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A theoretical study on aminoacid-based ionic liquids with acid gases and water

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ABSTRACT

The properties of 1-ethyl-3-methylimidazolium glycinate ionic liquid mixed with CO_2, SO_2 and H_2O were studied using a computational chemistry approach considering classical molecular dynamics simulations and quantum chemistry calculations using density functional theory. Studies as a function of mixture composition, pressure and temperature allowed a detailed characterization at the nanoscopic level of the interaction between the acid gases and the ionic liquid as a model for the use of aminoacid-based ionic liquids for acid gas capture purposes. Likewise, the properties of aqueous mixtures were analysed considering the ubiquitous presence of water in acid gas capture industrial processes. Insights on the characteristics and strength of gas molecules – ionic liquid interactions were inferred from simulations, and thus, showing the arrangement and dynamics of gas molecules around the ions.

1. Introduction

The interest on the application of ionic liquids, ILs, for carbon capture purposes has led to a large number of studies in the recent years [1,2,3,4,5,6]. The reason on this interest stands on the possibility of tuning ILs properties through suitable combinations of ions for fulfilling technological requirements according to a sustainable chemistry approach [7,8,9] and thus, the large number of possible ILs which can be considered for the treatment of flue gases coming from fossil-fuelled power plants. Therefore, ILs have been considered among the most promising options for developing carbon capture technologies being viable from technological and economical viewpoints [10,11]. Nevertheless, several problems have been considered for the application of conventional ILs [12], including poor biodegradability [13] toxicity [14] or economic issues rising from their high cost [15], which would hinder their application to large scale operations such as CO_2 absorption [16,17] and they have led to some authors claims that ILs – based technologies for CO_2 capture would not be available in the next two decades [18]. Nevertheless, many of these difficulties can be overcome if studies are shifted from conventional ILs [19,20,21] to new types of ILs considering more suitable and task-specific ions [22] from the large library of possible candidates [23,24].

For the purpose of developing suitable ILs for CO_2 capture, computational chemistry tools may play a pivotal role. These theoretical approaches allow to infer the most suitable anion – cation combinations for improving affinity toward CO_2 molecules [25,26], and at the same time leading to viable physicochemical properties which would allow scaling up the capturing processes to large scale industrial application [22,27]. In particular, classical molecular dynamics (MD) simulations and quantum chemistry studies using Density Functional Theory (DFT) have been thoroughly applied for the analysis of ILs–CO_2 systems. MD studies allow a characterization of molecular factors controlling CO_2 solubility in ILs [28,29], as well as relevant physicochemical properties, such as viscosity, in neat ILs [30] or in ILs + CO_2 mixed systems [31], which is highly relevant for process design purposes. Regarding DFT calculations, they provide an accurate quantification of short range IL–CO_2 interactions, calculating binding energies and preferential interaction sites, which can be used for the screening and designing the most suitable ions [32,33]. Therefore, MD + quantum chemistry combined theoretical studies would provide a detailed nanoscopic characterization of IL + CO_2 systems [34,35].

The suitability of ILs for the treatment of flue gases is even more remarkable when considering the high SO_2 solubility in ILs reported in several studies [36,37], which shows that ILs can be designed for the simultaneous absorption of both acid gases [38]. A remarkable factor that

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must be considered when studying the solubility of acid gases in ILs is the presence of water in the flue gases; water molecules have a great affinity for many ILs and thus they are readily absorbed when ILs are placed in contact with flue gases. Therefore, the presence of water may lead to a decrease of CO_2 or SO_2 solubility [39,40], although this disrupting effect is very minor or even favorable for some types of ILs [41,42,43].

As a continuation of our previous works on the suitability of ILs belonging to different families for acid gas capturing purposes [32,34,44,45,46], a study on ILs based on aminoacid ions (AILs) is reported in this work. AILs show several suitable properties for CO_2 capture, such as efficient CO_2 capturing ability through chemisorption [47,48], natural origin of raw materials or their moderate viscosities [49,50], although it has also been reported that AILs are biologically active compounds which may lead to some toxicity problems [51]. The AIL 1-ethyl-3-methylimidazolium glycinate ([EMIM][GLY], Fig. 1) was selected in this work as representative of the AILs family for acid gases capturing purposes considering its moderate viscosity [50], which is crucial for acid gas treatment purposes. The thermal stability of AILs containing alkylimidazolium cations was studied by Ohno and Fukumoto [49] confirming that they start to decompose only above 200 °C, which is suitable for acid gas capturing purposes. Likewise, AILs tend to possess higher vapor pressures than conventional ionic liquids based on anions such as chloride or bis(trifluoromethylsulfonyl)imide. The behaviour of [EMIM][GLY] + CO_2, + SO_2 and + H_2O mixtures as a function of temperature, pressure and mixtures composition was studied using MD. Likewise, the strengths and molecular characteristics of interactions between ions and CO_2, SO_2 and H_2O molecules were studied using DFT calculations. The combined MD + DFT approach leads to insights on the properties and structuring of AILs – acid gas mixtures from the nanoscopic viewpoint, inferring the most remarkable factors controlling acid gas absorption by AILs and the effect of absorbed gases and water on AILs liquid properties.

2. Methods

2.1. Molecular dynamics simulations

Fig. 1 shows the structures and their atom labeling for ions used along this work. The forcefield parameterizations used along this work for $[EMIM]^+$, $[GLY]^-$, CO_2 and SO_2 were reported in previous works [52,53]. Water was described according to the SPC-E model [54]. Regarding atomic charges for ions, it should be remarked that they were calculated for ionic pairs from DFT calculations (ChelpG for B3LYP/6-311++g(d,p) optimized interacting ionic pairs), leading to ±0.91 total charge for $[EMIM]^+/[GLY]^-$ ions [55]. The considered force field parameterization is no reactive, and thus, only physical interactions were considered in this work; nevertheless, the information obtained in this work would allow to infer the mechanisms of ion – CO_2 interactions before chemical reactions and is in agreement with similar approaches developed in the literature [56].

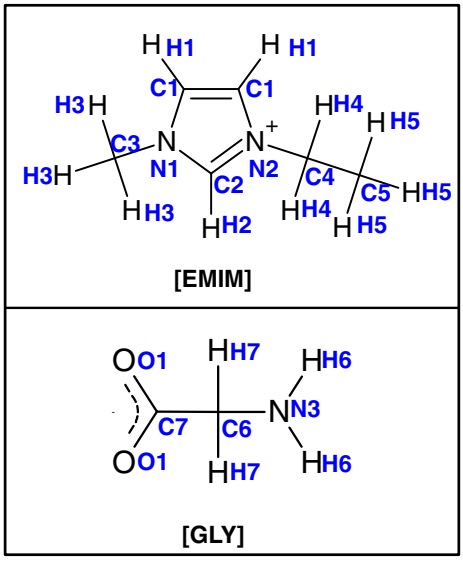

Fig. 1. Atom labeling for ions used along this work.

In order to prepare realistic [EMIM][GLY] + CO_2 or + SO_2 or + H_2O mixtures for MD simulations, the solubility of these compounds in [EMIM][GLY] was predicted using COSMO-RS calculations (COSMOthermX, [57]) considering previously optimized structures for isolated ions at B3LYP/6-311++g** level (calculated with Gaussian 09, Revision D.01) [58], for which COSMO files were calculated at the BVP86/TZVP/DGA1 level and used for gas solubility predictions as a function of pressure and temperature. MD studies were carried out at 303 and 373 K, for simulating both moderate and high temperature conditions, resembling those of near real flue gas conditions observed in fossil-fuelled power plants. Therefore, absorption isotherms for CO_2, SO_2 and H_2O in [EMIM][GLY] were predicted in a reasonable pressure range to cover gas mole fractions in [EMIM][GLY] wide enough to analyse the effect of concentration on the properties of mixtures, Fig. S1 (Supplementary Material). Thus, the simulation systems reported in Table S1 (Supplementary Material) were inferred from COSMOthermX predictions and used for MD simulations. The highest solubility of SO_2, and especially of H_2O, in comparison with CO_2, led to different pressure ranges used for the MD studies.

For the mixtures compositions reported in Table S1 (Supplementary Material), initial simulation boxes were built using the Packmol program [59], from which several heating (up to 500 K) and quenching steps were carried out to assure equilibration and minimize the effects of the sluggish character of ILs and its effect on the dynamics and reliability of MD simulations. Nevertheless, it should be remarked that [EMIM][GLY] is moderately viscous IL (47.75 mPa × s at 303.15 K and 8.38 mPa × s at 353.15 K) [50]. After equilibration runs, assured through constant total potential energy, MD production runs (10 ns) in the NPT ensemble at the corresponding pressures and temperatures (Table S1, Supplementary Material) were carried out. All MD simulations were carried out using MDynaMix v.5.2 [60], with temperature and pressure being controlled with the Nose–Hoover method, with 0.1 ps and 1 ps time constants, respectively. The coulombic interactions were handled with the Ewald summation method (cut-off radius of 15 Å) [61]. The equations of motion were solved with the Tuckerman–Berne double time step algorithm (long and short time steps of 1 and 0.1 fs, respectively) [62]. Lennard-Jones cross terms were calculated according to the Lorentz-Berthelot mixing rules. The cutoff for Lennard-Jones interactions was established in 12 Å.

2.2. Quantum chemistry calculations

Density Functional Theory calculations at the M062X/aug-cc-pVTZ level for IL – CO_2, IL – SO_2, and IL – H_2O clusters were carried out using the Gaussian 09 (Revision D.01) package [58]. Several cluster stoichiometries and interaction sites were considered for analysed IL – acid gas and IL – water short-range interactions and exploring the potential energy surfaces. In order to provide adequate guidance on this, electrostatic potential based on the electron density of each ion were calculated and they are displayed in the Supplementary Material (Fig. S2).

3. Results and discussion

The results reported in Table S1 and Fig. S1 (Supplementary Material) for the absorption isotherms in [EMIM][GLY] shows $CO_2 < SO_2 << H_2O$ solubility. Therefore, [EMIM][GLY] is a highly hygroscopic IL,