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# Gas solubility in ionic liquids (ILs): UNIFAC-IL model extension

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## Abstract

Prediction of thermodynamic behavior is essential for the early design stage of separation processes including solvent selection, process optimization and its performance evaluation. In order to better utilize ionic liquids (ILs) as solvents in gas separation processes, the UNIFAC-IL model of IL-liquid solute systems is extended to IL-gas systems by using experimental data from published works and pseudo-experimental data specifically generated from a calibrated COSMO-RS model. In this work, we consider in the model development a total number of 100 ILs from 6 cation families (i.e. imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, guanidium) and 24 anion families (i.e. bis(trifluoromethanesulfonyl) amide, tetrafluoroborate, hexafluorophosphate, dimethylphosphate, heptafluorobutyrate, trifluoroacetate, trifluoromethanesulfonate, methylsulfonate, methylsulfate, ethylsulfate, nitrate, p-toluenesulfonate, 2-(2-methoxyethoxy)ethylsulfate, chloride, bromide, dicyanamide, tetracyanoborate, tris(pentafluoroethyl)trifluorophosphate, lactate, levulinate, saccharinate, succinamate, tetrafluoroethanesulfonate, bis(2,4,4-trimethylpentyl)phosphinate), and 13 gases including CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, N<sub>2</sub>O, CO, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>. The extended UNIFAC-IL-Gas model consists of two sub-models, namely the UNIFAC-IL-Gas (Exp.) model and the UNIFAC-IL-Gas (Pseudo-Exp.) model. The training and testing of the UNIFAC-IL-Gas (Exp.) model is based on 100% experimental data, while the training of the UNIFAC-IL-Gas (Pseudo-Exp.) model is based on pseudo-experimental data, but its testing is also based on 100% experimental data.

**Keywords:** Ionic liquids (ILs), gas solubility, UNIFAC-IL, COSMO-RS, pseudo-experimental data

## 1. Introduction

Unlike most conventional organic solvents, ionic liquids (ILs) are usually non-volatile, have good stability and possess tailor-made properties such as high solubility and selectivity<sup>1</sup>. For this reason, they have been considered as potential alternatives to volatile organic solvents in many separation processes including gas separation,<sup>2-5</sup> extractive distillation<sup>5-10</sup> and liquid-liquid extraction.<sup>11-15</sup> In the past few decades, various ILs with different functions have been synthesized by combining different cations and anions. It has been found that some ILs have very distinct solvation capacities for different gases, indicating the high-potential of using ILs as solvents in gas separations.<sup>16</sup> Meanwhile, work regarding the utilization of ILs as solvents in gas separation tasks from CO<sub>2</sub> capture to shale gas purification have been widely studied.<sup>3-5,17-26</sup>

The performance of an IL-based gas separation process, as well as other solvent-based separation processes, largely depends on the solvent thermodynamic properties which are strongly determined by its molecular structure. Therefore, the selection of a suitable IL with desired thermodynamic properties for a specific gas separation task is of great importance. Considering that numerous ILs are possible composed of different cations and anions, the experimental trial and error method for IL screening is inevitably very time consuming and cost intensive, aside from being non-systematic. Therefore

predictive thermodynamic models that can support efficient, cost-effective and systematic selection of ILs are highly desirable.

A reliable predictive thermodynamic model can both identify structure-property relationships and provide the phase equilibria information of the systems. By far, predictive thermodynamic models including activity coefficient models (e.g. NRTL, UNIQUAC, UNIFAC),<sup>27-35</sup> equations of state models (e.g. GC EOS, CPA EOS, SAFT-based EOS)<sup>36-38</sup> and Ab initio methods (e.g. COSMO-RS, COSMO-SAC)<sup>39-41</sup> have been introduced to the IL containing systems. Most recently, Dong et al., proposed a united COSMO-UNIFAC model that combines COSMO-SAC and UNIFAC models for systems containing ILs.<sup>42,43</sup> Among these thermodynamic models, COSMO-RS and UNIFAC are the two most commonly studied methods for modelling of IL-containing systems. The COSMO-RS model is a predictive method first proposed by Klamt and Eckert (2000)<sup>44</sup> and it only requires molecular structure information. Banerjee et al. (2006)<sup>45</sup> used this model to predict binary VLE of systems containing imidazolium-based ILs and their work confirms that the presence of ILs in the vapor phase can be neglected even at very low pressures. Zhang et al. (2008)<sup>17</sup> applied the COSMO-RS model to predict the Henry's law constants of CO<sub>2</sub> in 408 ILs and it was found that ILs selected by this method present enhanced capability of capturing CO<sub>2</sub>, in contrast to ILs reported in literature. Based on the predicted selectivity and activity coefficient at infinite dilution using the COSMO-RS model, some suitable ILs are selected for extractive distillation processes and these screening ILs show better performance than their corresponding conventional solvents.<sup>40</sup> Zhou et al. (2012)<sup>46</sup> used the COSMO-RS model to predict the mutual solubilities of 1500 ILs with water at 298.15 K and the influence of the types of anion and cation and substituent groups on the mutual solubility of IL-water was also investigated in their work. Although the use of COSMO-RS model does not require experimental information, it typically offers mostly qualitatively correct results.<sup>47</sup> A way to improve the predictions from COSMO-RS is to use experimental data to calibrate the model and it is reported that all calibration models have better performance than the original COSMO-RS model.<sup>18,21,48-50</sup>

On the other hand, UNIFAC is usually preferred as it can provide reliable prediction results because the group interaction parameters in this model are regressed from experimental data. Additionally, UNIFAC is applicable for the thermodynamic prediction of those ILs for which experimental data is not unavailable, many of which may not even have been synthesized, although with potential practical application. Furthermore, UNIFAC can also be easily integrated into computer aided design methods (CAMD),<sup>51,52</sup> which have been suggested as one of the most efficient and systematic approaches to IL screening. To date, hundreds of UNIFAC group interaction parameters covering various IL groups (i.e. cations, anions) and conventional functional groups have been presented.<sup>5,6,15,29,32,34,50</sup> Kato and Gmehling<sup>29</sup> studied the thermodynamic behavior of 119 IL-liquid solute systems using both the original and modified UNIFAC models and then Nebig and Gmehling<sup>53</sup> revised and extended the modified UNIFAC model to the prediction of phase equilibria and excess properties for systems with ILs. The results show that the original UNIFAC especially modified UNIFAC method allows the reliable prediction of IL containing systems. Lei et al. (2009)<sup>28</sup>, Lei et al. (2012)<sup>34</sup> and Roughton et al. (2012)<sup>6</sup> extended the UNIFAC model to IL-solute systems by using different IL molecular decomposition methods. Since these extended UNIFAC-IL models can predict well the VLE of the systems with ILs, they can be used for screening/design suitable ILs for specific separation tasks. Most recently, Zhou et al. (2020)<sup>50</sup> largely extended the UNIFAC model for IL-liquid solute systems by using experimental data collected from literature and computational data generated from calibrated COSMO-RS models.

Remarkably, 39358 experimental data covering 21 conventional functional groups, 9 cation skeleton groups, and 29 anion groups was included in their work. In contrast, current UNIFAC-IL regression work of IL-gas systems is still limited to a few widely studied IL-CO<sub>2</sub> systems<sup>30,49,54</sup> and a small number of other gases such as H<sub>2</sub>, and gaseous hydrocarbon systems.<sup>4,35,43,49,54,55</sup> However, separation processes involving gases such as H<sub>2</sub>S and SO<sub>2</sub> are widely encountered in chemical and petrochemical industries, and therefore an extension of the UNIFAC-IL model to such IL-gas systems is highly desirable.

In the past decade, more and more solubility data of different gases in various ILs have been tested, which make it possible to extend the UNIFAC-IL model to their corresponding IL-gas systems. Although the solubility of CO<sub>2</sub> in ILs has been widely studied, experimental data for other gases (e.g. H<sub>2</sub>S, SO<sub>2</sub>) in many ILs are still not available. Moreover, most solubility data for gases are limited to those ILs that are composed of well-known cations (i.e. imidazolium, pyridinium and ammonium) and anions (i.e. bis(trifluoromethylsulfonyl)imide, tetrafluoroborate and hexafluorophosphate). In order to extend the UNIFAC-IL model to those IL-gas systems which do not have experimental data, reliable computational data generated from a priori prediction methods must be supplemented. In this respect, one of the quantum chemical calculation-based models, COSMO-RS, has been successfully applied in the generation of computational data for many IL-solute systems. Nonetheless, COSMO-RS only offers qualitatively correct results in some cases due to the high deviation between experimental and COSMO-RS computational properties. For this reason, this model is usually calibrated or modified before its application so as to improve the reliability of these computational data.<sup>49,50</sup>

Based on the solubility database built by Lei et al.,<sup>16</sup> we develop in this work a new database combining experimental data and COSMO-RS data with the aim of achieving a systematic extension of the UNIFAC-IL model to IL-gas systems. Besides this database, a model extension strategy is also proposed in this work (see Section 3.1). Compared to the previously reported UNIFAC-IL model, the UNIFAC-IL-Gas model presented in this work covering many more IL-gas systems, and many ILs and gases is for the first time introduced to the UNIFAC-IL model. This extended UNIFAC-IL-Gas model can provide reliable predictions of gas solubility in ILs and it offers prospect of screening ILs for many gas separations prior to their corresponding experimental work. For example, the removal of acid gases especially SO<sub>2</sub> and H<sub>2</sub>S is critical in the natural gas upgrading process, but currently screening suitable ILs for this process is not possible due to the insufficient experimental data or the limitation of the current UNIFAC-IL model. Therefore, the UNIFAC-IL-Gas model proposed in this work is a solution in this direction. In most previous works, the IL-liquid solute system and IL-gas system are separately incorporated into the UNIFAC-IL-Gas model. In order to combine the IL-solute and IL-gas systems in a single UNIFAC-IL-Gas model, some interaction parameters between IL and conventional main groups regressed from IL-liquid solute systems by Roughton et al.<sup>6</sup> have been adopted in this work. That is to say, this UNIFAC-IL-Gas model is not limited to IL-solute or IL-gas systems, but can be applied to IL-solute-gas systems, which is very important for the study of IL-based mixture solvent application in gas separation processes. In addition, the cation, anion and substituents of IL molecule are treated as separate functional groups in this work (see Section 3.2), which allows a larger and more flexible IL design space while using this UNIFAC-IL-Gas model.

## 2. Thermodynamic models

### 2.1. The COSMO-RS model

As a predictive thermodynamic model combining quantum chemical calculations and statistical thermodynamic approaches, COSMO-RS has been widely used to calculate the activity coefficients for many mixtures since it was first proposed by Klamt and Eckert.<sup>44</sup> In this model, the activity coefficient of a compound  $i$  in a solvent  $S$  ( $\gamma_S^i$ ) is computed from the chemical potential of the pure compound  $i$  ( $\mu_i^i$ ) and the chemical potential of  $i$  in the solvent  $S$  ( $\mu_S^i$ ), as shown in Eq1.

$$\ln \gamma_S^i = (\mu_S^i + \mu_i^i)/RT \quad (1)$$

where  $\mu_S^i$  can be calculated from the integration of the chemical potential of a surface segment  $\sigma$  in the solvent  $S$  ( $\mu_S(\sigma)$ ) over the surface of the compound  $i$  as follows.

$$\mu_S^i = \mu_{c,S}^i + \int p^i(\sigma) \mu_S(\sigma) d\sigma \quad (2)$$

where  $\mu_{c,S}^i$  is a combinatorial term describing the size and shape differences of different molecules in the solvent.  $p^i(\sigma)$  is a surface composition function (see Eq.3), also known as  $\sigma$ -profile, which represents the distribution of the polarization charges of each molecule and details of the relative amount of surface with polarity  $\sigma$  on the surface of the molecule.  $\mu_S(\sigma)$ , i.e.  $\sigma$ -potential, as a measure of the affinity of the solvent  $S$  to a surface of polarity  $\sigma$ , and is associated with the molecular surface interaction energies through a statistical thermodynamic procedure as described by Eqs.4-7.

$$p^i(\sigma) = \frac{n_{i(\sigma)}}{n_i} = \frac{A_{i(\sigma)}}{A_i} \quad (3)$$

$$\mu_S(\sigma) = -\frac{RT}{a_{eff}} \times \ln \left[ \int p_s(\sigma') \exp \left\{ \frac{a_{eff}}{RT} (\mu_S(\sigma') - e(\sigma, \sigma')) \right\} d\sigma' \right] \quad (4)$$

$$E_{misfit}(\sigma, \sigma') = a_{eff} e_{misfit}(\sigma, \sigma') = a_{eff} \frac{\alpha'}{2} (\sigma + \sigma')^2 \quad (5)$$

$$E_{HB}(\sigma, \sigma') = a_{eff} c_{HB} \min\{0, \min(0; \sigma_{donor} + \sigma_{HB}) \max(0; \sigma_{acceptor} - \sigma_{HB})\} \quad (6)$$

$$E_{vdW}(\sigma, \sigma') = a_{eff} (\tau_{vdW} + \tau'_{vdW}) \quad (7)$$

In Eq.3,  $n_{i(\sigma)}$  represents the number of segments with charge density  $\sigma$  that have a surface area  $A_{i(\sigma)}$ , while  $n_i$  represents the total number of segments in a single molecule with a total surface area  $A_i$ . In Eqs.4-7,  $a_{eff}$  is the effective contact area and  $\alpha'$  is an interaction parameter; interactions of electrostatics ( $E_{misfit}$ ) and hydrogen bonding ( $E_{HB}$ ) are described as functions of the polarization charges of two interacting surface segments  $\sigma$  and  $\sigma'$ . If the segments are located on a hydrogen bond donor or acceptor atom, these surface segments are expressed as  $\sigma_{donor}$  and  $\sigma_{acceptor}$ .  $c_{HB}$  and  $\sigma_{HB}$  are adjustable parameters of the hydrogen bond strength and the threshold for hydrogen bonding, respectively. The less specific van der Waals ( $E_{vdW}$ ) interactions are also considered with the element specific  $vdW$  interaction parameters  $\tau_{vdW}$  and  $\tau'_{vdW}$ .

As described above, COSMO-RS is an a priori approach that can predict activity coefficients of compounds in liquid mixtures without experimental data as its calculation only relies on compounds'  $\sigma$ -profiles. To date,  $\sigma$ -profiles of many cations and anions of ILs, as well as thousands of conventional molecules, have been included in the COSMO-RS database. Moreover, the  $\sigma$ -profiles of those compounds not included can easily be derived from quantum chemical calculations. Since COSMO-RS allows efficient and fast thermodynamic calculations without experimental data, it has been applied to many liquids or liquid mixtures, especially for those systems for which experimental data is unavailable. For the same reason, the COSMO-RS model has also received attention for the prediction of gas solubility in ILs, where the ions are treated separately as an electroneutral mixture, and distinct COSMO files are generated.

## 2.2. The Original UNIFAC model

Original UNIFAC proposed by Fredenslund et al.,<sup>56</sup> is a functional group based semi-empirical prediction method, where the activity coefficient for each species in the system is split into two components; a combinatorial  $\gamma_i^C$  and a residual component  $\gamma_i^R$ . For the molecule  $i$ , the activity coefficients are broken down as:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (8)$$

The combinatorial component of the activity is related to the entropic effects accounting for the size and shape of molecules, which can be expressed via the van der Waals volume ( $R_k$ ) and surface area ( $Q_k$ ) parameters for each functional group. The residual component of the activity is due to energetic interactions between groups present in the system, and represents the enthalpy contribution. It can be expressed as binary interaction parameters ( $\alpha_{nm}, \alpha_{mn}$ ).  $\gamma_i^C$  and  $\gamma_i^R$  can be calculated by Eqs.9-13 and Eqs.14-19, respectively.

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - 5q_i \left(1 - \frac{V_i}{F_i} + \ln \left(\frac{V_i}{F_i}\right)\right) \quad (9)$$

$$F_i = \frac{q_i}{\sum_j q_j x_j} \quad (10)$$

$$V_i = \frac{r_i}{\sum_j r_j x_j} \quad (11)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (12)$$

$$r_i = \sum_k v_k^{(i)} R_k \quad (13)$$

where  $F_i$  and  $V_i$  represent auxiliary properties for component  $i$ ; the pure component parameters  $q_i$  and  $r_i$ , respectively, denote relative molecular van der Waals surface areas and molecular van der Waals volumes, which are obtained from the sum of the group area  $Q_k$  and group volume parameters  $R_k$ , respectively.  $v_k^{(i)}$  is the number of groups of type  $k$  in molecule  $i$ .

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (14)$$

$$\ln \Gamma_k = Q_k \left(1 - \ln \left(\sum_m \theta_m \Psi_{mk}\right)\right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}} \quad (15)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (16)$$

$$X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_k v_k^{(i)} x_i} \quad (17)$$

$$\Psi_{nm} = \exp[-(\alpha_{nm}/T)] \quad (18)$$

$$\Psi_{mn} = \exp[-(\alpha_{mn}/T)] \quad (19)$$

where  $\Gamma_k$  and  $\Gamma_k^{(i)}$  denote the residual activity coefficient of group  $k$  and the residual activity coefficient of group  $k$  in pure component  $i$ , respectively;  $\theta_m$  is the fraction of group  $m$  in a mixture of the liquid phase and  $X_m/X_n$  is the fraction of group  $m$  or  $n$  in the mixture;  $\Psi_{nm}$  and  $\Psi_{mn}$  are the group interaction parameters which can be calculated through Eqs.18 and 19 based on the value of UNIFAC group interaction parameters ( $\alpha_{nm}, \alpha_{mn}$ ) between groups  $m$  and  $n$ .

Unlike COSMO-RS, the original UNIFAC model calculates the activity coefficient based on the van der Waals parameters (experiment-independent) of different functional subgroups and the binary interaction (experiment-dependent, temperature-independent) between the main groups of each component in the mixtures. Therefore, the predictive ability of the UNIFAC model is usually better than COSMO-RS, but its application, to some extent, is limited to systems where there are some available experimental data or parameters. Although the modified UNIFAC model<sup>57,58</sup> with

temperature-dependent interaction parameters has also been proposed because it can improve the model's prediction performance, the temperature has no noticeable impact on the activity coefficient for some IL-solute systems, especially IL-gas systems. For this reason, the original UNIFAC model is considered for the UNIFAC-IL model extension to IL-gas systems in this work. A large number of UNIFAC interaction parameters between conventional functional groups have been regressed and widely used.<sup>59,60</sup>

### 3. UNIFAC-IL-Gas model extension

#### 3.1. Model extension strategy

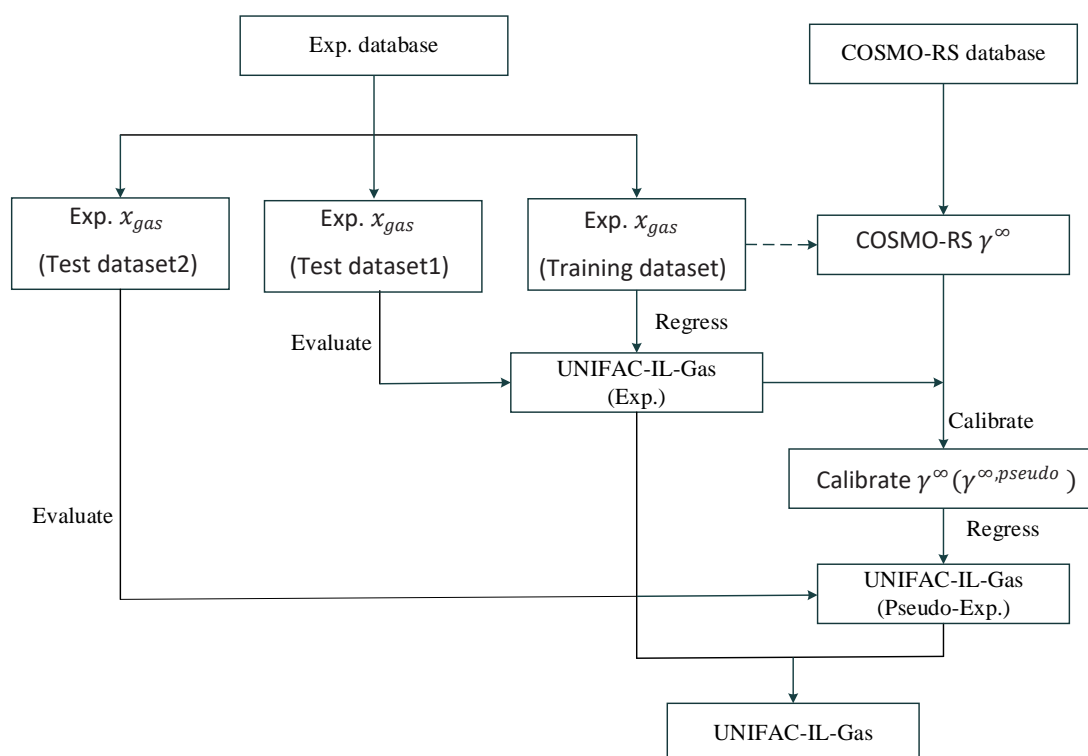


Figure 1. Hierarchical strategy for the extension of UNIFAC-IL-Gas model. (Exp. and Pseudo-Exp. indicate the source of data from experimental database and the calibrated COSMO-RS model)

Considering the large number of IL-gas systems in the UNIFAC-IL-Gas model extension, a hierarchical is proposed in this work (see Figure 1). Because testing is a very important part of the model extension, the experimental data coming from the Exp. database is divided into a training dataset and test datasets, and these datasets cover different IL-gas systems. Typically, 20-30% of data points are used for testing purposes. However, considering the limited number of experimental data for some systems, the percentage of the test dataset used will be adjusted accordingly (see Section 4). First, the UNIFAC-IL model is extended to the IL-gas systems by using experimental gas solubility data (i.e. the training dataset) from Exp. database and this UNIFAC-IL-Gas (Exp.) model is evaluated by using experimental data of Test dataset1 from Exp. database. Secondly, a wide range of computational infinite dilution

activity coefficients ( $\gamma^\infty$ ) of different gases in various ILs are specifically generated from COSMO-RS model, and then these  $\gamma^\infty$  are calibrated by using calculated  $\gamma^\infty$  from validated UNIFAC-IL-Gas (Exp.) model. Next, these calibrated  $\gamma^\infty$  ( $\gamma^{\infty,pseudo}$ ) are used for the regression of UNIFAC-IL-Gas (Pseudo-Exp.) model and its predictive capability is further evaluated by using experimental data of Test dataset2 from Exp. database. Finally, an extended UNIFAC-IL-Gas model combining UNIFAC-IL-Gas (Exp.) and UNIFAC-IL-Gas (Pseudo-Exp.) model is obtained.

### 3.2. Model extension method

Since UNIFAC is a functional group based thermodynamic model, the IL molecule should be first decomposed appropriately into separate functional groups for the UNIFAC-IL model extension. The three main decomposition approaches generally used for this purpose are in Figure 2.

- (I) The IL molecule is divided into one cation-based group and one anion group. This approach cannot reflect the structural variations of substituents in ILs.
- (II) The IL molecule is divided into several groups, but the skeletons of the cation and anion are treated as a one functional group. This approach cannot be easily extended due to its fixed combination of cations and anions.
- (III) The IL molecule is divided into several groups with the cation skeleton treated as a separate functional group. This approach enables the largest extension of the UNIFAC-IL model with an adequate consideration of the structural variation of cations, anions, and substituents in ILs. Meanwhile, it can significantly enlarge the design space and the flexibility for IL design in CAMD<sup>8,13</sup>. With these considerations, this decomposition approach is employed for both experimental data extension (Section 4.1) and pseudo-experimental data extension (Section 4.2) in this work.

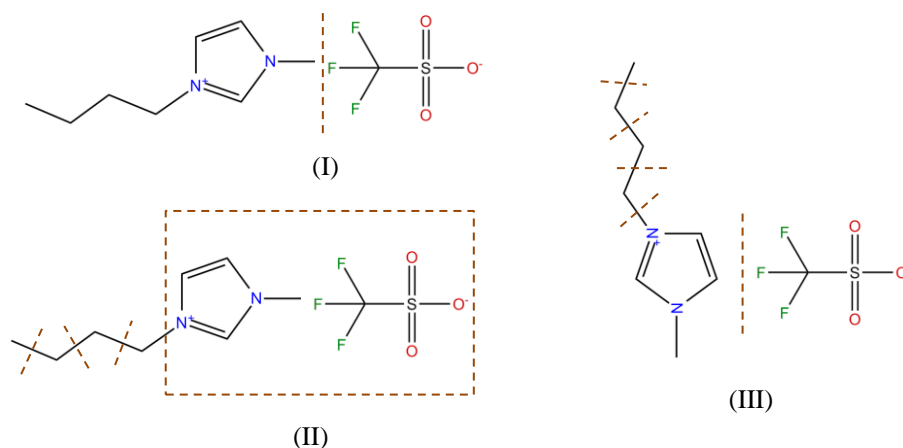


Figure 2. Three different decomposition approaches of IL for UNIFAC functional groups: Exemplified for 1-butyl-3-methylimidazolium trifluoroacetate ( $[C_4mIm]^+[CF_3SO_3]^-$ ). Figure adapted from Chen et al.<sup>8</sup>.

Based on 13 studied gases, 7 cation groups, 24 anion groups and 3 substituent groups from the group decomposition are included in the proposed UNIFAC-IL model extension to IL-gas systems. The van der Waals volumes and areas  $R_k$  and  $Q_k$  of these groups are either taken from literature or calculated as follows:

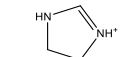
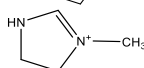



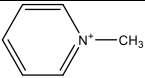
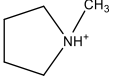
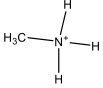
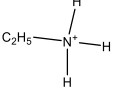
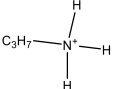
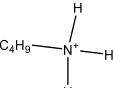
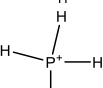
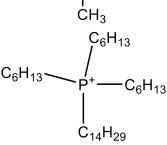
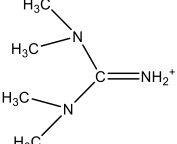
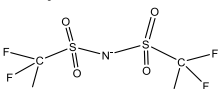
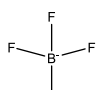
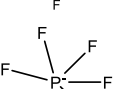
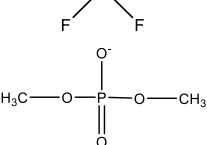
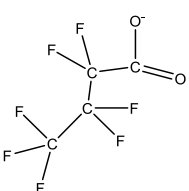
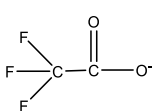
$$R_k = \frac{V_k \times N_A}{V_{VW}} \quad (20)$$

$$Q_k = \frac{A_k \times N_A}{A_{VW}} \quad (21)$$

where  $V_k$  and  $A_k$  denote, respectively, the van der Waals group volumes and surface areas of group  $k$  in each molecule, which can be calculated from correlations with molecular volumes and surface areas or from quantum chemical calculations.  $N_A$  is the Avogadro's number with a value of  $6.023 \times 10^{23}/mol$ , and  $V_{VW}$ ,  $A_{VW}$  are standard segment volume and surface area (of ethylene group in polyethylene) with values of  $15.17 \text{ cm}^3/mol$ ,  $2.5 \times 10^9 \text{ cm}^2/mol$ , respectively. The values of  $R_k$  and  $Q_k$  for all the involved functional subgroups are summarized in Table 1. Most of the  $R_k$  and  $Q_k$  values are taken from previously published work and the remaining parameters obtained in this work are calculated from COSMO-RS.

Table 1: Group's information of  $R_k$  and  $Q_k$  involved in the extension of the UNIFAC-IL-Gas model ( $R_k$  and  $Q_k$  obtained in this work are calculated from COSMO-RS)

Group No.	Main group	Subgroup	$R_k$	$Q_k$	Reference	Structure
1	CO <sub>2</sub>	CO <sub>2</sub>	1.3000	1.1200	61	
2	SO <sub>2</sub>	SO <sub>2</sub>	0.9011	0.8480	54	
3	H <sub>2</sub> S	H <sub>2</sub> S	1.7933	1.5022	This work	
4	NH <sub>3</sub>	NH <sub>3</sub>	1.2193	1.1786	This work	
5	N <sub>2</sub> O	N <sub>2</sub> O	1.8465	1.5860	This work	
6	CO	CO	1.0470	1.0600	35	
7	N <sub>2</sub>	N <sub>2</sub>	0.9340	0.9750	4	
8	O <sub>2</sub>	O <sub>2</sub>	1.1257	1.1940	4	
9	H <sub>2</sub>	H <sub>2</sub>	0.528	0.664	35	
10	CH <sub>4</sub>	CH <sub>4</sub>	1.1290	1.1240	61	
11	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	1.5740	1.4880	61	
12	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub>	1.8022	1.6960	62	
13	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>8</sub>	3.2002	2.3460	This work	
14	CH <sub>2</sub>	CH <sub>3</sub>	0.9011	0.8480	56	
		CH <sub>2</sub>	0.6744	0.5400	56	
		CH	0.4469	0.228	56	
15	OH	OH	1.0000	1.200	59	
16	CH <sub>2</sub> O	CH <sub>3</sub> O	1.1450	1.088	28	
		CH <sub>2</sub> O	0.9183	0.7800	28	
17	[Im]	[Im]	1.9471	0.8660	6	
		[mIm]	2.8482	1.7140	6	
18	[Py]	[Py]	2.6670	1.5530	6	

		[mPy]	3.5681	2.4010	6	
19	[Pyr]	[mPyr]	3.3873	2.9093	6	
20	[N]	[CH3N]	1.1865	0.9400	6	
		[C2H5N]	1.8609	1.4800	6	
		[C3H7N]	2.5353	2.0200	6	
		[C4H9N]	3.2097	2.5600	6	
21	[P]	[CH3P]	1.4931	0.9197	50	
22	[TDPH]	[TDPH]	29.7600	16.1100	This work	
23	[TMG]	[TMG]	3.2002	2.3459	This work	
24	[Tf2N]	[Tf2N]	5.7738	4.9320	6	
25	[BF4]	[BF4]	1.7856	1.4940	6	
26	[PF6]	[PF6]	7.0615	6.5787	6	
27	[DMP]	[DMP]	3.4127	3.2820	6	
28	[C3F7CO2]	[C3F7COO]	6.7579	3.9692	This work	
29	[TFA]	[CF3COO]	3.1773	3.2200	6	

30	[TfO]	[CF <sub>3</sub> SO <sub>3</sub> ]	3.4745	2.9796	6	
31	[MeSO <sub>3</sub> ]	[MeSO <sub>3</sub> ]	2.7126	2.3701	13	
32	[MeSO <sub>4</sub> ]	[MeSO <sub>4</sub> ]	3.4832	3.7280	6	
33	[EtSO <sub>4</sub> ]	[EtSO <sub>4</sub> ]	4.1576	4.1760	6	
34	[NO <sub>3</sub> ]	[NO <sub>3</sub> ]	1.6611	1.5289	13	
35	[TOS]	[TOS]	5.4854	4.5884	13	
36	[MDEGSO <sub>4</sub> ]	[MDEGSO <sub>4</sub> ]	6.6686	6.9840	6	
37	[Cl]	[Cl]	0.7660	0.7200	6	Cl <sup>-</sup>
38	[Br]	[Br]	0.9492	0.8320	6	Br <sup>-</sup>
39	[DCA]	[DCA]	2.4171	2.1337	13	
40	[TCB]	[TCB]	4.3314	3.6652	13	
41	[eFAP]	[eFAP]	9.4117	7.7294	13	
42	[L]	[L]	3.1347	2.3066	This work	
43	[LEV]	[LEV]	5.6143	3.6501	This work	
44	[SAC]	[SAC]	8.0206	4.6397	This work	
45	[SUC]	[SUC]	5.2374	3.3891	This work	



Like many other UNIFAC-IL extensions, the interaction parameters between conventional main groups are taken directly from the original UNIFAC parameter matrix. Meanwhile, in order to combine the IL-solute and IL-gas systems in one UNIFAC-IL-Gas model, some interaction parameters between IL and conventional main groups regressed from IL-solute systems by Roughton et al.<sup>6</sup> have been adopted. That is to say, this model is not limited to IL-solute or IL-gas systems, but can be applied in IL-solute-gas systems, which is very important for the study of IL-based mixture solvent application in gas separation processes. In addition, the interaction parameters between IL main groups (i.e. cations and anions) are assumed to be zero considering the strong interaction and weak dissociation of ion pairs. We should note that the interaction parameters between different gases are not involved or considered in the current model extension, as such parameters are typically not available in UNIFAC-tables. Figure 3 presents the group interaction parameter matrix of the extended UNIFAC-IL-Gas model. In this work, we consider in the model extension a total number of 100 ILs (see Appendix) from 6 cation families and 24 anion, and 13 gases including CO<sub>2</sub><sup>17,63-114</sup>, SO<sub>2</sub><sup>115-119</sup>, H<sub>2</sub>S<sup>25,90,120-128</sup>, NH<sub>3</sub><sup>129-131</sup>, N<sub>2</sub>O<sup>77,80,132-136</sup>, CO<sup>64,96,137-140</sup>, N<sub>2</sub><sup>64,71,80,96,134,139,141,142</sup>, O<sub>2</sub><sup>64,71,72,77,96,139,141-144</sup>, H<sub>2</sub><sup>64,71,75,96,137,139,142,143,145-148</sup>, CH<sub>4</sub><sup>64,76,91,141,142,149-153</sup>, C<sub>2</sub>H<sub>4</sub><sup>76,77,141</sup>, C<sub>2</sub>H<sub>6</sub><sup>64,76,91,101,134,141,154,155</sup>, C<sub>3</sub>H<sub>8</sub><sup>74,110,156</sup>.

## Results and discussion

### 3.3. Experimental data extension

In this section, 7034 experimental gas solubility data in ILs with a range of temperature, 283.15-384.15K, and pressure, 0.05-973 bar (see Table S3, S4, S6, in the Supporting Information) are applied for the UNIFAC-IL model extension. As shown in Figure 3, group interaction parameters with orange color in the extended UNIFAC-IL-Gas parameter matrix are regressed from IL-gas systems by minimizing the objective function, i.e. the average absolute relative deviation (AARD) % between experimental and calculated gas solubility (mole fraction of gas in IL), as shown in Eq. (22).

$$O.F. = AARD(\%) = \frac{1}{N} \sum_1^N \left| \frac{x_i^{exp} - x_i^{cal}}{x_i^{exp}} \right| \times 100\% \quad (22)$$

where  $i$  represents the data point and  $N$  denotes the total number of the regressed data points.  $x_i^{cal}$  and  $x_i^{exp}$  are the gas solubility in ILs that can be directly taken from the experimental database and calculated from phase equilibrium equation (see Eq.23), respectively.

$$x_{gas} = \frac{y_{gas} P \varphi(T, P, y_{gas})}{\gamma_{gas} P_{gas}^s} \quad (23)$$

In Eq. 23, the activity coefficient of gas ( $\gamma_{gas}$ ) can be calculated from UNIFAC-IL-Gas model and the mole composition of gas in the vapor phase ( $y_{gas}$ ) is assumed to be 1 due to the negligible vapor pressure of ILs.  $P$  represents the phase equilibrium pressure of the studied IL-gas system. The fugacity coefficient of gas ( $\varphi(T, P, y_{gas})$ ) can be calculated by the Peng-Robinson equation of state, while the saturated vapor pressure of gas ( $P_{gas}^s$ ) can be estimated from suitable correlations such as the Wagner, DIPPR, and Antoine equations. In this work, both DIPPR and Antoine equations were considered for different gases.

One of nonlinear programming solvers “lindoglobal” in GAMS (24.4.6) was used to solve this regression problem. Considering the complexity of this problem, the interaction parameters associated

with the IL-CO<sub>2</sub> systems are regressed first, and then the interaction parameters associated with other IL-gas systems are regressed. To evaluate the reliability of the regressed interaction parameters, as well as the predictive performance of the extended UNIFAC-IL-Gas (Exp.) model, nearly 75% of the involved experimental data points (i.e. training dataset) are used for the regression, while a certain number of remaining data points (i.e. Test dataset1) are used for prediction purposes.

The AARD (%) between the experimental and calculated  $x_{gas}$  of different gases in ILs range from 12% for gaseous hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>) to 22% for the gas dataset covering CO, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub> in the training dataset. As expected, the AARD (%) from the test dataset is higher than, but rather close to, its corresponding AARD (%) from the training dataset. The AARD (%) between the experimental and calculated  $x_{gas}$  of different gases in ILs for both the training and test datasets can be found in Table 2. To better illustrate the calculation results, comparisons between the experimental and calculated  $x_{gas}$  of all gases in ILs from the training and test datasets are presented in Figures 4 and 5, respectively. The resulting AARD (%) of prediction for the test dataset shows a reliable predictive ability of the extended UNIFAC-IL-Gas (Exp.) model. The new obtained group interaction parameters with their values are provided in Table S2 (Supporting Information).

Table 2: Summary of the extended UNIFAC-IL-Gases (Exp.) model for both training and test datasets

Gas dataset	Involved gases	Training dataset		Test dataset1	
		Data points	*AARD%	Data points	*AARD%
1	CO <sub>2</sub>	2345	14.5	1083	16.5
2	SO <sub>2</sub> , H <sub>2</sub> S, NH <sub>3</sub> , N <sub>2</sub> O	1533	12.7	395	19.2
3	CO, N <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub>	681	22.1	96	35.0
4	CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub>	877	11.5	24	14.2

\*AARD% of both training and test datasets are calculated from Eq. 22

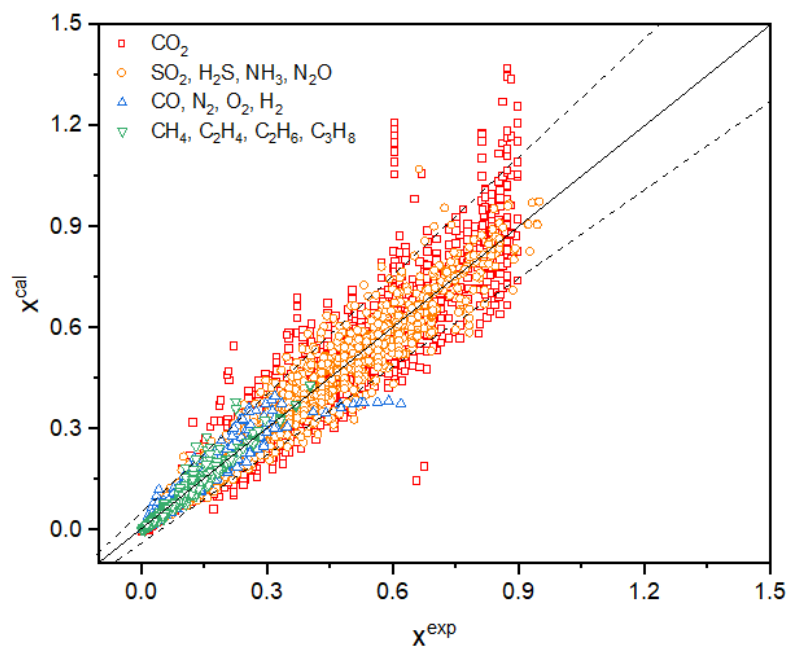


Figure 4. Comparison of experimental and UNIFAC-IL-Gas calculated gas solubilities of different gases in ILs from the training dataset

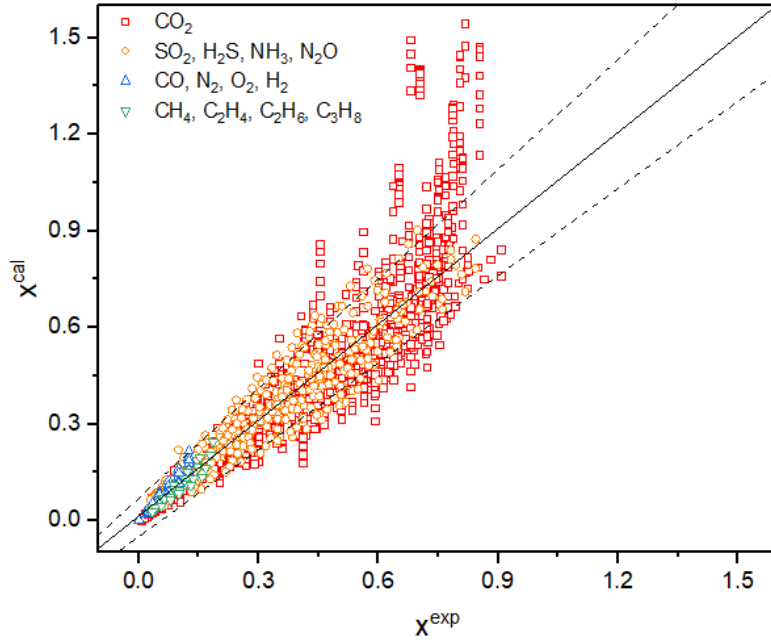


Figure 5. Comparison of experimental and UNIFAC-IL-Gas (Exp.) predicted gas solubilities of different gases in ILs from Test dataset1

### 3.4. Pseudo-experimental data extension

As mentioned above, computational data from the COSMO-RS calculation are very useful because of the insufficient experimental data for some important IL-gas systems. In this work, we only use the COSMO-RS model to generate computational data, but it is not included in the UNIFAC-IL-Gas model extension. Although gas solubility data can be generated directly from COSMO-RS calculations where the saturated vapor pressure is estimated by using the information of gas-phase energy, we use the pseudo-experimental data of infinite dilution activity coefficient since it allows consistent vapor pressure calculations (DIPPR or Antoine method) for both experiment and pseudo-experimental data based regression. To improve the reliability of the computational  $\gamma^\infty$  from COSMO-RS model, a number of calculated  $\gamma^\infty$  from validated UNIFAC-IL-Gas (Exp.) were used for calibrations. In this work, a linear calibrated COSMO-RS model involving temperature ( $T$ ) was employed, as shown in Eq.24. This calibration method for the COSMO-RS model has been used previously and suggested in several published works.<sup>18,21,48,49</sup> In the last part of this section, the testing results from Test dataset2 also verify the reliability of this calibration.

$$\gamma^{\infty,pseudo} = a\gamma^{\infty,COSMO-RS} + b + cT \quad (24)$$

where  $\gamma^{\infty,pseudo}$  and  $\gamma^{\infty,COSMO-RS}$  are the calibrated  $\gamma^\infty$  and the  $\gamma^\infty$  calculated directly from COSMO-RS, respectively. The adjustable parameters ( $a$ ,  $b$  and  $c$ ) of this linear calibrated model can be obtained by minimizing:

$$AARD(\%) = \frac{1}{N} \sum_{i=1}^N \left| \frac{\gamma_i^{\infty,exp} - \gamma_i^{\infty,pseudo}}{\gamma_i^{\infty,exp}} \right| \times 100\% \quad (25)$$

where  $\gamma_i^{\infty,pseudo}$  and  $\gamma_i^{\infty,exp}$  are the pseudo-experimental  $\gamma^\infty$  and experimental  $\gamma^\infty$  of data point  $i$ , respectively.  $N$  denotes the total number of the regressed data points. In this equation,  $\gamma_i^{\infty,exp}$  are calculated from validated UNIFAC-IL-Gas (Exp.) model.

In this section, we will calibrate the computational data generated from COSMO-RS. The purpose of this calibration is to narrow the difference between experimental and computational data. To complement the insufficient amount of experimental data, a total of 6,610  $\gamma^{\infty,COSMO-RS}$  covering various IL-gas systems under different temperatures (see Supporting Information) are computed directly from COSMOthermX software, where the  $\sigma$ -profiles of the IL functional groups and studied gases are taken from the IL Thermo database. The detailed information of  $\gamma^{\infty,pseudo}$  and  $\gamma^{\infty,COSMO-RS}$  for each gas is presented in Table 3. From the linear regression results, we can observe that all gases with calibration have lower AARD% between the COSMO-RS based computational  $\gamma^\infty$  and UNIFAC-IL-Gas (Exp.) model based calculated  $\gamma^\infty$ , and only 3 gases (i.e. O<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>) have AARD% higher than 20%. These linear calibrations for each gas can be validated from the testing results of AARD% between experimental  $x_{gas}$  and calculated  $x_{gas}$  from calibrated  $\gamma^\infty$ .

Table 3: Calibration of the COSMO-RS model for generating pseudo-experimental data. The calibration parameters refer to Eq. 24.

Gas	AARD% without calibration	Calibration parameters			AARD% with calibration	Number of data points used in calibration
		$a$	$b$	$c$		
SO <sub>2</sub>	4.5	1.0000	-0.0620	0.0002	4.0	30
H <sub>2</sub> S	54.0	0.8000	0.6850	-0.0010	8.5	30
NH <sub>3</sub>	74.5	1.6000	0.3370	-0.0001	7.2	30
CO	54.1	1.1500	-0.4710	0.0006	8.5	60
N <sub>2</sub>	22.2	1.5000	0.7060	-0.0030	8.8	30
O <sub>2</sub>	59.0	1.5210	2.1930	-0.0060	10.4	30
H <sub>2</sub>	57.1	2.5820	0.1970	-0.0010	22.6	90
N <sub>2</sub> O	19.5	0.8360	-0.2140	0.0006	3.8	60
CH <sub>4</sub>	35.3	0.6620	-0.1980	0.0080	16.6	60
C <sub>2</sub> H <sub>4</sub>	20.3	0.6390	1.6460	-0.0030	14.7	40
C <sub>2</sub> H <sub>6</sub>	37.2	0.7450	-1.3690	0.0050	31.7	90
C <sub>3</sub> H <sub>8</sub>	44.5	0.8000	-1.1810	0.0070	36.8	40

Based on the pseudo-experimental data from the calibrated COSMO-model, the remaining unknown group interaction parameters (Marked in blue) in the extended UNIFAC-IL-Gas parameter matrix are regressed by minimizing the AARD % between the experimental and calculated gas solubility, as shown in Eq. (26).

$$AARD(\%) = \frac{1}{N} \sum_1^N \left| \frac{\gamma_i^{\infty,pseudo} - \gamma_i^{\infty,cal}}{\gamma_i^{\infty,pseudo}} \right| \times 100\% \quad (26)$$

where  $\gamma_i^{\infty,pseudo}$  and  $\gamma_i^{\infty,cal}$  are the pseudo-experimental and calculated  $\gamma^\infty$  of data point  $i$ , respectively.  $N$  denotes the total number of the regressed data points.



Table 4 summarizes the AARD (%) between  $\gamma_i^{\infty,pseudo}$  and  $\gamma_i^{\infty,cal}$  of all pseudo-experimental data points. To evaluate the predictive performance of the obtained UNIFAC-IL-Gas (Pseudo-Exp.) model, a test dataset (i.e. Test dataset2) including 347 experimental data points is applied. The AARD (%) between the experimental  $x_{gas}$  and  $x_{gas}$  calculated from UNIFAC-IL-Gas (Pseudo-Exp.) model for the test dataset is also provided in Table 2. Compared to the extension of UNIFAC-IL-Gas (Exp.) model, the AARD (%) from pseudo-experimental data presents similar fitting results, but the predictive reliability of this UNIFAC-IL-Gas (Pseudo-Exp.) model is not as good as its corresponding UNIFAC-IL-Gas (Exp.) model. Nevertheless, pseudo-experimental data from the calibrated COSMO-RS model is still a good supplementary data source when experimental data are not available. To better illustrate the calculation results, comparisons between  $\ln(\gamma_i^{\infty,pseudo})$  and  $\ln(\gamma_i^{\infty,cal})$  of all pseudo-experimental data points are presented in Figure 6, and comparisons between the experimental and predicted  $x_{gas}$  from UNIFAC-IL-Gas (Pseudo-Exp.) model are given in Figure 7. The resulting AARD (%) of prediction for the test dataset shows an acceptable predictive performance of the extended UNIFAC-IL-Gas (Pseudo-Exp.) model. The values of these new group interaction parameters in UNIFAC-IL-Gas (Pseudo-Exp.) model are listed in Table S2 (Supporting Information).

Table 4: Summary of the extended UNIFAC-IL-Gas (Pseudo-Exp.) model for both training and test datasets

Gas dataset	Involved gases	Training dataset		Test dataset2	
		(pseudo-experimental data)		(experimental data)	
		Data points	AARD%	Data points	AARD%
2	SO <sub>2</sub> , H <sub>2</sub> S, NH <sub>3</sub> , N <sub>2</sub> O	2280	8.1	169	12.5
3	CO, N <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub>	2090	9.6	88	35.1
4	CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub>	2240	13.5	86	22.8

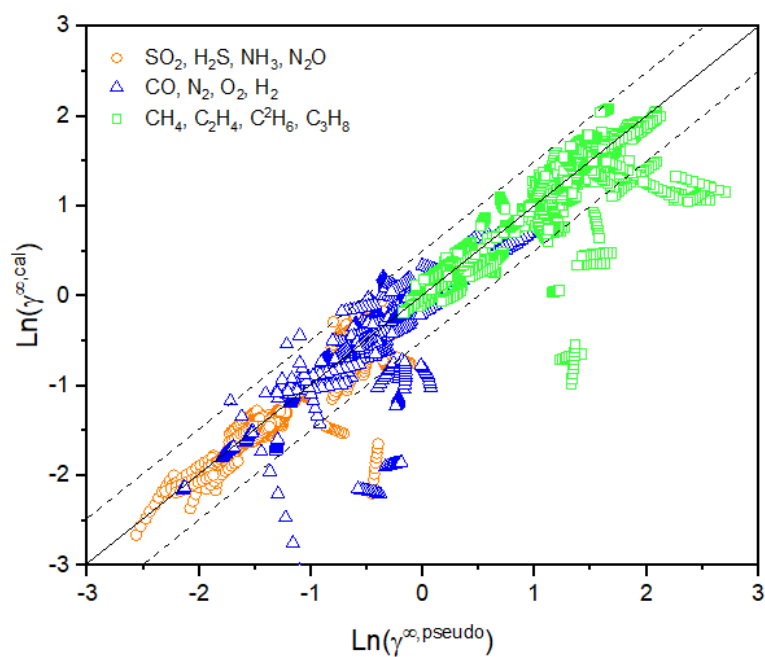


Figure 6. Comparison of the pseudo-experimental and model (UNIFAC-IL-Gas) calculated  $\gamma^\infty$  for different gases in ILs

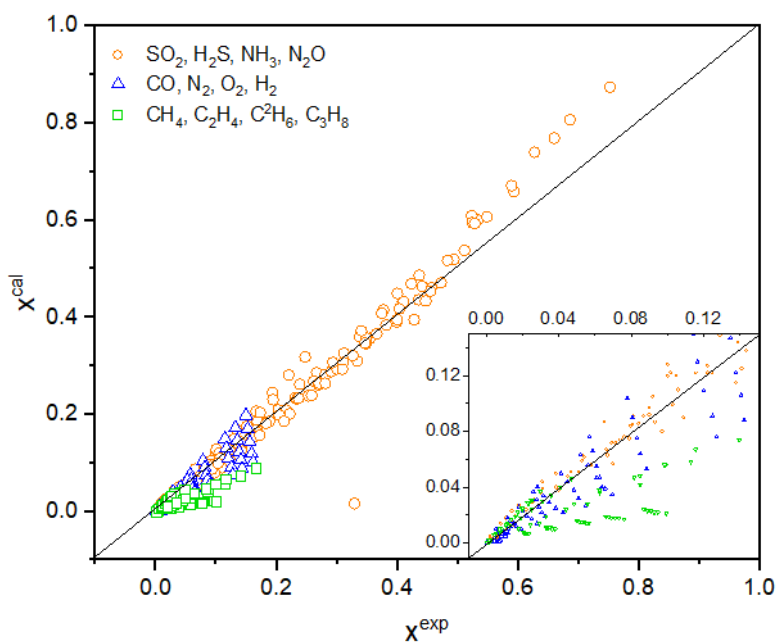


Figure 7. Comparison of the experimental and model (UNIFAC-IL-Gas) predicted gas solubility for different gases in ILs (experimental data are taken from Test dataset2)

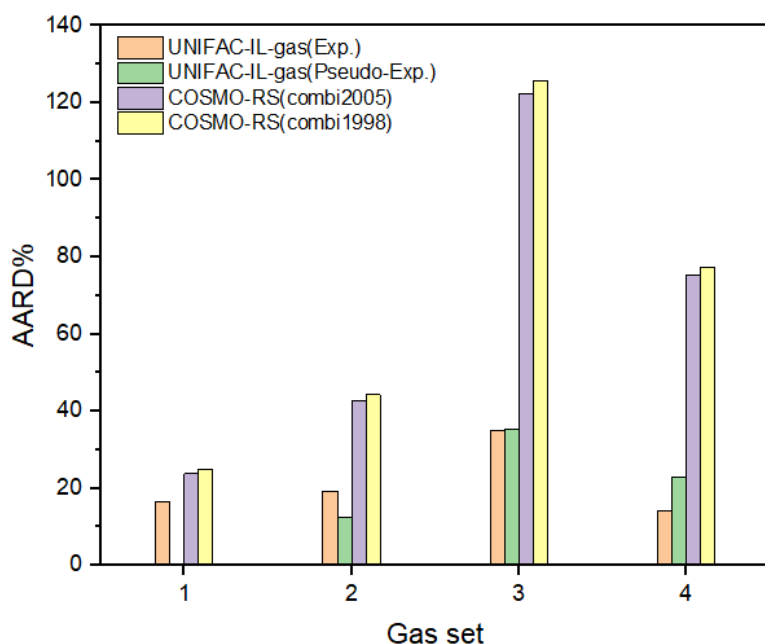


Figure 8: Comparisons between the prediction result (expressed as AARD%) from the UNIFAC-IL and COSMO-RS based model<sup>16</sup> for all studied gas datasets. (Gas dataset1: CO<sub>2</sub>; Gas dataset2: SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, NO<sub>2</sub>; Gas dataset3: CO, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>; Gas dataset4: CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>)

Among all studied IL-gas systems, gases (CO, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>) involved in the Gas dataset3 have relatively large deviation (about 30%) for both UNIFAC-IL-Gas (Exp.) and UNIFAC-IL-Gas (Pseudo-Exp.) models, as shown in Tables 2 and 4. This can be explained by the fact that these gases have lower vapor pressures compared with other studied gases, which usually leads to lower solubility in ILs, so their experimental data itself have higher deviation. Nevertheless, the extended UNIFAC model has much better predictive performance for CO, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> than COSMO-RS, for which AARD is over 100% (see Figure 8). In addition, it is found that there is no significant difference in the deviation of IL systems with different cation or anion families. However, a small number of data points for some IL-CO<sub>2</sub> systems show very large deviations, as shown in Figures 2 and 3. This can be explained as follows: (1) the system pressure of some data points for CO<sub>2</sub>-IL systems (e.g. 1-hexyl-3-methylimidazolium saccharinate and 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate) is very low or very high; (2) the number of data points for some CO<sub>2</sub>-IL systems (e.g. trihexyl tetradecyl phosphonium bis(2,4,4-trimethylpentyl)phosphinate, 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate) is very small; (3) the experimental data of some CO<sub>2</sub>-IL systems (mainly imidazolium dicyanamide) from different data sources have some deviations.

It is worth mentioning that the DIPPR and Antoine equations present different regression results for many IL-gas systems, especially for the gases with very low critical temperature. This can be explained by the fact that both the DIPPR and Antoine equations are sufficient for estimating the vapor pressure below the critical temperature and they provide similar vapor pressure values in the range of certain temperatures (e.g. CO 68.15-132.92 K). However, hypothetical vapor pressure extrapolated from these equations cannot express some gas systems well at temperatures above the critical temperature. In fact,

from a thermodynamic point of view, when the system temperature is higher than the critical temperature of the component, the liquid vapor pressure of the component no longer exists, and so, the vapor pressure (above the critical temperature) calculated from the DIPPR or Antoine equation is regarded as a pseudo-vapor pressure. In this work, the temperature of most studied IL-gas systems is much higher than the critical temperature of those involved gases and different vapor pressure equations present different regression results. This is one of the reasons why the AARD% of IL-gas systems is generally higher than for other IL-solutes systems. For this reason, we use either DIPPR or Antoine equation for different IL-gas systems based on their regression performance. It should be noted that when using this UNIFAC-IL-Gas model, the vapor pressure equation (DIPPR or Antoine) and coefficients must be consistent with the equation and coefficients used for each gas in this work. The details of the vapor calculation method and their corresponding equation parameters for all involved gases are provided in Table S8 (Supporting Information).

On the other hand, although the computational data generated from COSMO-RS have errors of its own, a calibration method is used to calibrate these computational data for reducing the impact of such inherent errors. Most importantly, the UNIFAC-IL-Gas (Pseudo-Exp.) model extended from these calibrated computational data (i.e. pseudo-experimental data) is verified by Test dataset2 containing 100% experimental data. In order to compare the prediction performance of the extended UNIFAC-IL-Gas models with COSMO-RS models, the prediction results of AARD% from the UNIFAC-IL and COSMO-RS based models for 4 gas datasets covering all studied gases are plotted in Figure 8. The prediction results from different versions (combi2005 and combi1998) of the COSMO-RS model are taken from Lei's work.<sup>16</sup> Clearly, both UNIFAC-IL-Gas (Exp.) and UNIFAC-IL-Gas (Pseudo-Exp.) models have much better predictive performance than the COSMO-RS models, especially for the gases included in Gas dataset3 and dataset4. These comparisons highlight the reliability and applicability of the extended UNIFAC-IL-Gas model developed in this work. This model can be easily used for screening suitable ILs for many gas separations such as natural gas upgrading and NH<sub>3</sub> recovery prior to their corresponding experimental work.

#### 4. Conclusions

A comprehensive database of IL gas-systems including experimental data from published works and pseudo-experimental data from calibrated COSMO-RS model have been developed. By using a hierarchical extension strategy, the UNIFAC-IL was extended to various IL-systems from a large number of experimental and pseudo-experimental data, and then a combined UNIFAC-IL-Gas model consisting of UNIFAC-IL-Gas (Exp.) and UNIFAC-IL-Gas (Pseudo-Exp.) was obtained. We should note that COSMO-RS model is only used to obtain pseudo-experimental data, and it is not involved in the UNIFAC-IL-Gas model extension. Overall, 13 gases, 3 conventional functional groups, 7 cation skeleton groups, and 24 anion groups are considered in this extended model. The calculation results of both training and test datasets, presented as comparisons between the experimental/pseudo-experimental and calculated gas solubility from the UNIFAC-IL-Gas model, show the reliable predictive performance of the UNIFAC-IL-Gas model obtained in this work.

This UNIFAC-IL-Gas model can be applied in solvent screening, process optimization and evaluation in the design stage of gas separation processes involving ILs. Moreover, this model can also be used for IL-based mixture solvents design since it combines IL-gas and other IL-solute systems, giving significant opportunity to potentially expand the application of ILs in gas separation processes. Furthermore, the current UNIFAC-IL-Gas model can be updated, or further extended, to new gas-IL systems that are currently not included in this study, once their experimental data becomes available.

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## Supporting Information

Tables S1-S8 summarize all the information used in the extension of the UNIFAC-IL-Gas model. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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#### Appendix : Ionic liquids covered in the UNIFAC-IL-Gas model

Abbreviation	Full name
[EMIM][Tf <sub>2</sub> N]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIM][Tf <sub>2</sub> N]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C <sub>5</sub> MIM][Tf <sub>2</sub> N]	1-methyl-3-pentylimidazolium bis(trifluoromethylsulfonyl)imide
[HMIM][Tf <sub>2</sub> N]	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[OMIM][Tf <sub>2</sub> N]	1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide
[HMMIM][Tf <sub>2</sub> N]	1-hexyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide
[HEMIM][Tf <sub>2</sub> N]	1-(2-hydroxyethyl)-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide

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[(OH) <sub>2</sub> IM][Tf <sub>2</sub> N]	1,3-dihydroxyimidazolium bis(trifluoromethylsulfonyl)imide
[(ETO) <sub>2</sub> IM][Tf <sub>2</sub> N]	1,3-diethoxyimidazolium bis(trifluoromethylsulfonyl)imide
[MTOC <sub>2</sub> MIM][Tf <sub>2</sub> N]	1-(2-methoxyethyl)-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide
[EMIM][BF <sub>4</sub> ]	1-ethyl-3-methylimidazolium tetrafluoroborate
[BMIM][BF <sub>4</sub> ]	1-butyl-3-methylimidazolium tetrafluoroborate
[HMIM][BF <sub>4</sub> ]	1-hexyl-3-methylimidazolium tetrafluoroborate
[OMIM][BF <sub>4</sub> ]	1-methyl-3-octylimidazolium tetrafluoroborate
[HEMIM][BF <sub>4</sub> ]	1-(2-hydroxyethyl)-3-methyl-imidazolium tetrafluoroborate
[EMIM][PF <sub>6</sub> ]	1-ethyl-3-methylimidazolium hexafluorophosphate
[BMIM][PF <sub>6</sub> ]	1-butyl-3-methylimidazolium hexafluorophosphate
[HMIM][PF <sub>6</sub> ]	1-hexyl-3-methylimidazolium hexafluorophosphate
[OMIM][PF <sub>6</sub> ]	1-methyl-3-octylimidazolium hexafluorophosphate
[HEMIM][PF <sub>6</sub> ]	1-(2-hydroxyethyl)-3-methyl-imidazolium hexafluorophosphate
MTOC <sub>2</sub> MIM[PF <sub>6</sub> ]	1-(2-methoxyethyl)-3-methyl-imidazolium hexafluorophosphate
[MMIM][MeSO <sub>3</sub> ]	1,3-dimethylimidazolium methylsulfonate
[EMIM][MeSO <sub>3</sub> ]	1-ethyl-3-methylimidazolium methylsulfonate
[BMIM][MeSO <sub>3</sub> ]	1-butyl-3-methylimidazolium methylsulfonate
[HMIM][MeSO <sub>3</sub> ]	1-hexyl-3-methylimidazolium methylsulfonate
[EMIM][MeSO <sub>4</sub> ]	1-ethyl-3-methylimidazolium methylsulfate
[BMIM][MeSO <sub>4</sub> ]	1-butyl-3-methylimidazolium methylsulfate
[HMIM][MeSO <sub>4</sub> ]	1-hexyl-3-methylimidazolium methylsulfate
[EMIM][EtSO <sub>4</sub> ]	1-ethyl-3-methylimidazolium ethylsulfate
[BMIM][EtSO <sub>4</sub> ]	1-butyl-3-methylimidazolium ethylsulfate
[HMIM][EtSO <sub>4</sub> ]	1-hexyl-3-methylimidazolium ethylsulfate
[EMIM][TFA]	1-ethyl-3-methylimidazolium trifluoroacetate
[BMIM][TFA]	1-butyl-3-methylimidazolium trifluoroacetate
[HMIM][TFA]	1-hexyl-3-methylimidazolium trifluoroacetate
[EMIM][TfO]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
[BMIM][TfO]	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[HMIM][TfO]	1-hexyl-3-methylimidazolium trifluoromethanesulfonate
[HEMIM][TfO]	1-(2-hydroxyethyl)-3-methyl-imidazolium trifluoromethanesulfonate
[MMIM][DMP]	1,3-dimethylimidazolium dimethylphosphate
[EMIM][DMP]	1-ethyl-3-methylimidazolium dimethylphosphate
[BMIM][DMP]	1-butyl-3-methylimidazolium dimethylphosphate
[HMIM][DMP]	1-hexyl-3-methylimidazolium dimethylphosphate
[EMIM][DCA]	1-ethyl-3-methylimidazolium dicyanamide
[BMIM][DCA]	1-butyl-3-methylimidazolium dicyanamide
[HMIM][DCA]	1-hexyl-3-methylimidazolium dicyanamide
[EMIM][TCB]	1-ethyl-3-methylimidazolium tetracyanoborate

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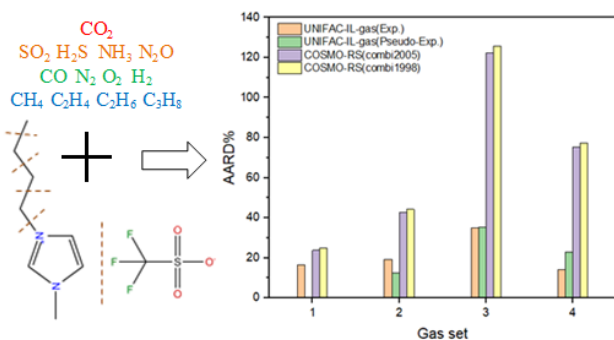
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[BMIM][TCB]	1-butyl-3-methylimidazolium tetracyanoborate
[HMIM][TCB]	1-hexyl-3-methylimidazolium tetracyanoborate
[EMIM][C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> ]	1-ethyl-3-methylimidazolium heptafluorobutyrate
[BMIM][C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> ]	1-butyl-3-methylimidazolium heptafluorobutyrate
[HMIM][C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> ]	1-hexyl-3-methylimidazolium heptafluorobutyrate
[EMIM][NO <sub>3</sub> ]	1-ethyl-3-methylimidazolium nitrate
[BMIM][NO <sub>3</sub> ]	1-butyl-3-methylimidazolium nitrate
[HMIM][NO <sub>3</sub> ]	1-hexyl-3-methylimidazolium nitrate
[EMIM][MDEGSO <sub>4</sub> ]	1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate
[BMIM][MDEGSO <sub>4</sub> ]	1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate
[HMIM][MDEGSO <sub>4</sub> ]	1-hexyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate
[HMIM][Cl]	1-hexyl-3-methylimidazolium chloride
[EMIM][Br]	1-ethyl-3-methylimidazolium bromide
[BMIM][Br]	1-butyl-3-methylimidazolium bromide
[HMIM][Br]	1-hexyl-3-methylimidazolium bromide
[EMIM][eFAP]	1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
[BMIM][eFAP]	1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
[HMIM][eFAP]	1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
[EMIM][SAC]	1-ethyl-3-methylimidazolium saccharinate
[BMIM][SAC]	1-butyl-3-methylimidazolium saccharinate
[HMIM][SAC]	1-hexyl-3-methylimidazolium saccharinate
[EMIM][SUC]	1-ethyl-3-methylimidazolium succinamate
[HMIM][SUC]	1-butyl-3-methylimidazolium succinamate
[BMIM][SUC]	1-hexyl-3-methylimidazolium succinamate
[BMIM][TFES]	1-ethyl-3-methylimidazolium tetrafluoroethanesulfonate
[EMIM][TFES]	1-butyl-3-methylimidazolium tetrafluoroethanesulfonate
[HMIM][TFES]	1-hexyl-3-methylimidazolium tetrafluoroethanesulfonate
[BMIM][LEV]	1-ethyl-3-methylimidazolium levulinate
[EMIM][LEV]	1-butyl-3-methylimidazolium levulinate
[HMIM][LEV]	1-hexyl-3-methylimidazolium levulinate
[EMPY][Tf <sub>2</sub> N]	1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide
[BMPY][Tf <sub>2</sub> N]	1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide
[HMPY][Tf <sub>2</sub> N]	1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide
[BPY][BF <sub>4</sub> ]	1-butylpyridinium tetrafluoroborate
[EMPYR][Tf <sub>2</sub> N]	1-ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[C <sub>3</sub> MPYR][Tf <sub>2</sub> N]	1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[BMPYR][Tf <sub>2</sub> N]	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[C <sub>5</sub> MPYR][Tf <sub>2</sub> N]	1-methyl-1-pentylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[HMPYR][Tf <sub>2</sub> N]	1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[C <sub>7</sub> MPYR][Tf <sub>2</sub> N]	1-heptyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[OMPYR][Tf <sub>2</sub> N]	1-methyl-1-octylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[BMPYR][eFAP]	1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate
[BMPYR][LEV]	1-butyl-1-methylpyrrolidinium levulinate
[N1,1,3,2-OH][Tf <sub>2</sub> N]	2-hydroxyethyltrimethylammonium bis(trifluoromethylsulfonyl)imide

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[N1,8,8,8][Tf <sub>2</sub> N]	N-methyl-N,N,N-trioctylammonium bis(trifluoromethylsulfonyl)imide
[N4,1,1,1][Tf <sub>2</sub> N]	N-butyl-N,N,N-trimethylammonium bis(trifluoromethylsulfonyl)imide
[MDEA][Cl]	2-[2-hydroxyethyl (methyl) amino]ethanol chloride
[TDPH][Tf <sub>2</sub> N]	trihexyl tetradecyl phosphonium bis(trifluoromethylsulfonyl)imide
[TDPH][Br]	trihexyl tetradecyl phosphonium bromide
[TDPH][eFAP]	trihexyl tetradecyl phosphonium tris(pentafluoroethyl)trifluorophosphate
[TDPH][phos]	trihexyl tetradecyl phosphonium bis(2,4,4-trimethylpentyl)phosphinate
[P1,4,4,4][MeSO <sub>4</sub> ]	tributyl methyl phosphonium methylsulfate
[P1,4,4,4][TOS]	tributyl methyl phosphonium p-toluenesulfonate
[TMG][L]	1,1,3,3-tetramethyl-guanidium lactate



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