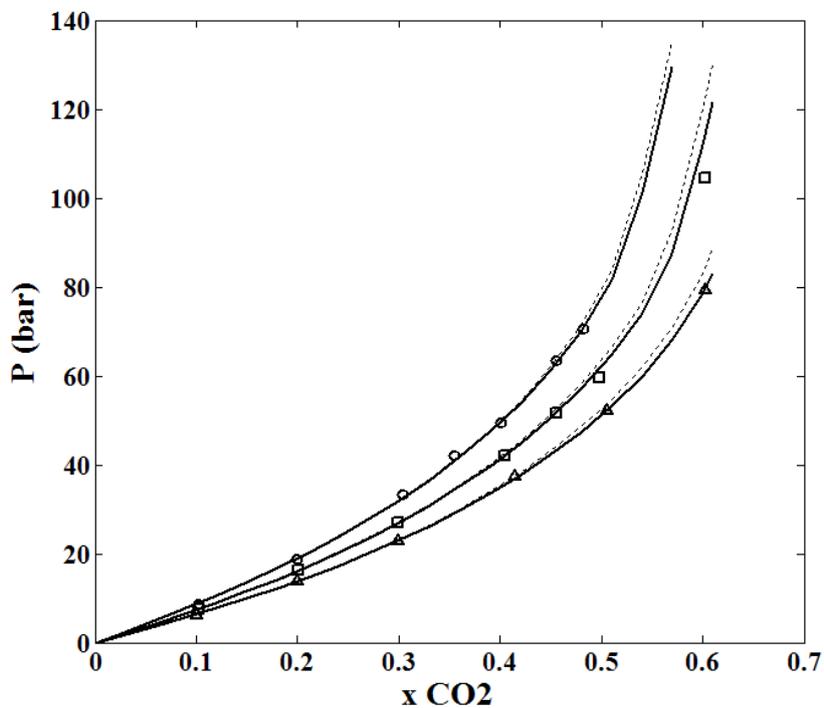

Figure 8. Effect of alkyl chain length on the cation and the solubility of CO$_2$ in ILs at 313.3 K, With the experimental Data Δ, [omim][BF$_4$]; □, [hmim][BF$_4$]; ○, [bmim][BF$_4$]; —, Mod. UNIFAC; ----, UNIFAC.

The effect of temperature on the solubility of CO_2 and H_2S in [emim][Tf$_2$N] and [bmim][Tf$_2$N] was investigated through Figures 9 and 10, respectively. As expected, the solubilities of CO_2 and H_2S 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.
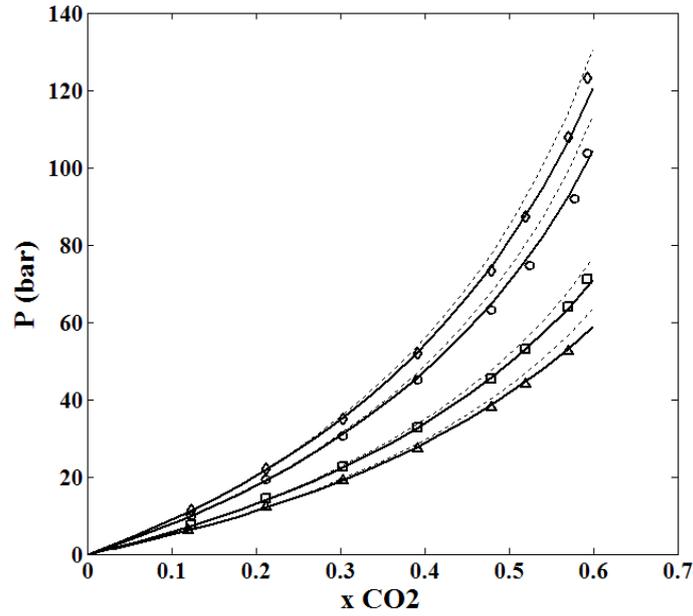

Figure 9. Effect of temperature on the solubility of CO_2 in [emim][Tf$_2$N], with experimental data, ◊, 351.6 K; ○, 341.76 K; □, 322.1 K; Δ, 312.1 K; —, Mod. UNIFAC; ----, UNIFAC.
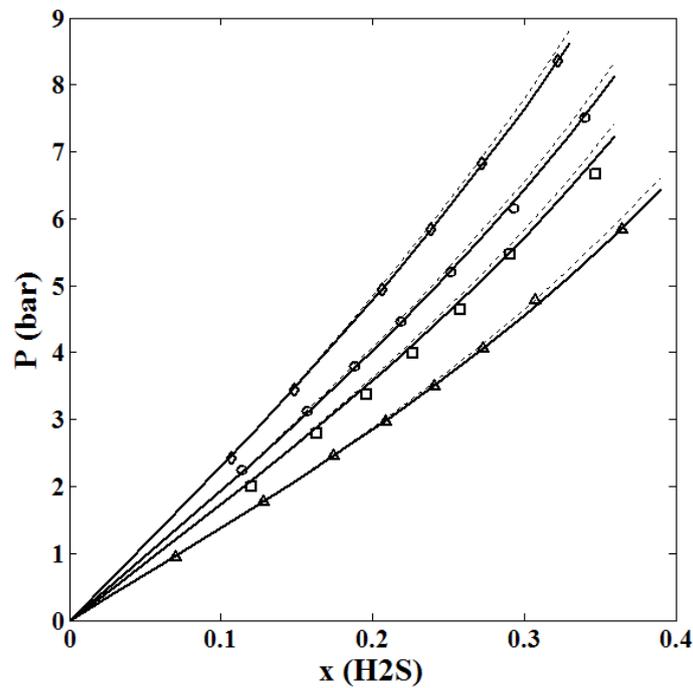

Figure 10. Effect of temperature on the solubility of H_2S in [bmim][Tf$_2$N], with experimental data, ◊, 333.15 K; ○, 323.15 K; □, 313.15 K; Δ, 303.15 K; —, Mod. UNIFAC; ----, UNIFAC.

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_2 and H_2S 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_2 and H_2S reduced by increasing the temperature. Also, in the case of CO_2, it was shown that the solubility is higher in the ionic liquids with $[Tf_2N]$ anion which contains fluoroalkyl groups. In addition, a longer alkyl groups leads to the higher solubility of CO_2 in the ILs. To study the effect of anion group in the case of H_2S, it was observed that while the solubility of H_2S for [bmim] base ILs can change in the order of $[PF_6]$ < $[BF_4]$ < $[Tf_2N]$, for [hmim] based ILs, H_2S solubility changes in the sequence of $[PF_6]$ < $[Tf_2N]$ < $[BF_4]$.

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 ($cm^2\ mol^{-1}$)
f	Fugacity
f_i	Fugacity of component i
H_i	Henry's constant of i
m	Molality (mol Kg^{-1})
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

α	Free-volume Parameter
φ	Volume/Segment fraction
Γ_k	Residual activity coefficient of group k
$\Gamma_k^{(i)}$	Residual activity coefficient of group k in pure I component
γ	Mole based activity coefficient
θ	Surface area fraction
Ψ_{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
∞	Infinite

Abbreviations

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

References

[1] A. Dashti, M. Raji, M.S. Alivand, A.H. Mohammadi, "Estimation of CO2 equilibrium absorption in aqueous solutions of commonly used amines using different computational schemes", Fuel, vol. 264, pp. 116616, 2020.

[2] R. Kato, J. Gmehling, J. Chem. "Systems with ionic liquids: Measurement of VLE and γ∞ data and prediction of their thermodynamic behavior using original UNIFAC, mod. UNIFAC (Do) and COSMO-RS(Ol)", Thyrmodyn., vol.37, pp. 603-619, 2005.

[3] M.H. Sedghkerdar, N. Mahinpey, Z. Sun, S. Kaliaguine, "Novel synthetic sol–gel CaO based pellets using porous mesostructured silica in cyclic CO_2 capture process", Fuel, vol. 127, pp. 101-108, 2014.

[4] M.H. Sedghkerdar, N. Mahinpey, "Modified Overlapping Grain Size Distributed Model for the Kinetic Study of CO_2 Capture by a Synthetic Calcium-Based Sorbent: Structural Changes from the Chemical Reaction and Sintering", Ind. Eng. Res. Chem. Vol. 58, pp.14000-14007, 2019,.

[5] A.H. Soleimanisalim, M.H. Sedghkerdar, D. Karami, N. Mahinpey, "Effects of second metal oxides on zirconia-stabilized Ca-based sorbent for sorption/catalyst integrated gasification", J. Environ. Chem. Eng., vol. 5, pp. 1281-1288, 2017.

[6] N. Mahinpey, M.H. Sedghkerdar, A. Aqsha, A.H. Soleimanisalim, "CO_2 Capture Performance of Core/Shell CaO-Based Sorbent Using Mesostructured Silica and Titania in a Multicycle CO_2 Capture Process", Ind. Eng. Res. Chem. Vol. 55, pp. 4532-4538, 2016.

[7] A. Shariati and C.J. Peters, "High-pressure phase behavior of systems with ionic liquids: II. The binary system carbon dioxide+ 1-ethyl-3-methylimidazolium hexafluorophosphate", J. Supercrit. Fluids, vol. 29, pp. 43-48, 2004.

[8] A. H. Jalili, M. Rahmati-Rostami, C. Ghotbi, M. Hosseini-Jenab, A. N. Ahmadi, "Solubility of H2S in Ionic Liquids [bmim][PF6], [bmim][BF4], and [bmim][Tf2N]", J. Chem. Eng. Data, vol. 54, pp. 1844-1849, 2009.

[9] S. N. V. K. Aki, B. R. Mellein, E. M. Saurer and J. F. Brennecke, "Liquid Phase Behavior of Imidazolium-Based Ionic Liquids with Alcohols", J. Phys. Chem. B, vol. 108, pp. 5113-5119, 2004.

[10] S. G. Kazarian, B. J. Briscoe, T. Welton, "Combining ionic liquids and supercritical fluids: in situ ATR-IR study of CO2 dissolved in two ionic liquids at high pressuresElectronic supplementary information (ESI) available: schematic view of the miniature high-pressure flow cell. See", Chem. Commun. vol. 20, pp. 2047, 2000.

[11] M.R. Ally, J. Braunstein, R. E. Baltus, S. Dai, D. W. Depaoli, J. M. Simonson. "Irregular ionic lattice model for gas solubilities in ionic liquids" Ind. Eng. Chem. Res. Vol. 43, pp. 1296-1301, 2004.

[12] B. Dębski, A. Hänel, R. Aranowski, S. Stolte Marta Markiewicz, T. Veltzke, I. Cichowska-Kopczyńska, "Thermodynamic interpretation and prediction of CO_2 solubility in imidazolium ionic liquids based on regular solution theory", J. Molec. Liq. Vol. 291 pp. 110477, 2019.

[13] M. Loreno, R.A. Reis, S. Mattedi, M.L.L. Paredes, "Predicting the solubility of carbon dioxide or methane in imidazolium-based ionic liquids with GC-sPC-SAFT equation of state", Fluid Phase Equil. Vol. 479, pp. 85-98, 2019.

[14] E. Lukoshkoa, F. Muteletb, K. Paduszyńskia, U. Domańska, Fluid Phase Equilib. 2015, 339, 105.

[15] A.Fredensuld, R. L. Jones, J. M. Prausnitz, "GroupContribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures,"AIChE J. vol. 21, pp. 1086-1099, 1975.

[16] T. Oshi and J .M. Prausnitz, "Estimation of solvent activities in polymer solutions using a group-contribution method" Ind. Eng. Chem. Process Des. Dev. Vol. 17, pp. 333-339.

[17] H. S. Elbro, A. Fredensuld and P. Rasmussen, "A new simple equation for the prediction of solvent activities in polymer solutions" Macromolecules vol. 23, pp. 4707-4714, 1990.

[18] A. Bondi, "Physical Properties of Molecular Crystals, Liquid and Gases", Wiley, New York, 1968.

[19] J. C. Lagarias, J. A. Reeds, M. H. wrright, P. E. Wright, "Convergence properties of the Nelder--Mead simplex method in low dimensions"J. Optimization vol. 9, pp. 112-147, 1998.

[20] C. S. Pomelli, C. Chiappe, A. Vidis, G. Laurenczy, P. J. Dyson, "Influence of the interaction between hydrogen sulfide and ionic liquids on solubility: experimental and theoretical investigation", J. Phys. Chem. B vol. 111, pp. 13014-9, 2007.

[21] L. A. Blanchard, Z. Gu and J. F. Brennecke, "High-Pressure Phase Behavior of Ionic Liquid/CO_2 Systems"J. Phys. Chem. B vol. 105, pp. 2437-2444, 2001.

[22] A. Fredenslund, J. Gmehling, P. Rasmussen, "Vapor-Liquid Equilbria Using UNIFAC, Elsevier", Amsterdam, 1977.

[23] B. Breure, S. B. Bottini, G-J. Witkamp, C. J. Peters, "Thermodynamic modeling of the phase behavior of binary systems of ionic liquids and carbon dioxide with the group contribution equation of state", J. Phys. Chem. B vol. 111, pp. 14265-14270, 2007.

[24] A. M. Schilderman, S. Raeissi, C. J. Peters, "Solubility of carbon dioxide in the ionic liquid 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide" Fluid Phase Equilib. Vol. 260, pp. 19-22, 2007.

[25] E.-K. Shin, B.-C. Lee, J.S Lim, "High-pressure solubilities of carbon dioxide in ionic liquids: 1-alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide" J. Supercrit. Fluids vol. 45, pp. 282-292, 2008.

[26] M. C. Kroon, A. Shariati, M. Constantini, J. Van Spronsen, G. J. Witkamp, R. A. Sheldon and C. J. Peters, " High-pressure phase behavior of systems with ionic liquids: Part V. The binary system carbon dioxide+ 1-butyl-3-methylimidazolium tetrafluoroborate", J. Chem. Eng. Data vol. 50, pp. 173-176, 2005.

[27] M. Constantini, V.A. Toussaint, A. Shariati, C. J. Peters and I. Kikic, "High-pressure phase behavior of systems with ionic liquids: Part IV. Binary system carbon dioxide+1-hexyl-3-methylimidazolium tetrafluoroborate", J. Chem. Eng. Data vol. 50, pp. 52-55, 2005.

[28] K. I. Gutkowski, A. Shariati, C. J. Peters, "High-pressure phase behavior of the binary ionic liquid system 1-octyl-3-methylimidazolium tetrafluoroborate+ carbon dioxide"J. Supercrit. Fluids vol. 39, pp. 187-191, 2006.

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

محمد هاشم صدق‌کردار[۱]*، وحید تقی خانی[۲]، سیروس قطبی[۲]، علیرضا شریعتی[۳]

۱. دانشگاه خلیج فارس، دانشکده نفت، گاز و پتروشیمی، بوشهر، ایران

۲. دانشگاه صنعتی شریف، دانشکده مهندسی شیمی و نفت، تهران، ایران

۳. دانشکده، نفت، گاز و پتروشیمی، دانشگاه شیراز، شیراز، ایران

مشخصات مقاله

※ عهده‌دار مکاتبات؛

رایانامه: sedghkerdar@pgu.ac.ir

تلفن: ۲۶۱۵ ۳۱۲۲ ۷۷ ۹۸+

چکیده

در این تحقیق، حلالیت گازهای اسیدی شامل CO_2 و H_2S در ۹ مایع یونی بر پایه ایمیدازول توسط یک مدل ضریب فعالیت اصلاح شده UNIFAC، 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. پارامتر های 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: