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Application of COSMO-RS and UNIFAC for Ionic Liquids based Gas Separation

Xinyan Liu^{a,b}, Teng Zhou^c, Xiangping Zhang^{b*}, Suojiang Zhang^b, Xiaodong Liang^a, Rafiqul Gani^d, Georgios M. Kontogeorgis^{a*}

^a Department of Chemical & Biochemical Engineering, Technical University of Denmark, DK 2800 Kgs. Lyngby, Denmark

^b Beijing Key Laboratory of Ionic Liquids Clean Process, CAS State Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

^c Process Systems Engineering, Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstr. 1, D-39106 Magdeburg, Germany

^d PSE for SPEED, Skyttemosen 6, DK-3450 Allerød, Denmark

*Corresponding authors

Email address: gk@kt.dtu.dk; xpzhang@ipe.ac.cn

Abstract

In recent years, due to their advantages on good stability, non-volatility, tunable viscosity and tailor-made properties, ionic liquids (ILs) have been regarded as novel potential solvents and alternative media for gas separation. However, the various cations and anions representing the ILs, together with limited experimental data, make it challenging to predict gas solubility in ILs and identify the optimal IL for a specific gas separation. In this work, a comprehensive Henry's law constants database is first established for gas-IL which supplements an already established extensive gas solubility database. Because of the insufficient experimental data for both IL-C₂H₄ and IL-C₂H₆ systems, the COSMO-RS model is used after validation to generate additional pseudo-experimental data. Then, together with the sufficient experimental data of CO₂-IL and CH₄-IL systems, UNIFAC-IL is developed for the prediction of four-component shale gas (CH₄, C₂H₄, C₂H₆, CO₂) solubility in ILs. A relatively good agreement between the model predicted and the experimental solubility data is observed. Moreover, the developed UNIFAC-IL model can be used to predict the solubility of gases in new ILs that are not included in parameter fitting due to its group contribution basis. For this reason, the model represents a very useful tool for task-specific design of ionic liquids for gas separations.

Keywords: Ionic Liquids (ILs); COSMO-RS; UNIFAC; Gas solubility; Henry's law constant

1 Introduction

Separation and purification technologies are widely used in modern industry and research area, such as gas separation, material production and environmental protection, and they are indispensable units in many industrial production processes. Currently, the commonly used gas separation technologies are energy intensive distillation, solvent based absorption, flux limited adsorption, and membrane-based operations. Distillation is extensively used for some light hydrocarbon gas separation processes in which the separated gas is recognized as an important raw gas for synthesizing many industrial chemicals. Such distillation processes usually involve columns with large numbers of trays operating at low temperatures and high pressures, which leads to a high energy consumption and negative environmental impact Tula et al., (2017). Thus, solvent based absorption technology is an alternative to overcome these disadvantages. It is widely

used for separating gas mixtures coming from power or chemical plants containing CO₂, H₂S and so on, which need to be removed in order to meet the emission standard of air pollutants. Currently, there are two kinds of solvents for these gases removing. One type is classified as chemical solvents such as monoethanolamine (MEA), methyldiethanolamine (MDEA) or diethanolamine (DEA) Afkhamipour et al., (2014). The other is a physical solvent where solvent-blends like Selexol Kapetaki et al., (2015) or Rectisol Sun et al., (2013) are applied. However, both of these two types of solvents have disadvantages, for example, the chemical solvent may lead to a high vaporization temperature; large solvent loss; high energy consumption for solvent regeneration; while the traditional physical solvents may result in a lower gas recovery because of the low gas capacity. Therefore, developing innovative, energy-saving and “green” solvents for related absorption technologies have received much attention by many researchers.

Recently, ionic liquids (ILs) have been considered as potential substitutes to the chemical solvents as well as the physical ones due to their non-volatility, good stability which can overcome the disadvantages of chemical solvents, and also because of their tailor-made properties such as high solubility and selectivity, which can also avoid the disadvantages of physical ones Cao et al., (2018). Blanchard et al. Blanchard et al., (1999) first reported in 1999 that CO₂ is soluble in [bmim][PF₆] under 8MPa, attracting more studies on gas solubilities in ILs. Zhang et al. Zhang et al., (2012) reviewed the research progress on CO₂ capture with ILs until 2012. The CO₂ capture capacities of pure ILs and IL mixtures are summarized and compared. Besides, the optimal design and economic assessment of IL-based process are also discussed. Lei et al. Lei et al., (2014a) studied the capture of gases using ILs, where the solubility data of a series of important gases such as CO₂, SO₂, CO, N₂, O₂ and some light hydrocarbon gases are reviewed over a wide range of temperatures and pressures. It is found that some ILs show very distinct solvation capacities for different gases, indicating a high-potential for their application to the corresponding gas separations. However, because of the numerous possible combinations of anions and cations present in ILs, the current available experimental IL-data is unable to represent them all and it is time-consuming to measure the solubility of each gas in all the ILs of interest. Therefore, in order to find ILs that are suitable as solvents for gas separation, it is important to have the appropriate predictive thermodynamic models which could be used for the design of IL-based gas separation processes. So far, several thermodynamic models have been applied for describing the IL-containing systems, such as equations of state (EoS) Hizaddin et al., (2015; Mota Martinez et al., (2015), empirical models Blath et al., (2011), and group contribution based methods Carlisle et al., (2008) (UNIFAC) Song et al., (2018), quantum chemical calculation based model (COSMO-RS) Fallanza et al., (2013; Han et al., (2018; Lyu et al., (2014; Song et al., (2017; Song et al., (2015; Zhou et al., (2014). Among them, COSMO-RS is a novel model for a priori prediction without relying on any experimental data. It has been widely used for an IL priori screening. As a typical group contribution-based model, UNIFAC model has received much attention for IL design by many researchers. Therefore, in this paper, both two models are taken into consideration for activity coefficient prediction.

The COSMO-RS model is first developed by Klamt et al Klamt et al., (2000). As a predictive method, the COSMO-RS calculation only requires molecular structure information. It has not only been used for predicting solubility of liquid species in ILs Zhou et al., (2012) but also applied for predicting the solubility of gases and screening suitable ILs for different gas mixture separations. Zhang et al. Zhang et al., (2008) use the COSMO-RS model to screen ILs only for CO₂ capture.

However, due to the high deviation between experimental and COSMO-RS predicted properties, it offers only qualitatively correct results Manan et al., (2009). In consideration of this, many authors developed modified COSMO-RS models in which directly linear correction on the Henry's law constant to reduce the systematic error associated with COSMOthermX prediction is proposed Farahipour et al., (2016; Zhao et al., (2015; Zhao et al., (2017). The COSMOthermX is the software based on COSMO-RS model. All of these modified models perform better than the original COSMO-RS model. It is found that the Henry's law constant is predicted through the vapor pressure of gas multiplying the activity coefficient of gas in IL. To validate the COSMOthermX calculation deeply, in this work, the vapor pressure calculated based on the gas energy file from a COSMO-RS approximation model Eckert, (2013) and the activity coefficient value predicted by COSMO-RS are both compared with experiments separately before application. The result shows a large error in vapor pressure prediction. Then linear correction only on the activity coefficient is proposed.

As a result, the simpler group contribution based UNIFAC model is mainly considered for the prediction of gas solubility in ILs. The classical UNIFAC model, with parameters regressed from experimental data, usually shows better predictions of phase equilibrium. The UNIFAC model has recently been extended to IL containing systems by Lei et al. Lei et al., (2012; Lei et al., (2009) for liquid solute-IL systems, and later for CO₂-IL systems Lei et al., (2014b). The predicted results agree well with the experiments. Due to the strong electrostatic interactions between cation and anion, they treat the cation and anion as one main group. However, with this approach it is difficult to flexibly tune cations and anions for IL design. In order to expand the IL design space, Roughton et al. Roughton et al., (2012) and Song et al. Song et al., (2018) developed a UNIFAC model to predict liquid-liquid equilibrium of IL systems where ILs are treated as three groups: cation, anion and substituents on the cation. In this work, we employ this strategy to establish a new UNIFAC-IL model to predict vapor-liquid equilibrium for IL-four-gas systems.

In this work, a comprehensive Henry's law constants database is first established for gas-IL which supplements an already established extensive gas solubility database. With the increasing interests on the substituted resources of conventional coal, a model shale gas, mainly containing CH₄, and some other gases such as C₂H₄, C₂H₆, CO₂, is selected as a case study to highlight the application of the developed predictive thermodynamic models. UNIFAC-IL is developed for the prediction of four-component shale gas (CH₄, C₂H₄, C₂H₆, CO₂) solubility in ILs. Because of the insufficient experimental data for both IL-C₂H₄ and IL-C₂H₆ systems, the COSMO-RS model is considered after validation as a supplementary tool for additional pseudo-experimental data. Detailed calculation sequences for both corrected COSMO-RS model and UNIFAC-IL model are shown in Fig.1.

Fig. 1. Calculation sequence for the model development

The paper is organized as follows. The database for experimental solubility and Henry's law constant of gas in IL is first established in section 2.1. Then the COSMO-RS theory and the UNIFAC model are introduced in 2.2 and 2.3 respectively. In section 3, the COSMO-RS based model is developed to predict the activity coefficient of the four gases in ILs. With sufficient experimental and predicted data from the database and COSMO-RS model, the UNIFAC-IL model is further developed. Results of some new group parameter regression and associated discussions for the performance of these two models compared with experiments are presented. Finally in the conclusion (section 4), the application of these two models are discussed and related perspectives has been stated.

2. Methods and tools

An IL-database is first established, containing experimental solubility data and Henry's law constants of various gases in different ILs. Based on this database, solubility data of the four gases (CH_4 , C_2H_4 , C_2H_6 , CO_2) are retrieved for UNIFAC-IL model development. And the activity coefficient data is applied for COSMO-RS model validation and correction.

2.1 IL-Database

The prerequisite for developing a thermodynamic model is to build a comprehensive database of measured property data. In this work, our IL-database consists of measured solubility data and Henry's law constants of various gases in a wide range of ILs at different conditions.

The Henry's law constant data, covering 11 different gases, including CO_2 and some light hydrocarbon gases, is summarized in Table 1 and details and the corresponding literature sources can be found in Tables S1-S11 of the supporting information.

Table 1 Database information on measured Henry's law constants

Gas	Number of ILs	Number of data points	Temperature range (K)
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CO ₂	36	210	283 - 363
CH ₄	22	138	283 - 363
C ₂ H ₄	14	38	283 - 333
C ₂ H ₆	10	41	283 - 363
C ₃ H ₈	6	12	303 - 363
C ₄ H ₁₀	1	7	303 - 363
N ₂ O	6	21	293 - 363
N ₂	9	46	283 - 363
H ₂	4	28	278 - 343
O ₂	3	19	283 - 343
CO	1	9	283 - 343
Predicted from the corrected COSMO-RS (Eq. 1,17-19)			
C ₂ H ₄	30	300	288 - 333
C ₂ H ₆	30	300	288 - 333

In this work, we mainly focus on the first four gases (see Table 1), which are the main components of shale gas. These experimental Henry's law constants are compared with those obtained with the COSMO-RS model and make, where necessary, corrections to get a more consistently correct data. As a result, the accuracy of these collected experimental data is very important. Therefore, in the literature survey, to obtain the reliable data to be applied, on the one side, we make sure that the reported data of Henry's law constants of each gas in ILs at various temperatures are measured under the same method, on the other hand, we choose the data to be consistent under same conditions in different sources. In details, we have observed that more data are available for IL-CO₂ systems and the same binary systems have been measured by several authors. The more reliable data points with reported small deviations are retained in the database; otherwise the data is removed. For instance, the Henry's law constant of CO₂ in [bmim][Tf₂N] under 298K is reported by several authors. The values in the range 32.8 to 43 are retained Lee et al., (2015; Muldoon et al., (2007; Sistla et al., (2011) while the value of 16.2 Pereira et al., (2013), which deviates a lot from all other values is considered to be an outlier and is thus deleted. Then based on the activity coefficient predicted by the corrected COSMO-RS model and experimental vapor pressure data additional Henry's law constant pseudo-experimental data of C₂H₄ and C₂H₆ in 30 ILs under various temperatures is calculated and added to the database.

Besides the Henry's law constant database, a solubility database covering 16 gases is also developed based on Lei's database Lei et al., (2014a). From literature review, some more data points of solubility property are added. Here, we only focus on the ILs which have physical absorption on the gas. The related information is given in Table 2, while detailed values and the corresponding literature sources can be found in the Supporting Information (Table S12-S27).

Table 2 Database information on measured solubility data

Gas	Number of ILs	Number of data points	Temperature range (K)
CO ₂	103	4742	271 - 453
CH ₄	8+2	313+42	283 - 453
C ₂ H ₄	3	254	283 - 333

C ₂ H ₆	13+1	474+29	283 - 368
C ₃ H ₈	2+1	33+50	280 - 380
C ₄ H ₁₀	1	16	280 - 340
N ₂ O	11+1	513+31	283 - 373
N ₂	8+1	118+29	283 - 343
H ₂	12	265	278 - 453
O ₂	12	582	283 - 413
CO	5	101	283 - 413
H ₂ S	15	722	298 - 403
NH ₃	7	225	282 - 355
SO ₂	16	301	282 - 413
C ₃ H ₆	1	16	280 - 340
C ₄ H ₈	1	16	280 - 340

Note: the number after “+” denotes our collected data.

2.2 COSMO-RS based model for Henry’s law constant

COSMO-RS combines an electrostatic theory of locally interacting molecular surface descriptors (which are available from quantum chemical (QC) calculations) with a statistical thermodynamics methodology. It is regarded as a valuable tool for predicting activity coefficients and thermo-physical properties Klamt et al., (2000).

The Henry’s law constant is determined through Eq.1

$$H_i^S = \gamma_i^{S,\infty} p_i^S \quad (1)$$

where p_i^S is the vapor pressure. $\gamma_i^{S,\infty}$ is the infinite dilute activity coefficient of compound i . In COSMO-RS model, the activity coefficient is calculated from the chemical potential μ_i^p of the pure compounds i and the chemical potential μ_i^j at infinite dilution in compound j , as seen in Eq. 2.

$$\ln(\gamma_i) = (\mu_i^j - \mu_i^p)/RT \quad (2)$$

where μ_i^j is the chemical potential of compound i in the liquid phase (compound j or mixture system s), μ_i^p is the chemical potential of pure compound i at the same temperature. The chemical potential of compound i in system S is readily available from the integration of $\mu_s(\sigma)$ over the surface of the compound, as given by Eq.3.

$$\mu_i^S = \mu_i^{c,S} + \int p_i(\sigma) \mu_s(\sigma) d\sigma \quad (3)$$

where $p_i(\sigma)$ is called “ σ -profiles”, the probability distribution of σ for all compounds i , which can describe the composition of the surface segment ensemble with respect to the interactions. The σ -profiles is defined by Eq. 4.

$$p_i(\sigma) = \frac{n_i(\sigma)}{n_i} = \frac{A_i(\sigma)}{A_i} \quad (4)$$

where $n_i(\sigma)$ is the number of segments with charge density σ that have a surface area $A_i(\sigma)$, and n_i is the total number of segments in a single molecule with a total surface area A_i . All of these surface area, charge density information is calculated through quantum chemical calculation which can be obtained directly from COSMO output file in COSMOthermX software.

In the COSMO-RS theory, the most important molecular interactions such as electrostatics (E_{misfit}) and hydrogen bonding (E_{HB}) are taken into account as functions of the polarization

charges of two interacting surface segments σ and σ' . The less specific van der Waals (E_{vdW}) interactions are described in a slightly more approximate way. The above-mentioned interactions are given by Eqs. 5-7 as follows:

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

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

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

where a_{eff} is the contact surface area; α' is an adjustable parameter (the energy factor); σ and σ' are net screening charge densities (SCDs). c_{HB} and σ_{HB} are adjustable parameters of the HB interaction energy. τ_{vdW} and τ'_{vdW} are element-specific parameters.

As a result, the chemical potential of a surface segment with SCD σ , i.e., σ -potential $\mu_s(\sigma)$, is given by Eq. 8.

$$\mu_s(\sigma) = -\frac{RT}{a_{eff}} \times \ln \left[\int p_s(\sigma') \exp \left\{ \frac{a_{eff}}{RT} (\mu_s(\sigma') - E_{misfit}(\sigma, \sigma') - E_{HB}(\sigma, \sigma')) \right\} d\sigma' \right] \quad (8)$$

In this study, the COSMOthermX (version C3.0, release 14.01) Eckert, (2013), where the COSMO-RS theory is implemented, is applied for the prediction of four gas solubilities (CH_4 , C_2H_4 , C_2H_6 , CO_2) in ILs. The σ -profiles of calculated ILs represented by different cations and anions are retrieved from the IL Thermo Database Eckert, (2013). And the σ -profiles of CH_4 , C_2H_6 and CO_2 are taken from software database. For C_2H_4 , the profiles are optimized by the Gaussian 09 B.01 software Frisch et al., (2010) at the B3LYP/6-31+ +G** theoretical level in the ideal gas phase using the quantum-chemical calculation option. Frequency analysis is performed to ensure that no imaginary frequency exists and to confirm the minimization of energy. The COSMO files of C_2H_4 are calculated by the Gaussian 03 Frisch et al., (2004) package using the BVP86/TZVP/DGA1 level of theory. Then, the COSMO files of these gases are used as input in the COSMOthermX code to perform further calculations.

In COSMOthermX, the activity coefficient is directly predicted by Eq. 2, and related chemical potentials are calculated based on Eq. 3-8. The Henry's law constant calculation is based on Eq. 1 where the vapor pressure of gas can be estimated either by a COSMO-RS approximation model Eckert, (2013) or empirical correlation models (such as the Wagner, DIPPR, and Antoine equations). By default, the software uses the first method to estimate vapor pressures. In this work, the DIPPR Lee et al., (2015) equation (Eq.9) is applied as a candidate for the prediction of the Henry's law constant of the four gases (CO_2 , CH_4 , C_2H_4 , C_2H_6) in ILs and corresponding measured data is retrieved from the Henry's law constant database for the comparison.

$$P_i^s(\text{Pa}) = \exp \left[A_i + \frac{B_i}{T} + C_i \ln T + D_i T^{E_i} \right] \quad (9)$$

A_i , B_i , C_i , D_i , and E_i are compound-specific parameters, the values of which can be found from the DIPPR database "<https://dippr.aiche.org/SampleDb>," ().

2.3 UNIFAC-IL model

The original UNIFAC model Fredenslund et al., (1975) (Eq.A1-A13 in the Appendix) is first developed for the prediction of activity coefficients in liquid mixtures. It is broadly considered to be a predictive thermodynamic model based on the concept of group contribution. Due to this

predictive character, the model can be applied for solvent screening on many purposes such as the separation of gas mixtures and liquid-liquid extraction Lei et al., (2009; Song et al., (2018).

In order to apply the UNIFAC model into IL-containing systems, the IL molecule must first be divided into groups. Three approaches which can be used for this purpose are the following:

1) The IL molecule is divided into one cation and one anion group Santiago et al., (2011; Santiago et al., (2010). For instance, [BMIM][BF₄] can be divided into [BMIM]⁺ and [BF₄]⁻. This method could not reflect the influence of various substitutes on cation or anion.

2) The IL molecule is divided into several groups including all the substituent groups, but the skeletons of cation and anion are treated as one electrically neutral group so that the additional Debye-Hückel term relating to long-range electrostatic contributions can be neglected Chávezzislas et al., (2014; Lei et al., (2014b). In this case, [BMIM][BF₄] can be expressed by two main groups, CH₂ and [MIM][BF₄]. This approach is widely applied not only in UNIFAC developments, but also for some GC-EoS models Bermejo et al., (2009; Breure et al., (2007; Mota Martinez et al., (2015).

3) Similar to method 2, the IL is divided into several groups including alkyl chains, but the skeletons of cation and anion are divided into two groups: the cation core and anion. For the same example, CH₂, [MIM]⁺, and [BF₄]⁻ are identified using this method. Due to the strong interaction and weak dissociation of ion pairs, the interaction parameters between the cation core and anion are assumed to be zero Roughton et al., (2012; Song et al., (2018). The third approach allows for the optimal selection of cation-anion combinations, which largely expands the IL design space. It is due to this reason that we have chosen the third approach in this work.

In the UNIFAC-IL model, the group parameters for volume R_k and surface area Q_k were determined using the following procedures:

1). The rules of Bondi can be used to estimate R_k and Q_k Bondi, (1964) (Eq.10-11).

$$R_k = \frac{V_k}{15.17} \quad Q_k = \frac{A_k}{2.5 \times 10^9} \quad (10-11)$$

2). For groups that have not been defined by the rules of Bondi, values from similar UNIFAC groups were used. For example, the volume and surface area parameters for a di-substituted pyridine group were assumed to be equal to those of a di-substituted pyridinium group Roughton et al., (2012).

3). Otherwise for some groups, values were obtained in literature sources using correlations to molecular volume or molecular simulation to determine volume and surface area parameters Lei et al., (2014b; Lei et al., (2009; Song et al., (2018), as seen in Eq.(12-13).

$$R_k = \frac{V_k \times N_A}{V_{VW}} \quad Q_k = \frac{A_k \times N_A}{A_{VW}} \quad (12-13)$$

where V_k and A_k are van der Waals group volumes and surface areas of group k , respectively. V_{VW} (15.17 cm³/mol) and A_{VW} (2.5*10⁹ cm²/mol) are standard segment volume and surface area as suggested by Bondi (correspond to the CH₂ group in polyethylene), respectively; and N_A is the Avogadro's number (6.023*10²³mol⁻¹). All the final values of R_k and Q_k are presented in Table 4.

In this case, for CO₂ and CH₄, we use the corresponding gas solubility data reported in the established database to calculate the experimental activity coefficients in ILs using (Eq. 14). And for C₂H₄ and C₂H₆, because of the insufficient experimental data and the good predictive performance for IL-C₂H₄ and IL-C₂H₆ systems, we use the predicted activity coefficients data

from the corrected COSMO-RS model and calculate the solubility under pressure of 1 bar to correlate the related parameters.

$$\gamma_{i,exp} = \frac{Py_i}{P_i^s x_i} \quad (14)$$

where P is the total pressure of the system, y_i and x_i are the mole fraction of gas i in vapor phase and in liquid phase respectively. P_i^s is the saturated vapor pressure of gas i , calculated from DIPPR (Eq.9) in this work.

The interaction parameters (a_{mn} and a_{nm}) between some common UNIFAC groups which have been reported, for example $\text{CH}_2\text{-CO}_2$, $\text{CH}_2\text{-CH}_4$, $\text{CH}_2\text{-C}_2\text{H}_4$ and $\text{CH}_2\text{-CH}_2\text{O}$. Their values were kept the same as those in the literatures Nocon et al., (1983; Skjoldjorgensen et al., (1979). The other group interaction parameters were considered as unknown parameters, which were regressed by minimizing the objective function, shown as Eq. (15) where $\gamma_{i,cal}$ indicates the activity coefficients calculated from UNIFAC and $\gamma_{i,exp}$ denotes the experimental values obtained from Eq. (14). One of the ICAS toolboxes (MoT) Morales-Rodríguez et al., (2008) has been applied to perform this regression. The predicted results are compared with experimental data using the average absolute relative deviation (AARD) given in Eq.(16).

$$Obj = \sum_{i=1}^{NP} \left(\frac{\gamma_{i,exp} - \gamma_{i,cal}}{\gamma_{i,exp}} \right)^2 \quad (15)$$

$$AARD = \frac{1}{NP} \sum_{i=1}^{NP} \left| \frac{\gamma_{i,exp} - \gamma_{i,cal}}{\gamma_{i,exp}} \right| \times 100\% \quad (16)$$

Where NP is the total number of data points.

3. Results and discussion

3.1 COSMO-RS model verification and correction

Before COSMO-RS model is applied to generate the additional pseudo-experimental data, it is necessary to validate and evaluate its deviation with experiments. As mentioned in the introduction, only the four-component shale gas (CH_4 , C_2H_4 , C_2H_6 , CO_2) is taken into consideration in this work.

As described in section 2.2, the vapor pressure of corresponding gas should be estimated to calculate the Henry's law constant. In order to find the most accurate method, both the COSMO-RS approximation model and DIPPR (Eq.9) are compared with the experimental data, as seen in Fig. 2. The results indicate that the empirical DIPPR equation performs much better for prediction of vapor pressures. Therefore, in this work, we first calculate the experimental activity coefficients from the experimental Henry's law constants and the gas vapor pressures obtained from the DIPPR equation. These activity coefficients are then used to validate and correct the COSMO-RS predictions.

Fig. 2. Comparison of the estimated vapor pressure with the experimental value (corresponding DIPPR equation (Eq.9) coefficients of CO_2 , CH_4 , C_2H_4 and C_2H_6 are shown in Table S28 of Supporting information.)

Comparisons between the experimental and COSMO-RS calculated activity coefficients for the four shale gas components (CO_2 , CH_4 , C_2H_4 , C_2H_6) are performed. As shown in Fig. 3, systematic deviations could be identified, which although from one side it is unfortunate, from the other side it indicates that it is possible to develop systematic corrections to the COSMO-RS model for the prediction of activity coefficients of shale gas components in ILs. Following this idea, we have proposed a temperature-dependent correction model, summarized in equations 17-19 (Table 3), for the light hydrocarbon gases (CH_4 , C_2H_4 and C_2H_6).

For CO_2 , as seen in Fig. 3, the predicted activity coefficients usually underestimate the experimental values. While the experimental value ranges from 0.02 to 2.0, the predicted results vary in a much smaller scale (from 0.1 to 0.6). Therefore, it is difficult to find one universal model to correct the COSMO-RS predicted values, as for the light hydrocarbon gases.

Fig. 3. Experimental γ_{exp}^{∞} versus COSMO-RS predicted infinite dilution activity coefficients γ_{cosmo}^{∞} ; a) CO_2 , b) CH_4 , c) C_2H_4 , d) C_2H_6

As in Table 3, the corrected COSMO-RS models include two parameters, one is the temperature, the other is the activity coefficient from COSMO-RS which can be calculated directly from COSMOthermX software after the σ -profiles of the IL (in cation and anion, respectively) and gas have been retrieved from the IL Thermo database Eckert, (2013). The related calculation theory has been stated in section 2.2. Then the corrected activity coefficients of each gas in specific IL under various temperatures are calculated.

The accuracy of these models is shown in Fig. 4 and their relative deviations are reported in Table 3 together with the deviations from the original COSMO-RS predictions. Detailed information of the data points' value can be found in Table S29 of the Supporting information. It can be seen that the predicted values from these models are in much better agreement with the experimental data except for CH_4 (for which the deviation of about 50%, even after the correction, is still quite large). In both C_2H_4 -IL and C_2H_6 -IL systems, as a validation for the corrected COSMO-RS model, the experimental activity coefficient data in two ILs is retrieved and calculated for extrapolated validation (seen the test set in Fig.4). The results are turned out to be consistent with experiments. Therefore, pseudo experimental data are generated only for the C_2H_4 -IL and C_2H_6 -IL systems.

Table 3 Corrected COSMO-RS model for the infinite dilution activity coefficient of three light hydrocarbon gases (CH₄, C₂H₄, C₂H₆) in ILs

Gas	Corrected model, T in K		AARD with experimental γ^∞	
			Before correction	After correction
CH ₄	$\gamma_{cor}^\infty = 0.771\gamma_{cosmo}^\infty + 2.687 - 0.0087T$	Eq.(17)	123.4%	50.6%
C ₂ H ₄	$\gamma_{cor}^\infty = 1.582\gamma_{cosmo}^\infty + 1.268 - 0.00466T$	Eq.(18)	29.5%	6.3%
C ₂ H ₆	$\gamma_{cor}^\infty = 1.149\gamma_{cosmo}^\infty + 2.410 - 0.006699T$	Eq.(19)	19.5%	8.9%

Fig. 4. Experimental γ_{exp}^∞ versus corrected COSMO-RS calculated infinite dilution activity coefficients γ_{cor}^∞ ; a) CH₄, b) C₂H₄, c) C₂H₆

*This symbol corresponds to the test set ILs

In summary, COSMO-RS is a predictive model which is a positive feature but the performance is not always satisfactory for many IL-gas systems. The activity coefficient of gas in ILs, especially for C₂H₄ and C₂H₆, can be better estimated from the corrected COSMO-RS models which are developed based on experimental observations. Thus, total 600 data points of activity

coefficient among 60 IL-gas systems are added to the database. The ILs include all combinations of 3 kinds of cation ([EMIM], [BMIM], [HMIM]) with 9 kinds of common anion ([BF₄], [PF₆], [Tf₂N], [MeSO₄], [TfO], [DCA], [SCN], [DMP], [eFAP]) and another 3 ILs ([EMPY][Tf₂N], [BMPY][Tf₂N], [HMPY][Tf₂N]), totally 30 ILs with 2 gases (C₂H₄, C₂H₆) systems. These added data can be applied for further UNIFAC-IL model development. Fortunately, even though for CO₂ and CH₄, those semi-predicted values result in large errors from experiments, there is sufficient experimental solubility data in the database. As a result, for IL-CO₂ and IL-CH₄ systems, the UNIFAC-IL model is developed only based on these experimental data.

3.2 UNIFAC-IL model development

On the basis of sufficient experimental data and also the validated predicted values on activity coefficient of C₂H₄ and C₂H₆ in 30 ILs in the database, a UNIFAC-IL model among the four gases (CO₂, CH₄, C₂H₄, C₂H₆) is developed for improved predictions and also for IL design based on the group contribution principle. As a result, 19 main groups are identified. The group volume and surface area parameters are directly taken from literatures Dahl et al., (1991; Fredenslund et al., (1975; Lei et al., (2009; Nocon et al., (1983; Roughton et al., (2012; Song et al., (2018), and they are presented in Table 4. Based on the experimental solubility database, 37 pairs of group interaction parameters a_{mn} are fitted for 23 IL-CO₂ and 8 IL-CH₄ systems. And on the basis of predicted data in the database, another 23 pairs of group interaction parameters are fitted for 30 IL-C₂H₄ and 30 IL-C₂H₆ systems. Then same 600 data points as in the COSMO-RS model for IL-C₂H₄ and IL-C₂H₆ systems are calculated and also compared with experiments and values from corrected COSMO-RS model.

The optimization procedure is performed in a sequential fashion in order to decrease the number of adjustable parameters in each regression. Detailed order of optimization and the corresponding AARD can be found in Table 5. As indicated, during the first regression process, the parameters for groups CO₂, [IM]⁺, and [PF₆]⁻ are regressed using experimental data. The parameters between CO₂ and [IM]⁺ are then fixed when regressing the parameters for other anions. The same procedure has been followed for the IL-CH₄, IL-C₂H₄, IL-C₂H₆ systems. As mentioned in Section 2.3, the common UNIFAC group parameters (CO₂, CH₄, C₂H₄ with CH₂ and CH₂ with CH₂O) reported in the literature Nocon et al., (1983; Skjoldjorgensen et al., (1979) have been used directly in this work.

The obtained UNIFAC parameters are summarized and shown in Fig. 5. The comparison between experimental and calculated values for the infinite dilution activity coefficients of IL-CO₂ and IL-CH₄ systems is shown in Fig. 6. And the systems of IL-C₂H₄ and IL-C₂H₆ which have the experimental data are also compared with both corrected COSMO-RS and UNIFAC predicted values, as shown in Fig. 7, the corresponding data information can be found in Table S30 in the Supporting Information.

Table 4 UNIFAC parameters of dimensionless group volume R_k and surface area Q_k used in this work

Group No.	Main group	Subgroup	R_k	Q_k	Reference source	Structure
1	CO ₂	CO ₂	1.3000	1.1200	Nocon et al., (1983)	
2	CH ₄	CH ₄	1.1290	1.1240	Nocon et al., (1983)	
3	C ₂ H ₄	C ₂ H ₄	1.5740	1.4880	Nocon et al., (1983)	
4	C ₂ H ₆	C ₂ H ₆	1.8022	1.6960	Dahl et al., (1991)	
5	CH ₂	CH ₃	0.9011	0.8480	Fredenslund et al., (1975)	
		CH ₂	0.6744	0.5400	Fredenslund et al., (1975)	
6	CH ₂ O	CH ₂ O	0.9183	0.7800	Lei et al., (2009)	
7	[IM]	[IM]	1.9471	0.8660	Roughton et al., (2012)	
		[MIM]	2.8482	1.7140	Roughton et al., (2012)	
8	[PY]	[PY]	2.6670	1.5530	Roughton et al., (2012)	
		[MPY]	3.5681	2.4010	Roughton et al., (2012)	
9	[BF ₄]	[BF ₄]	1.7856	1.4940	Roughton et al., (2012)	
10	[PF ₆]	[PF ₆]	7.0615	6.5787	Roughton et al., (2012)	
11	[Tf ₂ N]	[Tf ₂ N]	5.7738	4.9320	Roughton et al., (2012)	
12	[Br]	[Br]	0.9492	0.8320	Roughton et al., (2012)	
13	[SCN]	[SCN]	1.9446	1.1752	Roughton et al., (2012)	
14	[CH ₃ SO ₄]	[CH ₃ SO ₄]	3.4832	3.7280	Roughton et al., (2012)	
15	[DCA]	[DCA]	2.4171	2.1337	Song et al., (2018)	
16	[NO ₃]	[NO ₃]	1.6611	1.5289	Song et al., (2018)	
17	[Cl]	[Cl]	0.7660	0.7200	Roughton et	

					al., (2012)	
18	[TfO]	[TfO]	3.4745	2.9796	Song et al., (2018)
19	[eFAP]	[eFAP]	9.4117	7.7294	Song et al., (2018)

Table 5 Order of optimization and the corresponding AARD values between experimental or corrected COSMO-RS value and estimated infinite dilution activity coefficients from UNIFAC

Sequence of fitting	Systems	Number of data points used in parameter regression	AARD of each system (%)
1	[EMIM][PF ₆]-CO ₂ [BMIM][PF ₆]-CO ₂ [HMIM][PF ₆]-CO ₂	231	6.1
2	[EMIM][BF ₄]-CO ₂ [BMIM][BF ₄]-CO ₂ [HMIM][BF ₄]-CO ₂	121	13.4
3	[BPY][BF ₄]-CO ₂	12	12.2
4	[EMIM][Tf ₂ N]-CO ₂ [BMIM][Tf ₂ N]-CO ₂ [HMIM][Tf ₂ N]-CO ₂	167	11.4
5	[(ETO) ₂ IM][Tf ₂ N]-CO ₂	16	6.0
6	[BMIM][CH ₃ SO ₄]-CO ₂ [HMIM][CH ₃ SO ₄]-CO ₂	40	15.1
7	[EMIM][TfO]-CO ₂ [BMIM][TfO]-CO ₂ [HMIM][TfO]-CO ₂	82	14.8
8	[EMIM][DCA]-CO ₂ [BMIM][DCA]-CO ₂	30	11.2
9	[BMIM][SCN]-CO ₂	34	12.0
10	[MMIM][DMP]-CO ₂	12	1.7
11	[BMIM][NO ₃]-CO ₂	54	6.8
12	[BMIM][Cl]-CO ₂	15	9.7
13	[BMIM][eFAP]-CO ₂	15	2.9
	Total No. of data points and total AARD of IL-CO ₂ systems	829	9.5
14	[BMIM][PF ₆]-CH ₄	74	25.2
15	[BMIM][BF ₄]-CH ₄	8	5.9
16	[BMIM][Tf ₂ N]-CH ₄ [HMIM][Tf ₂ N]-CH ₄	16	31.9
17	[HMPY][Tf ₂ N]-CH ₄	84	27.8
18	[BMIM][CH ₃ SO ₄]-CH ₄	10	30.5
19	[BMIM][DCA]-CH ₄	14	31.3
20	[EMIM][eFAP]-CH ₄	23	29.2
	Total No. of data points and total AARD of IL-CH ₄ systems	229	26.0

21	[EMIM][PF ₆]-C ₂ H ₄ [BMIM][PF ₆]-C ₂ H ₄ [HMIM][PF ₆]-C ₂ H ₄	30	1.6
22	[EMIM][BF ₄]-C ₂ H ₄ [BMIM][BF ₄]-C ₂ H ₄ [HMIM][BF ₄]-C ₂ H ₄	30	22.6
23	[EMIM][Tf ₂ N]-C ₂ H ₄ [BMIM][Tf ₂ N]-C ₂ H ₄ [HMIM][Tf ₂ N]-C ₂ H ₄	30	14.3
24	[EMIM][CH ₃ SO ₄]-C ₂ H ₄ [BMIM][CH ₃ SO ₄]- C ₂ H ₄ [HMIM][CH ₃ SO ₄]-C ₂ H ₄	30	24.1
25	[EMIM][TfO]-C ₂ H ₄ [BMIM][TfO]-C ₂ H ₄ [HMIM][TfO]-C ₂ H ₄	30	12.7
26	[EMIM][DCA]-C ₂ H ₄ [BMIM][DCA]-C ₂ H ₄ [HMIM][DCA]-C ₂ H ₄	30	19.0
27	[EMIM][SCN]-C ₂ H ₄ [BMIM][SCN]-C ₂ H ₄ [HMIM][SCN]-C ₂ H ₄	30	31.6
28	[EMIM][DMP]-C ₂ H ₄ [BMIM][DMP]-C ₂ H ₄ [HMIM][DMP]-C ₂ H ₄	30	17.8
29	[EMIM][eFAP]-C ₂ H ₄ [BMIM][eFAP]-C ₂ H ₄ [HMIM][eFAP]-C ₂ H ₄	30	15.3
30	[EMPY][Tf ₂ N]-C ₂ H ₄ [BMPY][Tf ₂ N]-C ₂ H ₄ [HMPY][Tf ₂ N]-C ₂ H ₄	30	15.4
	Total No. of data points and total AARD of IL-C ₂ H ₄ systems	300	17.4
31	[EMIM][BF ₄]-C ₂ H ₆ [BMIM][BF ₄]-C ₂ H ₆ [HMIM][BF ₄]-C ₂ H ₆	30	4.5
32	[EMIM][PF ₆]-C ₂ H ₆ [BMIM][PF ₆]-C ₂ H ₆ [HMIM][PF ₆]-C ₂ H ₆	30	5.0
33	[EMIM][Tf ₂ N]-C ₂ H ₆ [BMIM][Tf ₂ N]-C ₂ H ₆ [HMIM][Tf ₂ N]-C ₂ H ₆	30	31.2
34	[EMIM][CH ₃ SO ₄]-C ₂ H ₆ [BMIM][CH ₃ SO ₄]- C ₂ H ₆ [HMIM][CH ₃ SO ₄]-C ₂ H ₆	30	26.8
35	[EMIM][TfO]-C ₂ H ₆ [BMIM][TfO]-C ₂ H ₆ [HMIM][TfO]-C ₂ H ₆	30	39.1
36	[EMIM][DCA]-C ₂ H ₆ [BMIM][DCA]-C ₂ H ₆ [HMIM][DCA]-C ₂ H ₆	30	39.9
37	[EMIM][SCN]-C ₂ H ₆ [BMIM][SCN]-C ₂ H ₆ [HMIM][SCN]-C ₂ H ₆	30	40.0
38	[EMIM][DMP]-C ₂ H ₆ [BMIM][DMP]-C ₂ H ₆ [HMIM][DMP]-C ₂ H ₆	30	19.2
39	[EMIM][eFAP]-C ₂ H ₆ [BMIM][eFAP]-C ₂ H ₆ [HMIM][eFAP]-C ₂ H ₆	30	21.1
40	[EMPY][Tf ₂ N]-C ₂ H ₆ [BMPY][Tf ₂ N]-C ₂ H ₆ [HMPY][Tf ₂ N]-C ₂ H ₆	30	14.1
	Total No. of data points and total AARD of IL-C ₂ H ₆ systems	300	24.1

Main Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	CO2	CH4	C2H4	C2H6	CH2	CH2O	[lm]	[Py]	[DMP]	[BF4]	[PF6]	[Tf2N]	[SCN]	[CH3SO4]	[DCA]	[NO3]	[Cl]	[TfO]	[eFAP]
1	CO2	0.00	0.00	0.00	6339.00	-2114.13	168.31	-2206.35	644.03	-165.20	165.80	-2938.23	-2795.59	-9.15	-44.68	-2325.06	-237.67	-172.08	-48.42
2	CH4	0.00	0.00	0.00	-356.00		-31.98	0.07		-121.49	-31.97	0.00		24.40	19.38				-5.08
3	C2H4	0.00	0.00	0.00	-372.10		-166.49	-0.04	-335.49	3392.90	-165.47	0.00	1.02	935.61	937.49			130.83	89.03
4	C2H6	0.00	0.00	0.00	-9.92		24.89	0.05	2091.20	0.03	-137.45	952.90	10000.00	3877.53	4159.83			2340.31	484.12
5	CH2	107.70	1138.00	896.40	0.00	251.50	12481.33	-2766.70	-8.54	11447.19	9191.88	-3564.96	-3015.09	8355.84	7334.64	-2719.71	8488.15	394.93	8349.01
6	CH2O	453.18			83.36	0.00	-1035.91					-0.06							
7	[lm]	226.40	807.82	880.18	0.00	747.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	[Py]	116.93	314.55	-63.22	100.13		0.00	0.00											
9	[DMP]	-12.16		785.49	0.00		0.00		0.00										
10	[BF4]	7959.58	584.93	467.22	229.54		0.00			0.00									
11	[PF6]	224.47	807.65	877.62	1140.44		0.00				0.00								
12	[Tf2N]	-128.93	1.64	165.71	27.88	-3022.60	0.00					0.00							
13	[SCN]	302.39		371.47	-10.02		0.00						0.00						
14	[CH3SO4]	676.54	755.09	272.94	87.07		0.00							0.00					
15	[DCA]	492.19	269.81	375.32	60.69		0.00								0.00				
16	[NO3]	303.98			0.00		0.00									0.00			
17	[Cl]	948.93			0.00		0.00										0.00		
18	[TfO]	747.47		447.54	52.79		0.00											0.00	
19	[eFAP]	-49.39	248.36	224.33	20.37		0.00												0.00
Reported from literature																			
				This work fitted from Exp. data															
					This work fitted from Pre. Data														

Fig. 5. Fitted UNIFAC-IL group interaction parameters (Reported values from Ref.[42; 43];Pre.=Predicted data from COSMO-RS)

Fig. 6. Experimental γ_{exp}^{∞} versus UNIFAC calculated infinite dilution activity coefficients γ_{UNIFAC}^{∞} ; a) IL-CO₂ systems, b) IL-CH₄ systems

Fig. 7. Experimental γ_{exp}^{∞} versus both Predicted $\gamma_{cor_cosmo}^{\infty}$ and UNIFAC calculated infinite dilution activity coefficients γ_{UNIFAC}^{∞} ; a) IL-C₂H₄ systems, b) IL-C₂H₆ systems

As a result, the UNIFAC-IL model for the four-component shale gas (CH₄, C₂H₄, C₂H₆, CO₂) with various ILs (combined between two kinds of cation and 11 anions) systems is developed. The results predicted by the UNIFAC-IL model and the experimental data exhibit similar trends (see Fig.5 and 6), with the AARD 9.5%, 26.0%, 17.3%, 14.6% for IL-CO₂, IL-CH₄, IL-C₂H₄ and IL-C₂H₆ systems, respectively.

For IL-CH₄ system (see Fig.5b), there exists relatively large deviation. A general reason for this is that same group parameters from IL-CO₂ systems are directly used for IL-CH₄, IL-C₂H₄ and also IL-C₂H₆, it is difficult to obtain a global optimization result. Most in details, the reasons on the largest deviation for the IL-CH₄ systems (AARD = 26%) and the calculated activity coefficients change little at same temperature for each system (seen Fig. 6b) are as follows: 1) the low solubility of CH₄ in ILs; 2) limited solubility data of CH₄ in ILs and some solubility data under a wide range of pressure used for correlation; 3) for some ILs, the experimental data from more than one data sources, with some deviations from each other. Nevertheless, compared with

an average deviation of about 50% for the corrected COSMO-RS model for the IL-CH₄ systems, the predicted results by UNIFAC are in quantitatively better agreement with the experimental data. For IL-C₂H₄ and IL-C₂H₆ systems, because of the UNIFAC model is developed based on the corrected COSMO-RS values, the AARD of UNIFAC with experiments is a little bit larger than that of the corrected COSMO-RS (6.3%, 8.9%), but this UNIFAC model is easier available without any quantum chemical calculation.

In addition, this group division method provides the possibility for further IL screening and design for the shale gas separation. With these group interaction parameters, the activity coefficient of each gas in different combinations of cation, anion, and the substitutes can be easily estimated. Then, the IL with high solubility of CO₂ and high selectivity of CO₂ or other two light hydrocarbon gases to CH₄ can be screened out. This will be illustrated in a subsequent publication.

4. Conclusion and future perspectives

This work establishes first of all a database containing sufficient experimental data for Henry's law constant and solubility of several gases in ILs. Especially, as they are the conventional components of shale gas, measured data of CO₂ and three light hydrocarbon gases (CH₄, C₂H₄, and C₂H₆), together with some validated predicted values from a corrected COSMO-RS model, are included in the database. This database is used for the further development of UNIFAC-IL, and then the performance of both corrected COSMO-RS and UNIFAC-IL model is evaluated.

As our focus is on ILs screening and prediction purposes for shale gas separation, a UNIFAC-IL model is developed for the predictions of solubility of four shale gases (CH₄, C₂H₄, C₂H₆, CO₂) in ILs. Because of insufficient available experimental data for IL-C₂H₄ and IL-C₂H₆ systems, the COSMO-RS model is considered and validated as a supplementary tool for generation of additional data for C₂H₄ and C₂H₆ solubility in more ILs. In the first case, we have developed a corrected version of COSMO-RS model for all the four gases and a good prediction is obtained for the activity coefficient of C₂H₄ and C₂H₆ in ILs, with the average absolute relative deviation (AARD) of 6.2% and 8.9%, respectively. Then based on 600 predicted activity coefficient data points for C₂H₄, C₂H₆ in ILs and sufficient measured solubility data of CO₂, CH₄ in ILs, the UNIFAC-IL model is developed and interaction parameters between these four gases and 15 main groups presented in conventional ILs have been determined. The AARDs between calculated activity coefficients and experiments for the IL-CO₂, IL-CH₄, IL-C₂H₄ and IL-C₂H₆ systems are about 9.5%, 26.0%, 17.4%, 14.6% respectively. It is found that the proposed corrected version of the COSMO-RS model is able to predict the Henry's law constants of C₂H₄ and C₂H₆ in ILs, whereas for the cases of CO₂ and CH₄ where there is sufficient experimental data, the regressed UNIFAC-IL model performs better than COSMO-RS. Moreover, the developed UNIFAC-IL model can be used to predict the solubility of gases in new ILs that are not included in parameter fitting due to its group contribution basis. For this reason, the model represents a very useful tool for task-specific design of ionic liquids for gas separations.

This work provides a good basis for ILs screening and the basis of group contribution in UNIFAC makes it very useful for further IL design on shale gas separation processes, in which a systematic three-stage framework toward IL-based gas separation will be proposed and a hybrid IL-based process will be established.

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Appendix A.UNIFAC

In UNIFAC, the activity coefficient consists of a combinatorial part and a residual part, as shown in Eq. (A.1)

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

The combinatorial part is given by the following equations:

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - 5q_i \left(1 - \frac{V_i}{F_i} + \ln \left(\frac{V_i}{F_i} \right) \right) \quad \text{Eq.(A.2)}$$

$$F_i = \frac{q_i}{\sum_j q_j x_j} \quad V_i = \frac{r_i}{\sum_j r_j x_j} \quad \text{Eq.(A.3-A.4)}$$

$$r_i = \sum_k \nu_k^{(i)} R_k \quad q_i = \sum_k \nu_k^{(i)} Q_k \quad \text{Eq.(A.5-A.6)}$$

Where R_k and Q_k are the relative van der Waals group volumes and group surface areas, respectively. r_i and q_i are the dimensionless molecular van der Waals volumes and surface areas, which are calculated from the summation of group volumes and surface areas, respectively.

The residual part is determined by the equations:

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad \text{Eq.(A.7)}$$

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \psi_{mk} \right) - \sum_m \left(\frac{\Theta_m \psi_{km}}{\sum_n \Theta_n \psi_{nm}} \right) \right] \quad \text{Eq.(A.8)}$$

$$X_m = \frac{\sum_i \nu_m^{(i)} x_i}{\sum_i \sum_k \nu_k^{(i)} x_i} \quad \Theta_m^{(i)} = \frac{Q_m X_m^{(i)}}{\sum_n Q_n X_n^{(i)}} \quad \Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad \text{Eq.(A.9-A.11)}$$

$$\psi_{mn} = \exp \left(-\frac{a_{mn}}{T} \right) \quad \psi_{nm} = \exp \left(-\frac{a_{nm}}{T} \right) \quad \text{Eq.(A.12-A.13)}$$

Where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only compound i . X_m is the fraction of

group m in the mixture. ψ_{mn} is the group interaction parameter. a_{mn} characterizes the interaction energy between groups n and m .

Appendix B. Supplementary information

Supplementary information associated with this article can be found in the online version.

Abbreviations

COSMO-RS	Conductor-like Screening Model for Real Solvents
ILs	Ionic liquids
MEA	Monoethanolamine
MDEA	Methyldiethanolamine
DEA	Diethanolamine
EoS	Equation of state
UNIFAC	Universal quasichemical functional-group activity coefficients
CAMD	Computer-aided molecular design
QC	Quantum chemical
SCD	Surface charge density
AARD	Average absolute relative deviation
[EMIM]	1-ethyl-3-methylimidazolium
[BMIM]	1-butyl-3-methylimidazolium
[HMIM]	1-hexyl-3-methylimidazolium
[MMIM]	1,3-dimethyl-imidazolium
[OMIM]	1-octyl-3-methylimidazolium
[AMIM]	1-allyl-3-methylimidazolium
[BMPYRR]	1-butyl-1-methylpyrrolidinium
[thtdp]	Tributyl(tetradecyl)phosphonium
[BMPIP]	1-butyl-1-methylpiperidinium
[tes]	Triethylsulfonium
[toa]	Methyltrioctylammonium
[DCA]	Dicyanamide
[PF ₆]	Hexafluorophosphate

[BF ₄]	Tetrafluoroborate
[TfO]	Trifluoromethanesulfonate
[NO ₃]	Nitrate
[CH ₃ SO ₄]	Methylsulfate
[Tf ₂ N]	Bis(trifluoromethylsulfonyl)-imide
[FEP]	Tris(pentafluoroethyl)trifluorophosphare
[DEP]	Diethylphosphate
[phos]	Bis(2,4,4-trimethylpentyl)phosphinate

LIST OF SYMBOLS

p_i^s = vapor pressure of pure component i

P = pressure, Pa

T = temperature, K

x_i = composition of component i in liquid

y_i = composition of component i in vapor

γ_i = activity coefficient

E_{misfit} = misfit energy of two molecules.

α' = energy factor.

σ = charge density, Coulomb/m²

a_{eff} = contacted surface area, m²

E_{hb} = hydrogen interaction energy, Coulomb

μ_i = chemical potential.

E_{vdW} = interaction energy attributing to van der Waals force

$p_i(\sigma)$ = probability distribution of σ

H_{iA} = Henry's law constant of component i in solvent A, Pa

γ_i^∞ = the infinite dilution activity coefficient of component i

R_k = group parameters of volume

Q_k = group parameters of surface area

r_i = molecular van der Waals volumes

q_i = molecular surface area

Γ_k = group residual activity coefficient

$\Gamma_k^{(i)}$ = residual activity coefficient of group k in a reference solution containing only molecule of type i .

X_m = fraction of group m in the mixture

ψ_{mn}, a_{mn} = interaction parameters between groups n and m

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