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Solubility of greenhouse and acid gases on the $[C_4mim][MeSO_4]$ ionic liquid for gas separation and CO_2 conversion

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ABSTRACT

Ionic liquids (ILs) are an exciting class of compounds of high interest from a technological point of view. One of the applications that is raising more interest is their possible use as solvents to carry out the conversion of CO_2 into more valuable compounds. Theoretical approaches provide an attractive option to screen ILs properties and give quick answers to guide the experiments, becoming a crucial tool for process design. This work illustrates a practical example based on the solubility of greenhouse and acid gases on the butylmethylimidazolium methylsulfate $[C_4mim][MeSO_4]$ IL, in order to study its feasibility for gas separation and conversion. A simple but reliable molecular model is presented for the ionic liquid based on structural information and molecular simulations, and coarse-grained models are used to model the different gases. The absorption of relevant gases for the separation/conversion process (CO_2, CH_4, CO, H_2, SO_2, H_2S) in $[C_4mim][MeSO_4]$ is modeled and compared with experimental data using a minimum amount of binary data. From this information, the ternary diagrams of $[C_4mim][MeSO_4]$ with CO_2 and the acid gases SO_2 and H_2S are predicted, and the selectivity of CO_2 by respect all the gases is evaluated, with particular attention to the contaminants above mentioned.

1. Introduction

In the last 15 years, ionic liquids (ILs) have drawn academic and commercial attention due to their unusual chemical and physical properties that make them valuable alternatives to traditional compounds and solvents for different applications [1]. ILs are practically non-volatile, present a wide liquid range and are not flammable, among other characteristics. A considerable volume of research and review work has been published addressing their valuable properties and their design for a specific application by choosing the appropriate cation/anion combination. This design is provided through a previous systematic thermophysical characterization, which is a key requirement for practical applications. Experimental measurements are required to do this task, but they can hardly explore all the ranges of temperature and pressure of application without an important economic and timing penalty.

One of the current potential applications of ILs is its use as a solvent for carbon dioxide (CO_2) capture and separation [2,3]. CO_2 usually comes as a residue from plant effluent streams, mixed with other greenhouse gases (CH_4, CO) or hazardous pollutants, such as H_2S and SO_2. This process can be seen as an alternative to the conventional technology of using chemical absorption through an aqueous solution of amines, which has important drawbacks, including loss of solvent, corrosion of facility, and high energy demand regeneration of the absorbent [4]. ILs are a possible kind of novel media that, with an appropriate selection, could result in a non-contaminated target gas, particularly attractive for the separation of these gases. The resulting purified CO_2 can be further transformed into useful compounds employing the same ILs as catalysts/reaction media [5], what is of paramount importance from a standpoint of green chemistry. Additionally, supercritical carbon dioxide in combination with ILs can be used in continuous green biocatalytic processes [6,7]. In this manner, CO_2 is converted from a residue into an added value compound or into a catalytic co-solvent. However, these processes require, as mentioned, a first gas separation step, which is a key element for an adequate posterior processing.

At the current moment, there is still a need for a further understanding of the dependence of the gas behavior on the IL microscopic structure in order to enhance its design. Molecular modeling techniques provide an excellent framework to progress on this field [8]. Among many equations of state (EoSs), the

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soft-SAFT EoS [9] provides a physically grounded theoretical approach to describe the thermophysical properties and phase behavior of ILs and their mixtures in good agreement with the experimental data [10–12]. Hence, the purpose of this work is to exploit the possibilities of soft-SAFT as a powerful tool for the description of the behavior of ILs and similar compounds, by exploring their ability to solubilize CO_2 and several other contaminant gases in them. In particular, we have focused our efforts in developing a theoretical semipredictive framework to study the potential application of the butylmethylimidazolium methylsulfate, [C_4mim][$MeSO_4$], IL for gas separation and conversion purposes.

Alkyl sulfate ILs have been recently subject of attention since they are halide-free ILs that can be used as an alternative to the widely investigated anion-fluorinated ILs, such as those with hexafluorophosphate, tetrafluoroborate or bis(trifluoromethylsulfonyl)imide as anions, considering their low cost, ease of preparation, wide electrochemical window, and air stability [13]. They can be used in the halide-free synthesis of other ILs by metathesis [13], as well as in organocatalysis for the synthesis of dihydropyrimidinones and -thiones [14].

In order to consider the use of this family of ILs for CO_2 separation and conversion processes, it is fundamental to know and understand the gas solubility behavior when these ILs are used as solvents. Previous works have focused on the experimental measurements of the solubility of various gases in [C_4mim][$MeSO_4$]. Some of these studies also present interesting results obtained from theoretical modeling approaches. For instance, Kumełan and co-workers presented solubility data for several gases in [C_4mim][$MeSO_4$] in wide temperature ranges for CO_2 [15], CH_4 [16], H_2 [17] and CO [17]. They used the extended Henry's law through the virial expansion proposed by Pitzer for the activity coefficients calculations to correlate the data. Of particular interest for the present contribution is the work done by Shiflett and co-workers [18–20], where the solubility of H_2S and SO_2 in [C_4mim][$MeSO_4$] was measured. They showed how the chemical absorption controlled the SO_2 solubility in the IL [18,20], and even presented phase equilibria data for the ternary systems composed of those gases, the IL and CO_2. A cubic equation of state, based on the SRK EoS but with up to 4 binary interaction parameters, was developed for the description of the high pressure phase equilibria of gases + ILs systems and was applied to describe the reported experimental data. These contributions have shown that [C_4mim][$MeSO_4$] enhances significantly the selectivity of the CO_2/SO_2 and CO_2/H_2S mixtures, being a potential candidate to substitute classical solvents.

This article is organized as follows: a short description of the main features of the soft-SAFT equation is exposed in the next section. Then, the different molecular models used to describe the gases and the selected IL of this work are explained appropriately, highlighting the assumptions made for each particular case. The results section includes a variety of phase diagrams showing the solubility of the different gases in [C_4mim][$MeSO_4$], the calculation of the Henry's constant for each case and the selectivity to separate the other gases from CO_2. Additionally, particular attention is given to the removal of acid gases by studying the ternary diagram of these mixtures with CO_2 and the IL, looking for the best separation conditions. Finally, some concluding remarks are given in the last section.

2. Methodology

The soft-SAFT equation [9] is a well-established variant of the original Statistical Associating Fluid Theory (SAFT) equation of state [21]. Based on Wertheim's first-order perturbation theory [22–24], it provides a framework in which the effects of molecular shape and intermolecular interactions on the thermodynamic properties of a system are explicitly considered. The equation calculates the total free energy of the system as a sum of different independent contributions that account for several molecular effects. For associating and polar molecules, the soft-SAFT approach calculates the Helmholtz energy of the system as a sum of an ideal contribution, A^{ideal}, a reference term, A^{ref}, for the attractive and repulsive forces between the segments that form the molecules, a chain contribution, A^{chain}, for the connectivity of the segments in the molecules, a contribution due to site-site intermolecular association, A^{assoc}, and a polar term, A^{polar}:

$$A^{\text{total}} - A^{\text{ideal}} = A^{\text{res}} = A^{\text{ref}} + A^{\text{chain}} + A^{\text{assoc}} + A^{\text{polar}}. \tag{1}$$

A^{res} is the residual Helmholtz energy density of the system. The reference term of the soft-SAFT EoS is given by a Lennard–Jones (LJ) spherical fluid, considering repulsive and attractive interactions of the monomers in a single contribution. This intermolecular potential includes the sphere (segment) diameter of the monomers σ_{ii} and the dispersive energy between segments ε_{ii}/k_B. The equation of Johnson et al. [25], adjusted to molecular simulations of Lennard–Jones monomers, is used here to calculate the free energy of this term.

In order to extend the LJ contribution to mixtures, it is necessary to apply the van der Waals one-fluid theory, due to the fact that the original reference term does not explicitly consider mixtures.

$$\sigma_m^3 = \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} m_i m_j x_i x_j \sigma_{ij}^3}{\sum_{i=1}^{n}\sum_{j=1}^{n} m_i m_j x_i x_j}, \tag{2}$$

$$\varepsilon\sigma_m^3 = \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} m_i m_j x_i x_j \sigma_{ij}^3}{\sum_{i=1}^{n}\sum_{j=1}^{n} m_i m_j x_i x_j}. \tag{3}$$

The unlike size σ_{ij} and energy ε_{ij}/k_B soft-SAFT molecular parameters are obtained with the modified Lorentz–Berthelot (LB) combining rules:

$$\sigma_{ij} = \eta_{ij}\left(\frac{\sigma_{ii}+\sigma_{jj}}{2}\right), \tag{4}$$

$$\varepsilon_{ij} = \xi_{ij}(\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{5}$$

where ξ_{ij} and η_{ij} are the size and energy binary adjustable parameters, respectively. It is important to clarify that when both values are set to one, Eqs. (4) and (5) reduce to the classical LB combining rules and the model becomes predictive. Note that ξ_{ij} is equivalent to $(1-k_{ij})$, and η_{ij} is equivalent to $(1-l_{ij})$, the energy and size binary parameters most commonly used in classical equations of state.

The chain and association terms come from Wertheim's theory [22–24] and are formally identical in all SAFT equations:

$$A^{\text{chain}} = Nk_BT\sum_i x_i(1-m_i)\ln g_{LJ}, \tag{6}$$

$$A^{\text{assoc}} = Nk_BT\sum_i x_i \sum_a \left(\ln X_i^a - \frac{X_i^a}{2}\right) + \frac{M_i}{2}, \tag{7}$$

where N is the number of molecules, k_B is the Boltzmann constant and T is the temperature. The chain term is obtained using an equation fitted to molecular simulations of LJ chains [26]. The chain term includes the chain length parameter m_i, while the association term involves two additional parameters related to the volume (K^{HB}) and energy (ε^{HB}/k_B) of the association sites.

Eqs. (6) and (7) are expressed in a general form valid for n compounds. The only requirement to extend the treatment to mixtures is the evaluation of the cross-association volume (${K^{HB}}_{ij}$) and energy (${\varepsilon^{HB}}_{ij}/k_B$) parameters to account for the energy and volume of association between different compounds. In this work, the mean arithmetic of the cube root of ${K^{HB}}_{ij}$ and the geometric average for