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Prediction of CO_2 solubility in ionic liquids with QM and UNIQUAC models

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ABSTRACT

In recent years, ionic liquids shows their abilities in many processes, like enzymatic reactions, electrochemical applications, catalysis processes, or separation processes. In this work, CO_2 solubility in Ionic liquids has been calculated based on two thermodynamic models, i.e., the UNIQUAC model and the quantum model, based on COSMO-RS theory of interacting molecular surface charge. To investigate the accuracy of the considered models the predicted solubility of CO_2 in ionic liquids was compared with experimental data in a wide range of pressure and temperature. The ionic liquids [bmim][Bf_4], [bmim][Tf_2N], [emim][Tf_2N], [Omim][Pf_6], [Omim][Tf_2N], [emim][Bf_4] and [Hmim][Tf_2N] were used here to investigate the capability of the models in predicting CO2 solubility. It was found that the accuracy of COSMO-RS is good, but only for some ILs, whereas UNIQUAC is the most capable method in predicting the gas solubility.

1. Introduction

Ionic liquids (ILs) are usually defined as organic salts composed of large asymmetric organic cations and organic or inorganic anions with melting point at or below 100 °C [1]. ILs have some properties as instance, low vapor pressure, high electroelasticity, non-toxicity, high heat capacity, non-flammability, high thermal and chemical stability and good miscibility with polar and non-polar liquid are the main advantages of ILs compared to conventional amine solvents to CO_2 absorption [2]. ILs has much potential in electrolyte, heat storage, liquid crystals, solvents, analytic, lubricants and additives. Carbon dioxide is one of the greenhouse gases that harmful to health and effect on the weather of the world because of changes in temperature then it is important for human beings to emit it from flue gases. The sources of CO_2 emissions are natural and human activities. Emissions of CO_2 from its sources such as burning fossil fuels can be controlled by arresting CO_2 from the emission point and detaching it with activities like underground injection [3]. Three basic methods are used to separate gases 1-using solvent/sorbent; like Amine 2-Memberane 3-Cryogenics. Capture of carbon dioxide using ILs is one of the applications of the first method. Researchers have shown the high CO_2 absorption capacity and selectivity of ILs for CO_2 capture from its sources [4]. It is necessary to be able to describe the treatment of VLE data, therefor capable model is needed. There are different models to obtain activity coefficient, some of them has a theoretical base like COSMO-RS model, others like Wilson use experiment here these two types are used.

The quantum chemical basis of COSMO-RS is COSMO, the Conductor-like Screening Model, which belongs to the class of a QM continuum salvation model (CSMs) [5]. COSMO-RS combines an electrostatic theory with statistical thermodynamic methodology [6].

The standard procedure of COSMO-RS calculations consisting two major steps: quantum chemical COSMO calculations for the molecular species involved and COSMO-RS statistical calculations [7].

The purpose of this study is to show the ability of COSMO-RS and UNIQUAC model to predict the solubility of CO_2 in [bmim][Bf_4], [bmim][Tf_2N], [emim][Tf_2N], [Omim][Pf_6], [Omim][Tf_2N], [emim][Bf_4] and [Hmim][Tf_2N]. The UNIQUAC model is widely used to predict gas solubility because of its simplicity and flexibility [8–13]. Two models were compared with experimental data in a wide range of pressure and temperature. The fantastic model of COSMO-RS, without needing experimental data, has recently been used by many researchers to check out its capability in thermodynamic properties prediction [14–16].

2. Theory

2.1. QM (COSMO-RS)

Since in the COSMO-RS viewed all molecular interactions consist of local pairwise interactions of surface segments, the statistical averaging can be done in the ensemble of interacting surface pieces. To describe the composition of the surface segment ensemble with respect to the interactions (which depend on σ only), only the probability distribution of σ has to be known for all compounds *i*. Such probability distributions $P_i(\sigma)$ are called "σ-profiles". The σ-profile of the whole system/mixture

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Table 1
Surface volume and area, critical properties and acentric factors.

Component	r	q	Tc(K)	Pc(bar)	ω
[bmim][Tf_2N]	11.2	9.86	1269.9	27.65	0.3
[emim][Bf_4]	6.51	5.16	596.2	23.6	0.808
[Omim][Tf_2N]	13.9	12.0	923.02	18.7	1.331
[Omim][Pf_6]	13.3	9.32	810.8	14	0.938
[emim][Tf_2N]	9.89	8.78	788.05	33.1	1.225
[bmim][Bf_4]	7.86	6.17	643.2	20.4	0.887
[Hmim][Tf_2N]	12.6	10.9	769.14	19.6	0.798
CO_2	1.3	1.12	304.2	73.9	0.224

$P_s(\sigma)$ is just a sum of the σ-profiles of the components i weighted with their mole fraction in the mixture x_i.

$$p_s(\sigma) = \sum_{ies} x_i p_i(\sigma) \tag{1}$$

$$\mu_s(\sigma) = -\frac{RT}{a_{eff}} \ln\left[\int p_s(\sigma')\, exp\left(\frac{a_{eff}}{RT}\left(\mu_s\left(\sigma'\right) - e(\sigma,\sigma')\right)\right) d\sigma'\right] \tag{2}$$

$\mu_s(\sigma)$ is a measure for the affinity of the system S to a surface of polarity σ.

The chemical potential (the partial Gibbs free energy) of compound i in system S is readily available for integration of the σ-potential over the surface of i:

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

$$\mu_i^{c,s} = \frac{\partial G_{c,s}}{\partial x_i} = RT\left[\lambda_0 \ln r_i + \lambda_1\left(1 - \frac{r_i}{\bar{r}} - \ln\bar{r}\right) + \lambda_2\left(1 - \frac{q_i}{\bar{q}} - \ln\bar{q}\right)\right] \tag{4}$$

$$G_i^{c,s} = RT\left[\lambda_0 \sum_i x_i \ln r_i - \lambda_1 \ln\left(\sum_i x_i r_i\right) - \lambda_2 \ln\left(\sum_i x_i q_i\right)\right] \tag{5}$$

r_i is the molecular volume and q_i is the molecular area of compound i. The total volume and area of all compounds in the mixture are defined:

$$\bar{r} = \sum_i x_i r_i \tag{6}$$

$$\bar{q} = \sum_i x_i q_i \tag{7}$$

The chemical potential μ_i^s allows for the prediction of almost all thermodynamic properties of compounds or mixtures, such as activity coefficients, excess properties or partition coefficients and solubility.

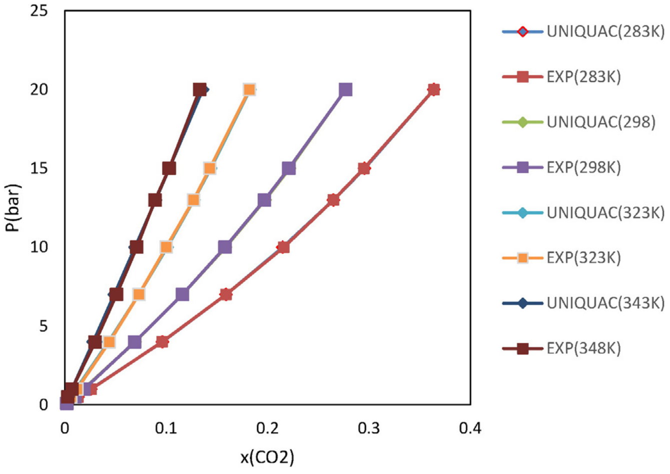

Fig. 1. P-x diagrams of the CO_2 + [bmim][Bf_4] mixtures.

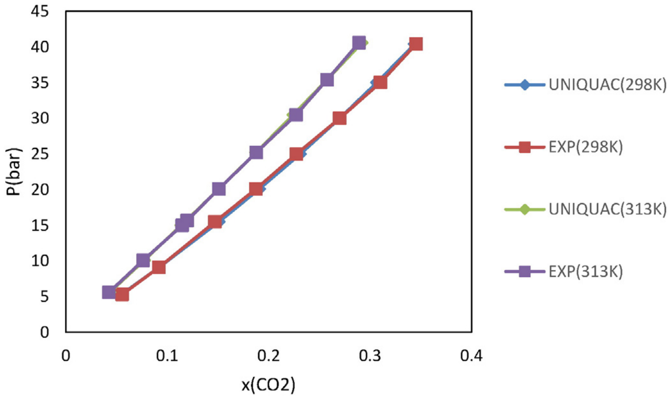

Fig. 2. P-x diagrams of the CO_2 + [emim][Bf_4] mixtures.

$$\gamma_s^x = \exp\left[\left(\mu_s^x - \mu_x^x\right)/kT\right] \tag{8}$$

$\mu_x^x$is the chemical potential in the pure liquid substance.

For each compound j the mole fraction x_j is varied until the partial pressure of the compound, which is calculated from Eq. (9), is equal to the given reference pressure p.

$$p_j = p_j^0 x_j \gamma_j \tag{9}$$

The p_j^0 is the pure compound vapor pressures for compound$j$. x_j is the mole fraction of the compound in the liquid, and γ_j are the activity coefficients of the compounds as predicted by COSMO-RS model. The ideal behavior of the gas phase is assumed. In each iteration step x_j will vary, compute γ_j in the given solvent or solvent mixture with a finite portion of compound j according to x_j and from that, calculate the partial pressure of the compound p_j according to Eq. (9). This process is repeated until the difference of the computed partial vapor pressure p_j and the given reference pressure p is less than a given threshold.

2.2. Uniquac

The UNIQUAC was initially published as Statistical Thermodynamics of Liquid Mixtures. The universal quasi-chemical theory or in short UNIQUAC consist of two parts describing g^E. First, combinatorial part describes the dominant entropic contribution, second, residual part that describes intermolecular forces that are responsible for enthalpy of

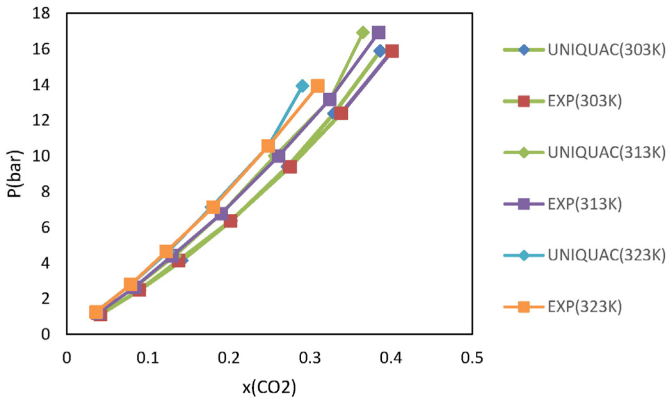

Fig. 3. P-x diagrams of the CO_2 + [Omim][Tf_2N] mixtures.