

## Prediction of Ammonia Solubility in Ionic Liquids Using UNIFAC Model

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Ionic liquid is a new type of green solvent, because of the nonvolatility, good dissolution properties, and high chemical stability. It is expected to replace the current extensive use of volatile solvents, to design environmental friendly new chemical process. However each cations and anions different from each other, combination into a huge number of ionic liquids, if its physical and chemical properties determined through the experiment, the cost is high. So it is highly needed to develop an effective and reliable method to predict the thermodynamic properties of the systems containing ionic liquid. Ammonia (NH<sub>3</sub>) solubility studies about the design and production of natural gas plays an important role. In this paper the solubility of NH<sub>3</sub> in different ionic liquids are studied, and compared with the results predicted by UNIFAC model.

The accurate calculation of the NH<sub>3</sub> solubility in ILs is important in natural gas purification. UNIFAC model is selected to predict the solubility of NH<sub>3</sub>, which can decrease a plenty of experimental work in the laboratory. The new group NH<sub>3</sub> is defined by regression of the experimental data collected from the literatures published to obtain the group-group interaction parameters between the components of NH<sub>3</sub> and ionic liquids. The consistency test is carried out to examine the accuracy of prediction results. The solubility predicted by UNIFAC model is verified a perfect agreement with the experimental data provided in the literature at temperature range from 282.2 K to 355.8 K and pressure up to 25 bar, with an average relative deviation (ARD) less than 10 %. The results demonstrate that for system studied in this work, UNIFAC model can realize the solubility prediction successful. This predictive model is useful for predicting the NH<sub>3</sub> solubility in imidazolium-based ionic liquids and providing the phase equilibrium data for the application of liquid natural gas and the relevant mass transfer separation in chemical engineering.

### 1. Introduction

As an integral part of chemical raw materials, ammonia occupies an important position in agricultural production, using in making urea, ammonium nitrate, ammonium chloride and potassium phosphate compound fertilizer, etc. But it is also a kind of pollution gases of the atmosphere, which can cause serious damage to people's health. Ammonia recovery mainly includes the preparation of concentrated ammonia process and preparation of liquid ammonia. There still exist some drawbacks, like high cost in operation and extra waste. The approach of absorption in an efficient liquid should be considered.

As a type of green solvent, ionic liquids (ILs) absorbed more and more attention in recent years (Lei et al., 2014) and more recently (Zhu et al., 2016), and used in various fields of chemical research, especially for its non-toxicity, nonvolatility, and good dissolution properties. Using ILs for gases separation and absorption is a good choose. A growing number of experimental studies have explored the solubility of NH<sub>3</sub> in common ILs, and shown that NH<sub>3</sub> had a highly solubility in ILs, however these cannot meet the practical needs. The requirement of predictive thermodynamic models is so heavily for investigating the research of ILs. The predictive thermodynamic models are able to describe the properties such as vapor-liquid equilibrium (VLE), solubility, and selectivity of gases in the mixtures of ILs. UNIFAC model (Hector et al., 2014) is used in thermodynamic property prediction without requirement of experimental data. Molecules are divided into groups using UNIFAC model and the interaction parameters between groups are considered only, which is highly applied in the systems that

lack of phase equilibrium data. Lei et al. (2014) predicted the solubility of CO<sub>2</sub> in ILs using UNIFAC model, obtained the interaction parameters between CO<sub>2</sub> and ILs groups through correlating the experimental data. Yunus et al. (2012) used UNIFAC model to fit the CO<sub>2</sub> solubility experiment data in [C<sub>4</sub>py][Tf<sub>2</sub>N] ionic liquid, and the predictive results shows good agreement with experimental data. This is the first work to apply the UNIFAC model to IL-NH<sub>3</sub> systems. In this work, UNIFAC model was researched to obtain the interaction parameters between NH<sub>3</sub> and ILs groups, aimed at predicting the solubility of NH<sub>3</sub> in ILs and analysis the influence of anions and cations of ILs on solubility of NH<sub>3</sub>, the ARDs were also calculated.

## 2. UNIFAC model

When NH<sub>3</sub> is in equilibrium with an ionic liquid system, it can be described as:

$$y_1 p \varphi_1(T, p, y_1) = x_1 \gamma_1 p_1^s \quad (1)$$

Where  $x_1$  and  $y_1$  are the mole fractions of NH<sub>3</sub> in liquid and gas phase respectively;  $\varphi_1(T, p, y_1)$  is the gas fugacity coefficient in gas phase calculated by R-K equation (Redlich et al., 1949);  $p$  is the pressure in system;  $p_1^s$  is the gas saturated vapor pressure obtained by Antoine equation (Fogg et al., 1991);  $\gamma_1$  is the gas activity coefficient in liquid phase determined by the UNIFAC model.

UNIFAC model is activity coefficient model that developed from UNIQUAC model combined with group structural analysis. In UNIFAC model, the activity coefficient is divided into two parts: combinatorial term  $\gamma_i^C$  determined by molecular size and shape and residual term  $\gamma_i^R$  determined by intermolecular interaction. The equation is written as:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2)$$

$\ln \gamma_i^C$  can be described as :

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - 5q_i \left[ 1 - \frac{V_i}{F_i} + \ln \left( \frac{V_i}{F_i} \right) \right] \quad (3)$$

$$F_i = \frac{q_i}{\sum_j q_j x_j}; \quad V_i = \frac{r_i}{\sum_j r_j x_j} \quad (4)$$

In the equation above,  $q_i$  and  $r_i$  are the surface parameters and volume parameters of pure components molecules respectively. They are written as:

$$q_i = \sum_k v_i^k Q_k; \quad r_i = \sum_k v_i^k R_k \quad (5)$$

Where  $v_i^k$  is stand for the number of group  $k$  in molecule  $i$ ;  $Q_k$  and  $R_k$  are surface parameters and volume parameters of group  $k$  respectively.

$\ln \gamma_i^R$  can be described as:

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (6)$$

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_{m=1}^N \theta_m \varphi_{mk} \right) - \sum_{m=1}^N \left( \frac{\theta_m \varphi_{km}}{\sum_{n=1}^N \theta_n \varphi_{nm}} \right) \right] \quad (7)$$

$$\ln \Gamma_k^{(i)} = Q_k \left[ 1 - \ln \left( \sum_{m=1}^N \theta_m^{(i)} \varphi_{mk} \right) - \sum_{m=1}^N \left( \frac{\theta_m^{(i)} \varphi_{km}}{\sum_{n=1}^N \theta_n^{(i)} \varphi_{nm}} \right) \right] \quad (8)$$

$$\theta_m = \frac{Q_m X_m}{\sum_{n=1}^N Q_n X_n}; \quad \theta_m^{(i)} = \frac{Q_m X_m^{(i)}}{\sum_{n=1}^N Q_n X_n^{(i)}} \quad (9)$$

$$X_m = \frac{\sum_{i=1}^M v_m^{(j)} x_i}{\sum_{i=1}^M \sum_{n=1}^N v_n^{(j)} x_i}; X_m^{(i)} = \frac{v_m^{(i)}}{\sum_{k=1}^N v_k^{(i)}} \quad (10)$$

$$\varphi_{n,m} = \exp[-(a_{nm} / T)] \quad (11)$$

Where  $x_i$  is the mole factor of component  $i$ ;  $X_m$  is the mole factor of group  $m$  in mixture solution;  $M$  is number of component,  $N$  is the group number.  $\varphi_{nm}$  is the group interaction parameters, and  $a_{nm}$  is the energy group interaction parameters that has no relation with the temperature.

### 3. Results and discussion

#### 3.1 Group interaction parameters regressing

In this work, five ILs were discussed to analysis the capability of UNIFAC model for  $\text{NH}_3$  solubility prediction in different pressure and temperature.

In using UNIFAC model, the ILs molecules are required to be divided into basic groups.  $\text{NH}_3$  molecule is regarded as a main group, for ILs, is also divided into several groups, the selection of main groups are treated as electrically neutral. As for  $[\text{BMIM}][\text{BF}_4]$ , it is divided into one  $\text{CH}_3$  group, three  $\text{CH}_2$  group, and one  $[\text{MIM}][\text{BF}_4]$  group.

The surface parameters ( $R_k$ ) and volume parameters ( $Q_k$ ) of ILs groups are obtained from literature (Lei et al., 2009), the group interaction parameters of ILs- $\text{CH}_2$  can be found from literature (Lei et al., 2009), and the unknown group interaction parameters between  $\text{NH}_3$  and ILs are regressed from the experimental data collected from literatures in this work.

In regression of group interaction parameters, the objective function  $OF$  defined as:

$$OF = \min \frac{1}{N} \sum_1^N \left| \frac{x_{cal} - x_{exp}}{x_{exp}} \right| \quad (12)$$

Where  $x_{exp}$  and  $x_{cal}$  stand for the experimental date and calculation data of  $\text{NH}_3$  solubility in ILs;  $N$  is the number of experimental data points.

Table 1: Group interaction parameters of UNIFAC model regressing

m	n	$a_{mn}$	$a_{nm}$
$\text{NH}_3$	$\text{CH}_2$	151	293
$\text{NH}_3$	$\text{MIMPF}_6$	877	-107
$\text{NH}_3$	$\text{MIMBF}_4$	148	486
$\text{NH}_3$	$\text{MIMTF}_2\text{N}$	5	788

Through minimizing the objective function, the group interaction parameters of UNIFAC model is listed in Table 1. The effectiveness is connected with the experimental data number and accuracy, the experimental data of  $\text{NH}_3$  solubility in ILs is still limited now, a large amount experiments should be completed by a large of researchers. As shown in Table 2, absolute relative deviations (ARDs) in most cases are less than 10 %. Figures 1a, 1b, 1c, and 1d show the solubility of  $\text{NH}_3$  in  $[\text{EMIM}][\text{BF}_4]$ ,  $[\text{BMIM}][\text{BF}_4]$ ,  $[\text{HMIM}][\text{BF}_4]$ ,  $[\text{OMIM}][\text{BF}_4]$ . Figures 2a, 2b and 2c show the solubility of  $\text{NH}_3$  in  $[\text{BMIM}][\text{PF}_6]$ ,  $[\text{BMIM}][\text{BF}_4]$  and  $[\text{BMIM}][\text{Tf}_2\text{N}]$ . It can be seen that the predictive values and the experimental data are coincident and with the same trend.

Table 2: The ARDs of UNIFAC model in prediction solubility of  $\text{NH}_3$  with experimental data

Ionic liquids	T range (K)	p range (bar)	ARDs%	ref
$[\text{BMIM}][\text{PF}_6]$	283.4 - 355.8	1.38 - 23.85	8.7	(Yokozeki et al., 2007)
$[\text{BMIM}][\text{Tf}_2\text{N}]$	283.3 - 347.6	1.14 - 24.88	9.0	(Yokozeki et al., 2007)
$[\text{EMIM}][\text{BF}_4]$	293.15 - 333.15	1.4 - 6.3	3.6	(Li et al., 2010)
$[\text{BMIM}][\text{BF}_4]$	282.2 - 355.1	0.91 - 23.75	11.7	(Yokozeki et al., 2007)
	293.15 - 333.15	0.7 - 8.3	7.5	(Li et al., 2010)
$[\text{HMIM}][\text{BF}_4]$	293.15 - 333.15	1.7 - 7.1	6.4	(Li et al., 2010)
$[\text{OMIM}][\text{BF}_4]$	293.15 - 333.15	1 - 6.1	9.8	(Li et al., 2010)

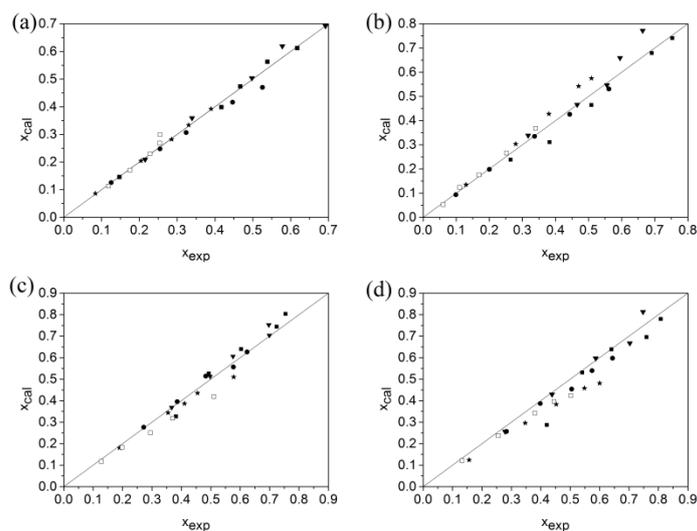


Figure 1: Comparison between experimental data and the values with different temperature. (a) [EMIM][BF<sub>4</sub>]; (b) [BMIM][BF<sub>4</sub>]; (c) [HMIM][BF<sub>4</sub>]; (d) [OMIM][BF<sub>4</sub>]. ■ 293.15 K; ● 298.15 K; ▼ 313.15 K; □ 323.15 K; ★ 333.15 K.

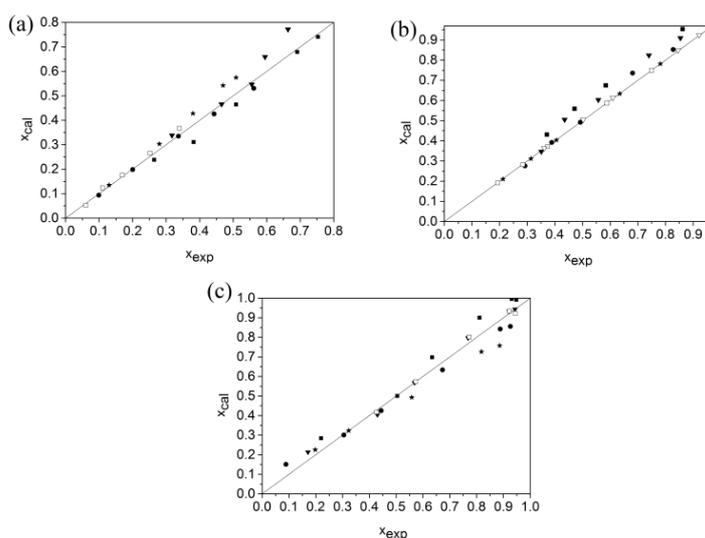


Figure 2: Comparison between experimental data and the values predicted by UNIFAC model of the ammonia solubility in ionic liquids with different temperature. (a) [BMIM][BF<sub>4</sub>]; (b) [BMIM][PF<sub>6</sub>]; (c) [BMIM][Tf<sub>2</sub>N]

### 3.2 Structure-property relation of ILs for NH<sub>3</sub>

The correlation in anion and cation of ILs and solubility of NH<sub>3</sub> should be predictive with Henry constant ( $H(T)$ ) which can be written as:

$$H(T) = \lim_{x_i \rightarrow 0} \frac{f_i}{x_i} = \gamma_i^\infty p_i^s(T) \quad (13)$$

Where,  $H(T)$  means the Henry constant of NH<sub>3</sub>,  $K_p$  is the gas fugacity,  $K_p$ ;  $\gamma_i^\infty$  stands for the infinite dilution activity coefficients, obtained by UNIFAC model;  $p_i^s(T)$  the gas saturated vapour pressure,  $K_p$ ;  $x_i$  is the mole factor of component NH<sub>3</sub> in ILs.

The Henry constant of NH<sub>3</sub> in different ILs were analysis, which are consistent with experimental data. Figure 3 shows the impact of anion of ILs on solubility of NH<sub>3</sub>. With the same cation, Henry constant are in order of [Tf<sub>2</sub>N]<sup>-</sup> > [BF<sub>4</sub>]<sup>-</sup> > [PF<sub>6</sub>]<sup>-</sup>. For cation, with the same anion [BF<sub>4</sub>]<sup>-</sup>, Figure 4 shows that with the number of carbon

increasing the henry constant decreasing, which is in accordance with experimental data. These indicated that with the same cation, along with the carbon number increasing, the solubility increasing. With the alkyl chain length longer the asymmetry characteristics of ILs is increasing, and ILs molecular inter-atomic forces is weak, the forces between the ILs molecules and  $\text{NH}_3$  molecules is stronger, the solubility of  $\text{NH}_3$  in ILs is become greater. Increasing the number of carbon or change the anion of ILs to increase the solubility of  $\text{NH}_3$  is feasible.

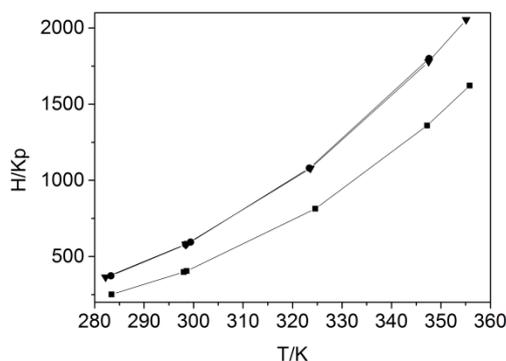


Figure 3: Henry constants ( $H$ ) of ammonia in ionic liquids with different temperature predicted by the UNIFAC model. ■ [BMIM][PF<sub>6</sub>]; ▼ [BMIM][Tf<sub>2</sub>N]; ● [BMIM][BF<sub>4</sub>]

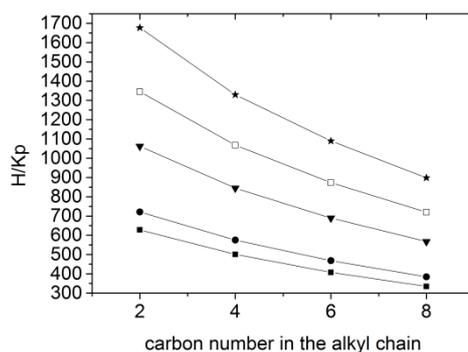


Figure 4: Henry constants ( $H$ ) of ammonia in ionic liquids at different temperature predicted by UNIFAC model. ■ 293.15 K; ● 298.15 K; ▼ 313.15 K; □ 323.15 K; ★ 333.15 K.

#### 4. Conclusions

In this work, a study of  $\text{NH}_3$ -ILs was carried out to analysis the feasibility of UNIFAC model. Through nonlinear regressing of the experimental data, the group interaction parameters of UNIFAC were obtained. The ARDs were calculated to verify the validity of this algorithm. With ARDs less than 10 %, the results shown agreement trend with experimental data, which indicates the UNIFAC predictive model can used in  $\text{NH}_3$  solubility prediction. Henry constant is also predicted and shown agreement with experimental data. With the influence of cations and anions of ILs on solubility analysis, concluded that increasing the number of carbon or change the anion of ILs are effective method to increase the solubility of  $\text{NH}_3$ , which are beneficial for  $\text{NH}_3$  absorption and separation in industry.

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