I&EC research
Industrial & Engineering Chemistry Research

Article

pubs.acs.org/IECR

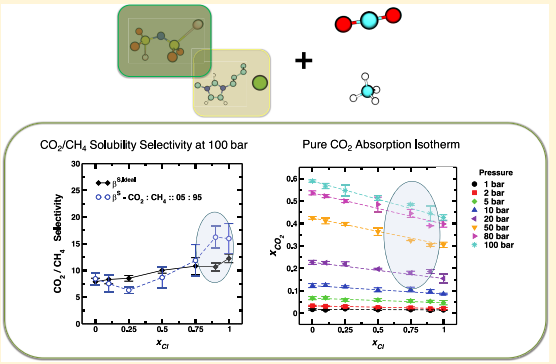
Monte Carlo Simulations of Pure and Mixed Gas Solubilities of CO_2 and CH_4 in Nonideal Ionic Liquid−Ionic Liquid Mixtures

Utkarsh Kapoor and Jindal K. Shah*

School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma 74078, United States

Supporting Information

ABSTRACT: The knowledge of mixed gas solubility in ionic liquids at high pressures, which becomes relevant in applications such as tertiary oil recovery and landfill gas utilization, is critical for the design of gas separation technologies. In this study, we examine ionic liquid mixtures for tuning the solubility of carbon dioxide (CO_2) and methane (CH_4). Using Gibbs ensemble Monte Carlo simulations, absorption isotherms of pure CO_2 and CH_4 are computed in the binary ionic liquid mixtures containing the common cation 1-*n*-butyl-3-methylimidazolium $[C_4mim]^+$ and the anions chloride Cl^- and bis-(trifluoromethanesulfonyl)imide $[NTf_2]^-$ using five molar compositions at 353 K and the pressures ranging from 1 to 100 bar. Additionally, mixture gas solubilities of CO_2 and CH_4 with the starting gas phase mole ratios of 5:95 and 15:85 at a total pressure of 100 bar are determined and compared with the ideal predictions obtained from the solubilities calculated in pure ionic liquids. Results show that the mixture solubilities deviate from the ideal mixing rule at high pressures with improved solubilities in ionic liquid mixtures having up to 10% of $[C_4mim][NTf_2]$ in $[C_4mim]Cl$. Furthermore, for the entire ionic liquid mixture composition range, the CO_2/CH_4 solubility selectivities exhibited a nonlinear behavior. Interestingly, simulated CO_2/CH_4 solubility selectivities at the mole ratios of 05:95 and 15:85 do not differ significantly from the ideal solubility selectivities suggesting independent gas absorption, except for 05:95 at 10% of $[C_4mim][NTf_2]$ in $[C_4mim]Cl$. Thus, there is a potential for improving CO_2/CH_4 selectivity in pure $[C_4mim]Cl$ with the addition of a small amount of $[C_4mim][NTf_2]$ ionic liquid.



INTRODUCTION

Gas separation is one of the most important unit processes in the chemical and petrochemical industries. Contaminants in the form of acid gases such as CO_2 have negative impacts on both the quality and viability of the natural gas fields.[1] Industrially, CO_2 removal is achieved by absorbing it in volatile organic solvents such as aqueous alkanolamine, which suffers from a number of disadvantages related to the loss of solvent due to volatilization, corrosion, and high energy demand to regenerate the solvents, increasing the cost of the operation.[2−4]

Ionic liquids have been suggested as promising gas separating agents and potential replacements for current materials.[5−8] Room temperature ionic liquids are molten salts with melting temperatures below 100 °C. They are comprised entirely of ions—the cation is usually highly asymmetric and of organic nature, whereas the anion can be either organic or inorganic. Charge delocalization and complex structures frustrate ordered packing, lowering the melting point. One of the attractive features of ionic liquids is that the cation−anion combinations can be varied almost at will, providing considerable freedom to adjust material properties of interest for a given application. One of the vibrant research areas in the field of ionic liquids is that of gas separation, especially those involving polar and nonpolar gas mixtures such as CO_2 and CH_4,[7−11] suggesting that these solvents are useful in absorption-based separations.[12−14] A number of research articles focused on experimental[9,10,15−20] and computational[8,21−24] work have been published with emphasis on gas solubility in various ionic liquids. These studies are only representative; for a thorough understanding of the field, we recommend the recently published article by Chen and co-workers[25] for a comprehensive collection of gas solubility research in ionic liquids.

In general, at the same temperature and pressure conditions, solubility of pure gases in ionic liquids follows the following order: SO_2 (H_2S) > CO_2 ≈ N_2O > C_2H_4 > C_2H_6 > CH_4 > Ar > O_2 > N_2 > CO > H_2.[25] The ordering suggests that it might be possible to utilize ionic liquids for separating gas mixtures. It is really interesting to note that experimental studies have supported the idea that when a gas having higher solubility in ionic liquids is mixed with a gas which possesses lower solubility in ionic liquids, the gas with higher solubility enhances the other gas solubility while its own solubility is reduced.[20,26,27] For instance, mixed gas solubility of CO_2/H_2 in

Special Issue: Chuck Eckert Festschrift

Received: June 21, 2019
Revised: August 8, 2019
Accepted: August 12, 2019
Published: August 12, 2019

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

various ionic liquids namely $[C_2mim][NTf_2]$,[28] $[C_4mim][PF_6]$,[15] and $[C_4mim][BF_4]$[29] have shown an increase in solubility selectivity of H_2. On the contrary, computational study involving solubility of CO_2/O_2 and SO_2/N_2 in $[C_6mim][NTf_2]$ by Shi and Maginn[30] does not support the argument and it is speculated that the observed solubility behavior can depend on the operating conditions. Furthermore, some authors have proposed that the presence of small quantities of water in the ionic liquid sample can affect the solubility behavior significantly.[31]

Although the topic of capturing a mixture of CO_2 and CH_4 simultaneously with ionic liquids is of great interest, availability of the relevant data is scarce. Hert et al.[20] concluded that the presence of CO_2 improves the solubility of CH_4 in $[C_6mim][NTf_2]$. Computational investigation, with the need to advance in supported ionic liquid membrane technology, by Budhathoki et al.[22] found only slight nonideal behavior of CO_2/CH_4 solubility selectivity and permselectivity in bulk $[C_4mim][NTf_2]$ ionic liquid at 333 K, and thus, the authors suggested that mixed gas properties can be safely estimated from pure gas data under ideal assumptions. However, the same authors, in another study,[23] showed that the permselectivity of CO_2 over CH_4 can be enhanced by using confinement.

Based on our previous studies[32,33] we believe that another approach to precisely tune the gas solubilities is to consider binary mixtures of ionic liquids that offer control over CO_2 solubility when the ionic liquid mixture composition is varied. To our knowledge, the only available data for binary ionic liquid mixtures is that reported by Finotello et al.[34] The authors conducted a systematic study of the gas solubility and solubility selectivity of CO_2/CH_4 in the binary mixtures of 1-ethyl-3-methylimidazolium $[C_2mim]$ bis-(trifluoromethanesulfonyl)imide $[NTf_2]$ and $[C_2mim]$ tetrafluoroborate $[BF_4]$. They concluded that although the solubility selectivity could be described by regular solution theory the ionic liquid mixtures of $[C_2mim][BF_4]_x[NTf_2]_{1-x}$ with $x = 0.90$ and 0.95 displayed enhanced solubility selectivity for CO_2 over CH_4.

In this article, we aim to provide the gas solubility data for pure CO_2 and CH_4, and their mixtures in the binary ionic liquid mixtures composed of the common cation $[C_4mim]^+$ paired with Cl^- and $[NTf_2]^-$. We employ the Gibbs ensemble Monte Carlo approach to compute the solubility and selectivity. The choice of the ionic liquid mixture is based on the fact that our previous studies have shown that these ionic liquid mixtures are characterized by local organization of anions around the cation that differs markedly from those of pure ionic liquid. The consequence of this behavior is that, although the Henry's constant for CO_2 in these ionic liquid mixtures is predictable from an ideal mixing rule, the dissolution mechanism is different from that in the pure ionic liquids.[32,33] However, it is not clear if the local ionic arrangements in these ionic liquid mixtures will impact CH_4 solubility and CO_2/CH_4 selectivity.

FORCE FIELD

The force field parameters for carbon dioxide (CO_2) and methane (CH_4) molecules were obtained from Shi and Maginn[24] and TraPPE,[35] respectively. Ionic liquid mixtures containing the cation 1-*n*-butyl-3-methylimidazolium $[C_4mim]^+$ and the anions chloride Cl^- and bis-(trifluoromethanesulfonyl)imide $[NTf_2]^-$ were modeled using a united atom classical force field developed by Liu and coworkers.[36,37] In this force field, methyl ($-CH_3$), methylene ($-CH_2-$), and trifluoromethane ($-CF_3$) groups are treated as a single interaction site, while heteroatoms such as oxygen, sulfur, and imidazolium ring hydrogen atoms, due to their importance in hydrogen bonding interactions with the anions, are modeled explicitly (schematic included in Figure S1 of the Supporting Information); and the total charge on the ion moieties is ±0.8. The force field was selected to be consistent with our previous studies regarding the structure and dynamics of the same binary ionic liquid mixtures[32] and the calculation of Henry's constants for CO_2 in these mixtures using free energy calculations performed using the Bennett Acceptance Ratio (BAR) approach.[33] Furthermore, our recent work, where we evaluated the predictive capability of four different classical force field models for phase equilibria properties of different gases in multiple ionic liquids, also suggested that performance of force field models for gas solubility data and temperature dependent trends aligns better with experimental results for force field models with scaled noninteger charges in comparison to the integer charge models.[38]

The intermolecular and intramolecular interactions were represented according to the following functional form:

$$E_{tot} = \sum_{bonds} K_r(r - r_0)^2 + \sum_{angles} K_\theta(\theta - \theta_0)^2 + \sum_{dihedrals} K_\chi[1 + \cos(n\chi - \delta_\chi)] + \sum_{impropers} K_\psi[1 + \cos(n\psi - \delta_\psi)] + \sum_{i=1}^{N-1}\sum_{i<j}^{N}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \left(\frac{q_i q_j}{r_{ij}}\right)\right\} \quad (1)$$

The energetic contributions due to bonds, angles, dihedrals, and improper torsions are described by the terms involving K_r, K_θ, K_χ, and K_ψ, respectively. The Lennard-Jones (LJ) 12−6 potential is used to express van der Waals interactions, for which ϵ_{ij} and σ_{ij} denote the size and energy parameters between atoms *i* and *j*. q_i and q_j are the partial charges placed on the atomic sites *i* and *j*, respectively, and describe the electrostatic interactions in the system via the Coulomb's law. As proposed for the model, the Lorentz−Berthelot combining rule was used to compute interactions between two different atom types. Intramolecular interactions between the terminal atoms in a dihedral, the so-called 1−4 interactions, were scaled by a factor of 0.5 for both the LJ and electrostatic interactions, while the nonbonded interactions between the atoms connected by bonds and angles were excluded.[37]

SIMULATION DETAILS

The absorption isotherms of CO_2 and CH_4 and their mixtures in the binary ionic liquid mixture system of $[C_4mim]Cl_x[NTf_2]_{1-x}$ (x = 0.0, 0.10, 0.25, 0.5, 0.75, 0.90, 1.0) were computed using the isothermal−isobaric Gibbs ensemble Monte Carlo (GEMC-NPT) approach as implemented in the CASSANDRA package.[39] Pure gas solubilities were calculated at pressures ranging from 1 to 100 bar (specifically; 1, 2, 5, 10, 20, 50, 80, and 100 bar). The low pressure range was selected to extract the Henry's constants, for making a comparison with those obtained in our previous study[33] and also for computing the ideal selectivities, while the high

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

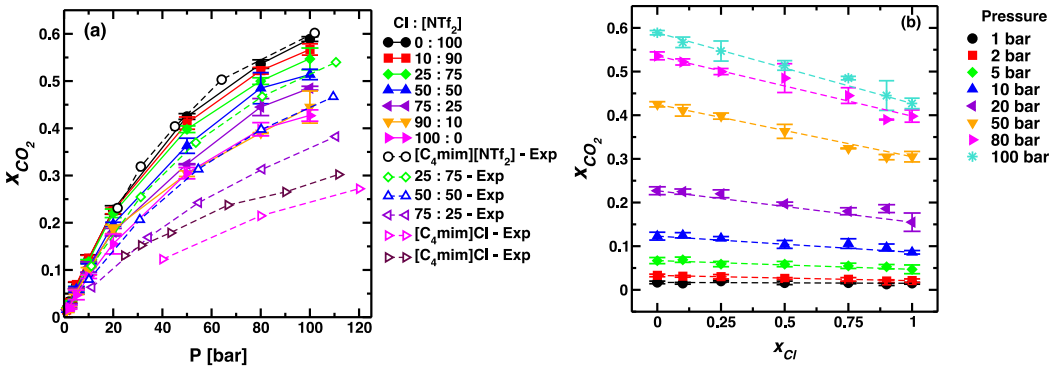


Figure 1. Solubilities of CO_2 in binary ionic liquid mixtures of $[C_4mim]Cl_x[NTf_2]_{1-x}$ at 353 K (a) shown as a function of different pressures of 1, 2, 5, 10, 20, 50, 80, and 100 bar; and (b) as a function of molar composition computed at a given pressure. Standard deviations were calculated from three independent trials for all mixture compositions. Note that the lines joining data points in (a) are only guides to the eye while dotted lines in (b) represent the mixing rule (eq 2). The available literature values for pure $[C_4mim][NTf_2]$ are taken from Carvalho et al.,[41] those for pure $[C_4mimCl]$ are taken from Taguchi et al.[43] and Jang et al.,[42] while those for IL mixtures are taken from Hiraga et al.[44]

pressure regime was probed to assess the nonideality of the gas absorption when mixtures are considered. CO_2 and CH_4 mixed gas solubilities were computed at 100 bar pressure with starting CO_2/CH_4 mole ratios of 05:95 and 15:85 in the gas phase. All the simulations were performed at a temperature of 353 K to ensure a liquid phase of ionic liquids used in this work and maintain consistency with our previous studies.[32,33]

A system size consisting of 256 ion pairs was used for all the ionic liquid compositions, except at $x = 0.10$ and $x = 0.90$, for which 250 ion pairs were simulated. For pure gas solubilities, the ionic liquid phase was generated by randomly placing the ions in a three-dimensional periodic cubic box. The initial density of these systems was set identical to that obtained from our previous molecular dynamics study[32] while the gas phase contained 500 molecules of either CO_2 or CH_4 molecules. Though the system size of the ionic liquid used for mixed gas solubilities remained the same, the number of CO_2/CH_4 molecules were chosen as 100/1900 and 150/850 to reflect 05:95 and 15:85 molar ratios in the gas phase. The initial configuration was prepared using CASSANDRA, employing a configurational bias methodology. The full description of the configurational bias algorithm implemented in CASSANDRA can be found elsewhere.[40] Briefly, conformational degrees of freedom of articulated molecules such as the cation $[C_4mim]^+$ and $[NTf_2]^-$ are sampled by breaking the molecules in fragments. These fragments are generated in such a way that each fragment contains a branch point (atoms connected to more than one atom) and all the atoms bonded to it. Adjacent fragments share a common bond about which the relative orientations of the two fragments are sampled. For $[C_4mim]^+$, the imidazolium ring and the two carbon atoms connected to the ring constitute a fragment. For each of the fragments, 100000 snapshots resulting from the sampling of bond angle distributions are generated prior to an actual simulation. During the course of a simulation, one of the samples is selected at random and the molecule is reassembled by placing the fragments one at a time. For the transfer of gas molecules, the configurational bias insertion method involves generating 12 randomly selected trial positions for the placement of the gas molecule in the receiving box. In the case of CO_2, the molecule is also given a random orientation. Out of the 12 positions, a trial site is selected based on the Boltzmann weight of the van der Waals and electrostatic energy (for CO_2) calculated with the atoms within 6.5 Å of the COM of the molecule.

A MC simulation consisted of moves to equalize temperature in each box, the pressure of the two boxes, and the chemical potential of the gases between the two phases. To achieve thermal equilibration, three types of MC moves were carried out: (i) translation of the center-of-mass (COM) of a molecule; (ii) rotation of the molecule about a randomly chosen axis (x, y, or z) with the COM placed at the origin; and (iii) conformational changes through a fragment-based sampling approach, as described above.[40] The probability of performing each of these moves was set to 30% for all the simulations. Pressure equilibration was ensured through the volume displacement moves, with a frequency of 0.5%. Unlike the constant volume GEMC, the volume displacement was carried out independently for each of the boxes. Due to the negligible vapor pressure of ionic liquids, only gas molecules were exchanged between the two phases to enforce the equality of chemical potential. Such particle transfer was attempted with 9.5% probability. The LJ and electrostatic interactions were truncated at 12 Å, consistent with the ionic liquid force field. Appropriate tail corrections were added to the LJ potential. The long-range component of the electrostatic interactions was calculated using the Ewald method. All the simulations were equilibrated for 25 million Monte Carlo (M MC) steps, followed by subsequent production runs of 50 M MC steps. The final 10 M MC steps were used to compute the averages. The statistical uncertainties were calculated by conducting three independent trials, where different initial configurations were obtained using different random seeds.

RESULTS AND DISCUSSION

Pure Gas Absorption. *CO_2 Solubility.* The CO_2 absorption isotherms at pressures ranging from 1 to 100 bar and the temperature of 353 K as a function of the anion composition are presented in Figure 1(a). Also included are the comparisons of the CO_2 solubilities obtained in this work with the available experimental data. The simulation results for CO_2 mole fractions in the $[C_4mim][NTf_2]$ ionic liquid are predicted in excellent agreement with the experimental measurements,[41] even at high pressures where it is known that the sampling becomes challenging[22] due to high solubility of CO_2. Simulation results also capture the experimentally

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

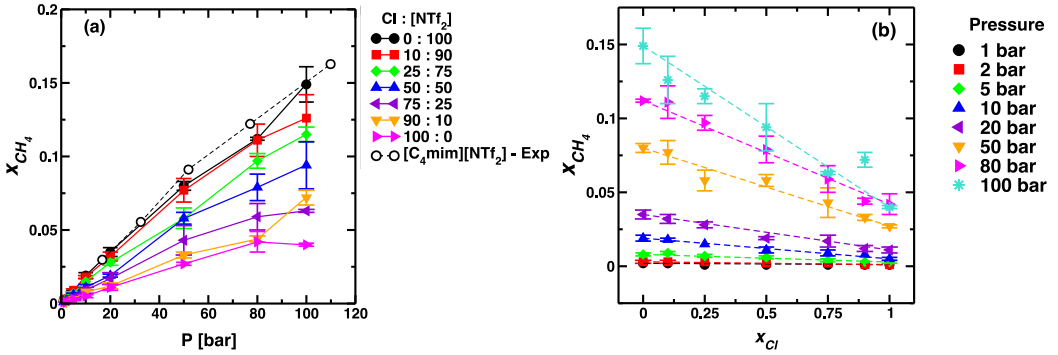


Figure 2. Solubilities of CH_4 in binary ionic liquid mixtures of $[C_4mim]Cl_x[NTf_2]_{1-x}$ at 353 K (a) shown as a function of different pressures of 1, 2, 5, 10, 20, 50, 80, 100 bar; and (b) as a function of molar composition computed at a given pressure. Standard deviations were calculated from three independent trials for all mixture compositions. Note that the lines joining data points in (a) are only guides to the eye while the dotted lines in (b) represent the mixing rule (eq 2). The available literature values for pure $[C_4mim][NTf_2]$ are taken from Raeissi et al.[17] for the same pressure range and temperature conditions, while the data for pure $[C_4mim]Cl$ for the same operating conditions is not available to the best of our knowledge.

observed nonlinear trend for CO_2 solubilities with pressure such that the CO_2 mole fraction is a linear function of pressure at low to moderate pressures and approaches an asymptotic limit as the gas phase pressure is increased. This phenomenon is related to a significant decrease in the void volume in the ionic liquid with pressure.

A comparison of the CO_2 solubility data in $[C_4mim]Cl$ generated with simulations and those obtained experimentally at high pressure suggests that the simulation results are consistently higher than the experimental data.[42−44] We recently reported[33] a similar observation that the Henry's constant for CO_2 in $[C_4mim]Cl$ calculated using the MD-BAR approach was underpredicted relative to the experimental values reported by Hiraga et al.,[44] suggesting that the simulations predict low-pressure CO_2 solubilities in $[C_4mim]Cl$ that are higher than the experimental measurements. It is conceivable that the difference arises due to the difficulties in measuring CO_2 solubilities as $[C_4mim]Cl$ is viscous, and the melting point of $[C_4mim]Cl$ is not too far from 353 K. In fact, the experimental absorption isotherms included in Figure 1(a) clearly demonstrate that a considerable variation in the experimental measurements of CO_2 solubilities exists in this ionic liquid.

The absorption isotherms for CO_2 in the binary ionic liquid mixtures follow similar trends as noted for the pure ionic liquid systems; that is, at low pressures the CO_2 mole fraction varies linearly with the pressure while the CO_2 solubilities increase sublinearly at moderate to high pressures. Furthermore, the solubility of CO_2 at a given binary ionic liquid composition is seen to be intermediate between the corresponding pure ionic liquid CO_2 solubilities. To assess if the solubilities deviate from the ideal mixing behavior, mole fractions of CO_2 are plotted against the ionic liquid compositions in Figure 1(b) for different pressures. The CO_2 mole fraction, on the basis of the ideal mixing rule, can be calculated as

$$x_{ideal} = x_1X_1 + x_2X_2 \quad (2)$$

and is depicted as dotted lines in Figure 1(b). In eq 2, x_1 and x_2 refer to the mole fraction of CO_2 in pure ionic liquid; X_1 and X_2 denote the mole fractions of the ionic liquids on a CO_2-free basis. It is clearly evident that the solubilities are weakly dependent on the molar compositions of the ionic liquid mixtures at pressures below 10 bar. In this regime, the CO_2 mole fractions in binary ionic liquid mixtures can be accurately predicted by the ideal mixing rule (eq 2), which is consistent with our previous study demonstrating that the Henry's constants for CO_2 in this binary ionic liquid system can be approximated from the knowledge of the Henry's constants obtained for the pure ionic liquids.[33] As the pressure is increased, deviations from the ideal mixing behavior begin to appear. For example, CO_2 solubilities are consistently higher than those suggested by the ideal mixing behavior at 20 bar. Solubilities in excess to the ideal mixing values were also observed for higher pressures, especially for the ionic liquid mixture lean in $[NTf_2]^-$ ($x_{Cl} > 0.50$).

In our previous studies,[32,33] we showed that the $[NTf_2]^-$ anion is displaced from its favorable hydrogen bonding interaction, along the C−H vector, involving the most acidic imidazolium ring hydrogen in the ionic liquid mixtures; the positions above and below the plane of the imidazolium ring become more populated as the concentration of Cl^- increases. The rearrangement of $[NTf_2]^-$ is likely to enable an enhanced interaction between the CO_2 molecules and the $[NTf_2]^-$ anion. We believe that the presence of such non-native structures in $[C_4mim]\ Cl_x\ [NTf_2]_{1-x}$ ionic liquid mixtures is one of the major contributing factors for the deviation of CO_2 solubilities from the ideal mixing rule. Furthermore, at higher pressures, a slight reorientation of ion moieties can be expected. Zhao et al.[45] showed a marked conformation transition of the butyl chain of $[C_4mim]^+$ from anti to gauche under very high pressures. Our previous work[33] suggested that CO_2 approaches the cation majorly from the alkyl chain side. Thus, the conformation change of alkyl chain can further aid better CO_2 absorption, plausibly leading to the nonideality.

CH_4 Solubility. The CH_4 solubilities computed at different pressures and 353 K, as a function of Cl^- composition, are reported in Figure 2(a). The computed CH_4 absorption isotherm for $[C_4mim][NTf_2]$ in this work agrees well with that determined by Raeissi et al.[17] over the entire pressure range. To the best of our knowledge, no experimental data exists for CH_4 solubilities in $[C_4mim]Cl$ for comparing the CH_4 solubility predictions. The solubility of CH_4 in the pure ionic liquid systems is lower than the corresponding CO_2 solubilities. On the contrary to the nonlinear behavior of CO_2 absorption isotherms with pressure, the CH_4 solubilities exhibit linearity over a larger pressure range. In general, the solubilities of CH_4 in the mixtures are bracketed by those in the pure ionic liquids.

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

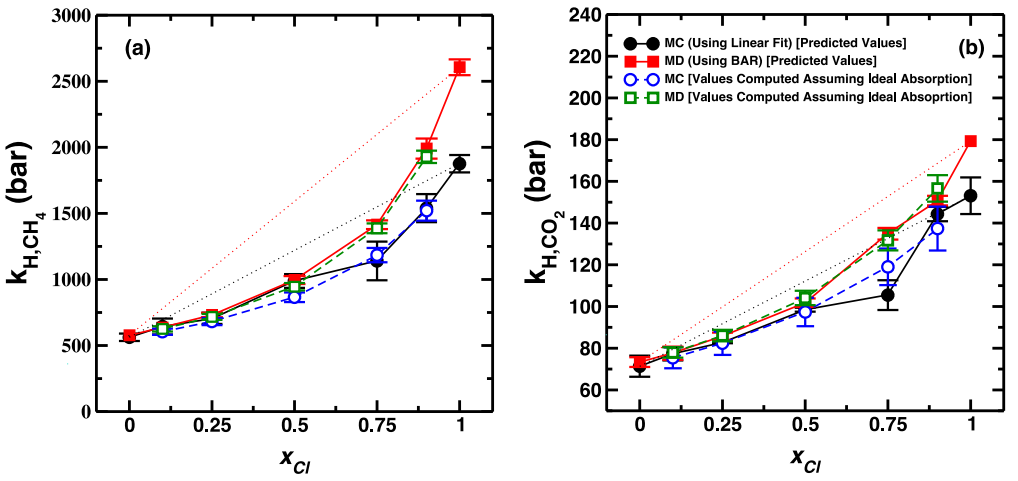


Figure 3. Comparison of Henry's constants of (a) CH_4 and (b) CO_2 calculated using MC simulations and those computed using the BAR technique employed in MD simulations for the mixture system of $[C_4mim]Cl_x[NTf_2]_{1-x}$. Standard deviations were calculated from three independent trials for all mixture compositions. Note that the lines joining data points are only guides to the eye while dotted lines represent the linear mixing rule. The values for CO_2-MD(BAR) are taken from our previous work.[33]

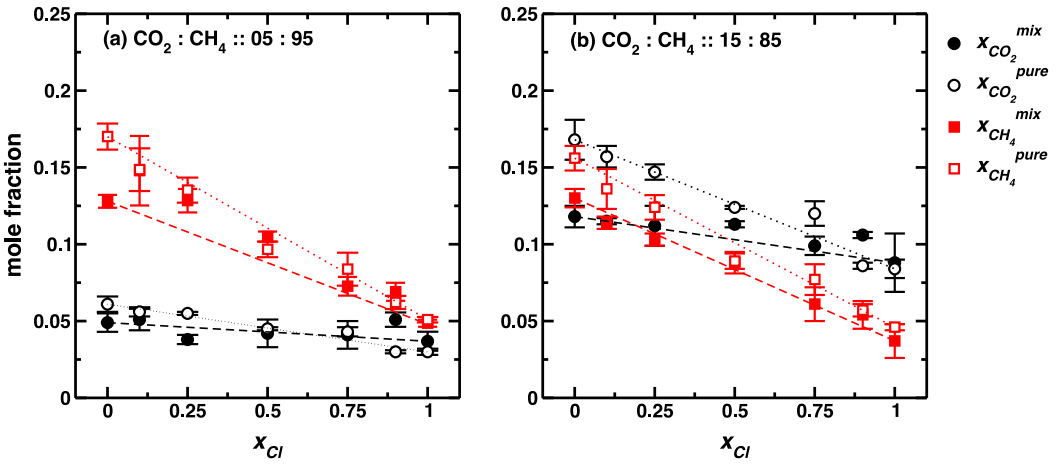


Figure 4. CO_2/CH_4 gas mixture solubility in a binary IL mixture of $[C_4mim]$ Cl_x $[NTf_2]_{1-x}$ as a function of molar composition computed at 353 K and total pressure of 100 bar compared with pure gas solubilities of CO_2 and CH_4 at 100 bar, respectively, (a) for the gas phase mixture ratio of CO_2/CH_4::05/95; and (b) for the gas phase mixture ratio of CO_2/CH_4::15/85. Standard deviations were calculated from three independent trials for all mixture compositions. Note that the dotted lines represent the mixing rule (eq 2).

The absorption data for CH_4 are plotted as a function of the Cl^- composition in Figure 2(b) to uncover deviations from the linear mixing rule (eq 2). The low pressure behavior (P < 20 bar) is accurately described by the linear mixing rule. Small departures from ideality are noted at P = 20 bar. However, the small solubilities and the associated statistical uncerainties make it challenging to identify ionic liquid compositions at which CH_4 solubility deviates significantly from the linear mixing rule. It is only at P = 100 bar and the Cl-$[NTf_2]$ mole ratio of 90:10 that there is a statistically significant enhancement in CH_4 solubility in comparison to the ideal behavior.

Henry's Constants. Henry's constants can be obtained from the absorption isotherms by taking a linear fit as pressure tends to zero. Figure S2 of the Supporting Information illustrates the linear fit process for the calculation of Henry's constants of CH_4 in $[C_4mim][NTf_2]$ ionic liquid. This procedure has been applied on each independent simulation trial to obtain the average Henry's constant values and the statistical uncertainties. However, as the isotherms have a nonlinear curvature, it is important to mention that Henry's constant values are heavily dependent on the range of data used for linear fit due to the curvature at high pressures. In this study, for CO_2, the data range is chosen based on the observed solubility value and, hence, is not the same for all the systems studied in this work. However, the data-range has been included in Table S3 of the Supporting Information, to help the reader reproduce the results if desired. On the contrary, due to very low CH_4 solubility, linear fits from P = 0 up to P = 50 bar are taken to calculate Henry's constants. This range is justified as the computed Henry's constant for CH_4 in $[C_4mim][NTf_2]$ is 560

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

bar (see Table S4, Supporting Information), which is close to the 541 bar determined experimentally from a linear fit of the solubility data between 15.9 to 50 bar.[17] As all the other ionic liquid mixtures exhibit CH_4 solubility lower than that found for $[C_4mim][NTf_2]$, the pressure range is adequate to extract the Henry's constants. We also performed infinitely dilute solvation free energy calculations for CH_4 with molecular dynamics simulations, employing the Bennett acceptance ratio (BAR) approach, represented as the MD-BAR technique in this work. The simulation protocol for these calculations is provided in the Supporting Information. The Henry's constants for CO_2 computed with MD-BAR are directly taken from our previous work.[33]

Figure 3 reports a comparison of the Henry's constants calculated using both GEMC and MD-BAR techniques for the gases along with the values estimated based on the Henry's constants in $[C_4mim][NTf_2]$ and $[C_4mim]Cl$ according to eq 3 for the ionic liquid-ionic liquid mixtures.

$$\frac{1}{H_{mix}} = \frac{X_1}{H_1} + \frac{X_2}{H_2} \tag{3}$$

For both the gases, the Henry's constants are strongly dependent on the molar compositions of the ionic liquid mixtures. Furthermore, it is seen that, within the statistical uncertainty, the linear mixing rule (eq 3) provides a reasonable approximation to the computed value at any given ionic liquid composition, regardless of the simulation technique used.

CO_2/CH_4 Mixture Solubility. Solubilities of CO_2/CH_4 gas mixtures in the binary ionic liquid mixture of $[C_4mim]$ Cl_x $[NTf_2]_{1-x}$ at 353 K and a total pressure of 100 bar were calculated for CO_2:CH_4 starting gas phase mole ratios of 05:95 and 15:85. The objective of this work was to determine if the two gases absorb independently. Additionally, it was also intended to discern the influence of nonideality in the molecular structures of the ionic liquid mixtures on the selectivity of CO_2 over CH_4.

Figure 4 presents the liquid phase compositions of CO_2 and CH_4 for the two starting gas phase mole ratios. Also included in this figure are the ideal liquid phase mole fractions of the two solutes estimated using Henry's law at the equilibrium gas phase partial pressures. The approach is justified because the partial pressures of CO_2 are low enough to be in the Henry's law regime. Similarly, the CH_4 solubility is described by Henry's law up to the pressures considered in this work. For pure $[C_4mim][NTf_2]$ ionic liquid, the amount of CO_2 absorbed for both the CO_2:CH_4 gas phase mole ratios of 05:95 and 15:85 is lower than that observed in the pure CO_2 gas system. Similar observations are made for CH_4 solubility. These trends suggest competitive absorption of the two gases. From a molecular perspective, the observation also indicates that a fraction of favorable interaction sites are common between CO_2 and CH_4. Our results for CH_4 solubility in the 05:95 mixture are in contrast to those reported by Budhathoki et al.[22] for the CO_2:CH_4 gas phase mole ratio of 04:96. The authors observed that while the solubility of CO_2 decreased relative to the pure CO_2 system, the amount of CH_4 was slightly higher than that for the pure CH_4 system, implying enhanced CH_4 absorption in the presence of CO_2. However, the competitive absorption mechanism is consistent between this work and that of Budhathoki et al.[22] when the starting CO_2 mole fraction increases in the gas phase. Unlike pure $[C_4mim][NTf_2]$ ionic liquid, the mixed gas solubilities of both CO_2 and CH_4 are similar to the pure gas solubilities in the pure $[C_4mim]Cl$ system, independent of their mole ratios.

Results from Monte Carlo (MC) simulations of mixture absorption and ideal gas solubility computation for the starting gas-phase mole ratio of 05:95 are presented in Figure 4(a) for the entire ionic liquid composition range. It can be seen that the MC results for CH_4 mole fractions in various ionic liquid mixtures are close to those predicted assuming ideal mixing except for the pure $[C_4mim][NTf_2]$ ionic liquid. On the other hand, the MC estimates of CO_2 solubilities can be approximated by the solubilities computed using ideal mixing behavior except when $x_{Cl} = 0.90$. We believe that this is due to the presence of non-native arrangement of the two anions around the cation as reported in our earlier publications.[32,33] Also, a consistent overlap of mixed gas CH_4 solubilities and the pure CH_4 gas solubilities across the entire composition range indicates that the presence of highly soluble gas CO_2 and the composition of the ionic liquid mixture do not lead to enhancement in the solubility of CH_4.

The equilibrium liquid-phase compositions of CO_2 and CH_4 for the starting gas-phase mole ratio of 15:85 at 100 bar are presented in Figure 4(b). We notice that the mole fraction of CO_2 in various ionic liquid mixtures steadily decreases as the concentration of Cl^- increases. A similar trend is observed for the liquid-phase mole fractions predicted from MC simulations for CH_4. For both the gases, the MC results consistently fall below those suggested by the ideal solubility calculations for $x_{Cl} < 0.50$, implying that the competitive absorption is dominant when Cl^- is the minority component. For equimolar and higher Cl^- concentrations, the MC calculations of mixture solubilities are well reproduced using the ideal solubility mechanism except for $x_{Cl} = 0.90$. Although the mixture solubilities closely follow the ideal gas solubility calculations, we stress that the physical dissolution mechanism of these gases is likely to be distinct from those in the pure ionic liquid. For example, we demonstrated that the Henry's constant of CO_2 in the same binary ionic liquid mixtures could be estimated using the ideal mixing behavior for the pure ionic liquid Henry's constants for CO_2, yet the CO_2 absorption mechanism is different, especially for ionic liquid mixtures rich in Cl^-.[33] Higher solubility of CO_2 at x_{Cl}= 0.90 than the ideal solubility is probably due to "free" $[NTf_2]^-$ in the system at this concentration.[32,33]

Solubility Selectivity. To account for the trends observed in mixed gas absorption isotherms, solubility selectivities were computed. Two different methods were employed. In the first method, solubility selectivities were directly calculated from the liquid and the gas phase compositions of the corresponding components obtained from the MC simulations as shown in eq 4

$$\beta^{S}_{CO_2/CH_4} = \left(\frac{x_{CO_2}/y_{CO_2}}{x_{CH_4}/y_{CH_4}}\right)_{P,T} \tag{4}$$

where x and y are the mole fractions in the liquid and gas phase, respectively, while the ideal solubility selectivities were determined by taking the ratio of Henry's constants, for a specific ionic liquid mixture, as shown in eq 5

$$\beta^{S,ideal}_{CO_2/CH_4} = \left(\frac{k_{H,CH_4}}{k_{H,CO_2}}\right) \tag{5}$$

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

The mixture selectivities computed via eq 4 for the two starting gas-phase mole ratios of CO_2:CH_4 are displayed in Figure 5 along with the ideal selectivity obtained from eq 5.

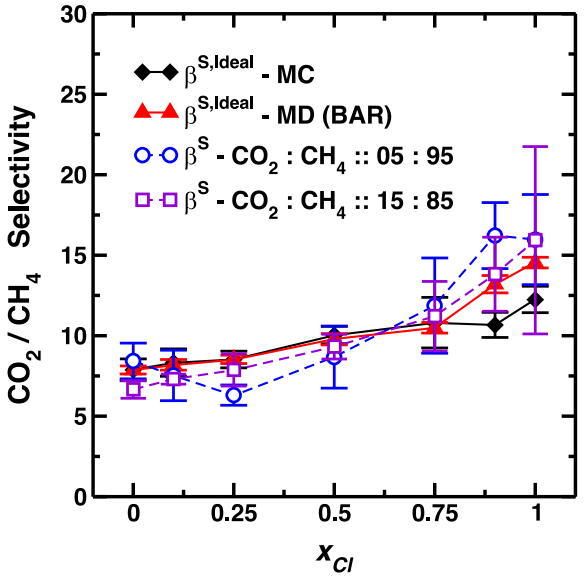


Figure 5. Comparison of CO_2/CH_4 gas mixture solubility selectivities ($\beta^{S}_{CO_2/CH_4}$), with CO_2:CH_4 gas phase mole ratios of 05:95 and 15:85, in binary IL mixture of $[C_4mim]Cl_x[NTf_2]_{1-x}$ as a function of molar composition computed at 353 K and total pressure of 100 bar with ideal solubility selectivities ($\beta^{S,ideal}_{CO_2/CH_4}$) computed using the ratio of Henry's law constants using both GEMC and BAR techniques. Standard deviations were calculated from three independent trials for all mixture compositions. Note that the lines joining data points are only guides to the eye.

The calculated values are also collected in Table 1. It is evident that the ideal solubility selectivities ($\beta^{S,ideal}_{CO_2/CH_4}$) obtained for the binary ionic liquid mixtures of $[C_4mim]Cl_x[NTf_2]_{1-x}$ at 353 K using both GEMC and MD-BAR methods are in very good agreement. The ideal selectivities range from ∼8 to ∼12 in going from the pure $[C_4mim][NTf_2]$ to pure $[C_4mim]Cl$. The increase in the selectivity is due to a less dramatic effect of the ionic liquid composition on the Henry's constant of CO_2 than that for CH_4. This is clearly borne out by nonlinear behavior of ideal selectivity as a function of ionic liquid composition. Further, the ideal solubility selectivity of ∼8 for pure ionic liquid $[C_4mim][NTf_2]$ is comparable to the experimental selectivity value of ∼7 published by Ramdin et al.[46] at the same temperature condition. The ideal selectivity is also comparable to 7.9 ± 0.5 reported by Budhathoki et al. for $[C_4mim][NTf_2]$ at 333 K.[22]

For pure $[C_4mim][NTf_2]$ ionic liquid, the computed mixture solubility selectivity ($\beta^{S}_{CO_2/CH_4}$) for the mole ratio of 05:95 is roughly equal to the ideal solubility selectivity computed from the ratio of the Henry's constants ($\beta^{S,ideal}_{CO_2/CH_4}$), whereas for the gas phase mole ratios of 15:85 the mixture solubility selectivity is lower than the ideal solubility selectivity. On the other hand, the mixture solubility selectivity in the pure $[C_4mim]Cl$ for both the starting gas-phase mole ratios can be estimated with the ideal selectivity assumption. In fact, for the entire composition range of ionic liquid mixtures the ideal assumption for the prediction of solubility selectivity seems to be irrespective of the gas-phase mole ratios except at x_{Cl} = 0.90 for 05:95 mol ratio. It is important to mention that the statistical uncertainties were calculated from three independent trials for all mixture compositions. A comparison of the selectivity obtained for the mixtures at x_{Cl} = 0.75, 0.90, and 1.00 for three vs five independent runs, shown in Table 2, demonstrates that the selectivity is rather invariant with increasing number of independent runs. However, the uncertainty in, some instances, is lower when five independent simulations are used. Nonetheless, results show that a small amount of $[C_4mim][NTf_2]$ in $[C_4mim]Cl$ (up to 10%) has the potential to improve the gas separation performance of the ionic liquid system, a result consistent with the gas mixture solubility isotherms. Similar observations have been reported previously for the enhancement in the solubility selectivity of CO_2 over both CH_4 and N_2 by adding 5−10% of $[C_2mim]$-

Table 1. CO_2/CH_4 Mole Percent Compositions in Liquid and Gas Phase and Solubility Selectivities in Binary Ionic Liquid Mixture of $[C_4mim]$ Cl_x $[NTf_2]_{1-x}$ at 353 K and a Total Pressure of 100 bar[a]

CO_2:CH_4	x_{IL}	x_{CO_2}	y_{CO_2}	x_{CH_4}	y_{CH_4}	β^{S}	$\beta^{S,\ Ideal(MC)}$	$\beta^{S,\ Ideal(MD)}$
05:95	0.00	0.049_6	0.044_1	0.128_4	0.956_1	8.43 ± 1.11	7.88 ± 0.68	7.87 ± 0.25
	0.10	0.051_7	0.043_1	0.148_{23}	0.957_1	7.53 ± 1.57	8.33 ± 0.85	8.19 ± 0.33
	0.25	0.038_3	0.045_0	0.128_8	0.955_0	6.31 ± 0.63	8.52 ± 0.52	8.53 ± 0.26
	0.50	0.042_9	0.045_1	0.105_3	0.955_1	8.67 ± 1.93	10.04 ± 0.54	9.78 ± 0.35
	0.75	0.041_9	0.045_1	0.073_6	0.955_1	11.87 ± 2.96	10.81 ± 1.57	10.49 ± 0.33
	0.90	0.051_5	0.044_1	0.069_6	0.956_1	16.22 ± 2.05	10.67 ± 0.78	13.20 ± 0.54
	1.00	0.037_6	0.045_1	0.049_2	0.955_1	15.97 ± 2.80	12.25 ± 0.82	14.54 ± 0.33
15:85	0.00	0.118_7	0.12_3	0.130_6	0.880_3	6.66 ± 0.55		
	0.10	0.115_2	0.122_1	0.114_4	0.878_1	7.30 ± 0.31		
	0.25	0.112_{13}	0.122_4	0.103_4	0.878_4	7.87 ± 1.00		
	0.50	0.113_2	0.122_1	0.088_7	0.878_1	9.32 ± 0.77		
	0.75	0.099_6	0.126_2	0.061_{11}	0.874_2	11.21 ± 2.16		
	0.90	0.106_2	0.124_1	0.054_9	0.876_1	13.82 ± 2.30		
	1.00	0.088_{19}	0.129_6	0.037_{11}	0.871_6	15.93 ± 5.82		

[a] x and y represent mole percent compositions in the liquid and gas phase, respectively. Standard deviations are computed from three independent simulations. For composition data subscripts represent uncertainties. For example, 0.049_6 = 0.049 ± 0.006.

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

Table 2. Comparison of Selectivity (β^S) Values Obtained for the Mixtures at x_{Cl} = 0.75, 0.90, and 1.00 Using Three vs Five Independent Simulation Runs, at 353 K and a Total Pressure of 100 bar

CO_2:CH_4	x_{IL}	β^S (3 runs)	β^S (5 runs)
05:95	0.75	11.87 ± 2.96	12.94 ± 3.99
	0.90	16.22 ± 2.05	15.71 ± 1.62
	1.00	15.97 ± 2.80	14.89 ± 2.94
15:85	0.75	11.21 ± 2.16	10.91 ± 1.60
	0.90	13.82 ± 2.30	14.18 ± 3.44
	1.00	15.93 ± 5.82	15.87 ± 4.70

$[NTf_2]$ in $[C_2mim][BF_4]$.[34] The authors rationalized the observation by suggesting lowering of the molar volume and a slight disruption of the hydrogen bond network of pure $[C_2mim][BF_4]$ ionic liquid. The observations made in our work in-part support the idea and provide further insight that the disruption of the preferential hydrogen bonding network leads to the possibility of nonideal structures, structures non-native to pure ionic liquid analogues, that not only can help improve the pure gas solubilities but also can enhance the solubility selectivity of the mixture of gases.

CONCLUSION

In this article, single component gas solubilities of CO_2 and CH_4 were computed in the binary ionic liquid mixtures of $[C_4mim]$ Cl_x $[NTf_2]_{1-x}$ (x = 0.0, 0.10, 0.25, 0.50, 0.75, 0.90, 1.0) at 353 K and pressures ranging from 0 to 100 bar computed using Gibbs ensemble Monte Carlo (GEMC) simulations. In addition, mixture gas solubilities were also determined for the starting gas-phase mole ratios of CO_2:CH_4 of 05:95 and 15:85 at 100 bar. Henry's constants of CO_2 and CH_4 were extracted from the single component absorption isotherms and compared against the results obtained with free energy calculations performed with MD-BAR. Selectivities of CO_2 over CH_4 were calculated from the respective Henry's constants and the mixture solubility data.

It was found that the solubility of CO_2 exhibited a linear dependence at low pressures while the rate of increase of CO_2 decreases as the pressure increased for the pure ionic liquids as well as the mixtures. It was observed that the CO_2 solubilities in the mixtures could be predicted from the solubility in the pure ionic liquids up to a pressure of 20 bar using a linear mixing rule. For higher pressures, nonideal behavior is noted for CO_2 solubilities such that the predictions from the linear mixing rule are consistently lower. The single-component solubility of CH_4, on the other hand, shows linear dependence on pressure up to 100 bar for all the ionic liquids examined in this work. Furthermore, the solubility of CH_4 in the ionic liquid mixtures is found to follow the ideal mixing rule, except only at 100 bar pressure and x_{Cl} = 0.90.

CO_2/CH_4 gas mixture solubility data in the binary ionic liquid mixtures of $[C_4mim]$ Cl_x $[NTf_2]_{1-x}$ suggest that, for the CO_2:CH_4 gas phase mole ratio of 05:95, the liquid-phase mole fractions of the two gases can be predicted with reasonable accuracy from the single-component absorption data. As the initial amount of CO_2 in the gas phase is increased, for example, the CO_2/CH_4 gas phase mole ratio of 15:85, competitive gas absorption mechanism is observed up to x_{Cl} = 0.50. Furthermore, despite a nonlinear trend in the solubility selectivity with ionic liquid composition, the CO_2/CH_4 selectivity is remarkably similar to the ideal selectivity for all the systems, except for the 05:95 mol ratio at x_{Cl} = 0.90, where the selectivity observed was markedly higher than the ideal selectivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b03384.

Raw data at 353 K for CO_2 and CH_4 pure gas solubilities at P = 1, 2, 5, 10, 20, 50, 80, 100 bar; mixed gas solubilities with molar ratio of CO_2/CH_4 as 05:95 and 15:85 in the gas phase and a total pressure of 100 bar; Henry's constants calculated using both Monte Carlo and molecular dynamics BAR techniques; and solubility selectivities; along with the chemical structure schematic (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: jindal.shah@okstate.edu.

ORCID

Utkarsh Kapoor: 0000-0002-4977-3405

Jindal K. Shah: 0000-0002-3838-6266

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.K.S. would like to thank the Editors for extending the invitation to contribute to the Charles Eckert Festschrift. We also acknowledge Prof. Neeraj Rai and Prof. Sapna Sarupria for useful discussions. This material is based upon work supported by the National Science Foundation (NSF) Award Number CBET-1706978. The authors gratefully acknowledge partial funding from the Oklahoma State University. Computational resources were provided by the High Performance Computing Center (HPCC) at the Oklahoma State University.

REFERENCES

(1) Hao, J.; Rice, P. A.; Stern, S. A. Upgrading Low-Quality Natural Gas With H_2S- And CO_2-Selective Polymer Membranes Part I. Process Design And Economics of Membrane Stages Without Recycle Streams. *J. Membr. Sci.* **2002**, *209*, 177−206.

(2) Liu, Y.; Zhang, L.; Watanasiri, S. Representing Vapor−Liquid Equilibrium for an Aqueous MEA−CO_2 System Using the Electrolyte Nonrandom-Two-Liquid Model. *Ind. Eng. Chem. Res.* **1999**, *38*, 2080−2090.

(3) Dupart, M. S.; Bacon, T. R.; Edwards, D. J. Understanding Corrosion in Alkanolamine Gas Treating Plants. Hydrocarbon Process. 1993, *92*, 156−160.

(4) Chang, H.; Shih, C. M. Simulation and Optimization for Power Plant Flue Gas CO_2 Absorption-Stripping Systems. *Sep. Sci. Technol.* **2005**, *40*, 877−909.

(5) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. Why is CO_2 So Soluble in Imidazolium-Based Ionic Liquids? *J. Am. Chem. Soc.* **2004**, *126*, 5300−5308.

(6) Lee, S.-H.; Kim, B.-S.; Lee, E.-W.; Park, Y.-I.; Lee, J.-M. The Removal of Acid Gases From Crude Natural Gas By Using Novel Supported Liquid Membranes. *Desalination* **2006**, *200*, 21−22.

(7) Finotello, A.; Bara, J. E.; Camper, D.; Noble, R. D. Room-Temperature Ionic Liquids: Temperature Dependence of Gas Solubility Selectivity. *Ind. Eng. Chem. Res.* **2008**, *47*, 3453−3459.

(8) Ramdin, M.; Balaji, S. P.; Vicent-Luna, J. M.; Gutiérrez-Sevillano, J. J.; Calero, S.; de Loos, T. W.; Vlugt, T. J. H. Solubility of the

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

Precombustion Gases CO_2, CH_4, CO, H_2, N_2, and H_2S in the Ionic Liquid [bmim][Tf_2N] from Monte Carlo Simulations. *J. Phys. Chem. C* **2014**, *118*, 23599−23604.

(9) Anderson, J. L.; Dixon, J. K.; Brennecke, J. F. Solubility of CO_2, CH_4, $C2H_6$, C_2H_4, O_2, and N_2 in 1-Hexyl-3-methylpyridinium Bis(trifluoromethylsulfonyl)imide: Comparison to Other Ionic Liquids. *Acc. Chem. Res.* **2007**, *40*, 1208−1216.

(10) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-n-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315−7320.

(11) Blanchard, L. A.; Brennecke, J. F. Green Processing using Ionic Liquids and CO_2. *Nature* **1999**, *399*, 1−2.

(12) Hojniak, S. D.; Silverwood, I. P.; Khan, A. L.; Vankelecom, I. F. J.; Dehaen, W.; Kazarian, S. G.; Binnemans, K. Highly Selective Separation of Carbon Dioxide from Nitrogen and Methane by Nitrile/Glycol-Difunctionalized Ionic Liquids in Supported Ionic Liquid Membranes (SILMs). *J. Phys. Chem. B* **2014**, *118*, 7440−7449.

(13) Shahkaramipour, N.; Adibi, M.; Seifkordi, A. A.; Fazli, Y. Separation of CO_2/CH_4 Through Alumina-Supported Geminal Ionic Liquid Membranes. *J. Membr. Sci.* **2014**, *455*, 229−235.

(14) Bara, J. E.; Gabriel, C. J.; Hatakeyama, E. S.; Carlisle, T. K.; Lessmann, S.; Noble, R. D.; Gin, D. L. Improving CO_2 Selectivity in Polymerized Room-Temperature Ionic Liquid Gas Separation Membranes Through Incorporation of Polar Substituents. *J. Membr. Sci.* **2008**, *321*, 3−7.

(15) Yokozeki, A.; Shiflett, M. B. Vapor−Liquid Equilibria of Ammonia+Ionic Liquid Mixtures. *Appl. Energy* **2007**, *84*, 1258−1273.

(16) Yokozeki, A.; Shiflett, M. B. Hydrogen Purification Using Room-Temperature Ionic Liquids. *Appl. Energy* **2007**, *84*, 351−361.

(17) Raeissi, S.; Peters, C. J. High Pressure Phase Behaviour of Methane in 1-Butyl-3- Methylimidazolium Bis-(Trifluoromethylsulfonyl)Imide. *Fluid Phase Equilib.* **2010**, *294*, 67−71.

(18) Anderson, J. L.; Dixon, J. K.; Maginn, E. J.; Brennecke, J. F. Measurement of SO_2 Solubility in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 15059−15062.

(19) Shiflett, M. B.; Yokozeki, A. Chemical Absorption of Sulfur Dioxide in Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.* **2010**, *49*, 1370−1377.

(20) Hert, D. G.; Anderson, J. L.; Aki, S. N. V. K.; Brennecke, J. F. Enhancement of Oxygen and Methane Solubility in 1-Hexyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl) Imide Using Carbon Dioxide. *Chem. Commun.* **2005**, *39*, 2603−3.

(21) Shi, W.; Sorescu, D. C.; Luebke, D. R.; Keller, M. J.; Wickramanayake, S. Molecular Simulations and Experimental Studies of Solubility and Diffusivity for Pure and Mixed Gases of H_2, CO_2, and Ar Absorbed in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Bis(Trifluoromethylsulfonyl)amide ([hmim][Tf 2N]). *J. Phys. Chem. B* **2010**, *114*, 6531−6541.

(22) Budhathoki, S.; Shah, J. K.; Maginn, E. J. Molecular Simulation Study of the Solubility, Diffusivity and Permselectivity of Pure and Binary Mixtures of CO_2 and CH_4 in the Ionic Liquid 1-n-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *Ind. Eng. Chem. Res.* **2015**, *54*, 8821−8828.

(23) Budhathoki, S.; Shah, J. K.; Maginn, E. J. Molecular Simulation Study of the Performance of Supported Ionic Liquid Phase Materials for the Separation of Carbon Dioxide from Methane and Hydrogen. *Ind. Eng. Chem. Res.* **2017**, acs.iecr.7b00763-10, *56*, 6775

(24) Shi, W.; Maginn, E. J. Atomistic Simulation of the Absorption of Carbon Dioxide and Water in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]. *J. Phys. Chem. B* **2008**, *112*, 2045−2055.

(25) Lei, Z.; Dai, C.; Chen, B. Gas Solubility in Ionic Liquids. *Chem. Rev.* **2014**, *114*, 1289−1326.

(26) Shiflett, M. B.; Niehaus, A. M. S.; Yokozeki, A. Separation of N_2O and CO_2 Using Room-Temperature Ionic Liquid [bmim][BF_4]. *J. Phys. Chem. B* **2011**, *115*, 3478−3487.

(27) Shiflett, M. B.; Niehaus, A. M. S.; Yokozeki, A. Separation of CO_2 and H_2S Using Room-Temperature Ionic Liquid [bmim][$MeSO_4$]. *J. Chem. Eng. Data* **2010**, *55*, 4785−4793.

(28) Solinas, M.; Pfaltz, A.; Cozzi, P. G.; Leitner, W. Enantioselective Hydrogenation of Imines in Ionic Liquid/Carbon Dioxide Media. *J. Am. Chem. Soc.* **2004**, *126*, 16142−16147.

(29) Toussaint, V. A.; Kühne, E.; Shariati, A.; Peters, C. J. Solubility Measurements of Hydrogen In 1-Butyl-3-Methylimidazolium Tetrafluoroborate and The Effect of Carbon Dioxide and A Selected Catalyst On The Hydrogen Solubility in The Ionic Liquid. *J. Chem. Thermodyn.* **2013**, *59*, 239−242.

(30) Shi, W.; Maginn, E. J. Molecular Simulation and Regular Solution Theory Modeling of Pure and Mixed Gas Absorption in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Bis-(Trifluoromethylsulfonyl)amide ([hmim][Tf_2N]). *J. Phys. Chem. B* **2008**, *112*, 16710−16720.

(31) Baltus, R. E.; Culbertson, B. H.; Dai, S.; Luo, H.; DePaoli, D. W. Low-Pressure Solu- bility of Carbon Dioxide in Room-Temperature Ionic Liquids Measured with a Quartz Crystal Microbalance. *J. Phys. Chem. B* **2004**, *108*, 721−727.

(32) Kapoor, U.; Shah, J. K. Preferential Ionic Interactions and Microscopic Structural Changes Drive Nonideality in Binary Ionic Liquid Mixtures as Revealed from Molecular Simulations. *Ind. Eng. Chem. Res.* **2016**, *55*, 13132−13146.

(33) Kapoor, U.; Shah, J. K. Molecular Origins of the Apparent Ideal CO_2 Solubilities in Binary Ionic Liquid Mixtures. *J. Phys. Chem. B* **2018**, *122*, 9763−9774.

(34) Finotello, A.; Bara, J. E.; Narayan, S.; Camper, D.; Noble, R. D. Ideal Gas Solubilities and Solubility Selectivities in a Binary Mixture of Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2008**, *112*, 2335−2339.

(35) Potoff, J. J.; Siepmann, J. I. Vapor-Liquid Equilibria of Mixtures Containing Alkanes, Carbon Dioxide, and Nitrogen. *AIChE J.* **2004**, *47*, 1676−1682.

(36) Liu, Z.; Chen, T.; Bell, A.; Smit, B. Improved United-Atom Force Field for 1-Alkyl-3- methylimidazolium Chloride. *J. Phys. Chem. B* **2010**, *114*, 4572−4582.

(37) Zhong, X.; Liu, Z.; Cao, D. Improved Classical United-Atom Force Field forImidazolium-Based Ionic Liquids: Tetrafluoroborate, Hexafluorophos- phate,Methylsulfate, Trifluoromethylsulfonate, Acetate, Trifluoroacetate, and Bis(trifluoromethylsulfonyl)amide. *J. Phys. Chem. B* **2011**, *115*, 10027−10040.

(38) Kapoor, U.; Banerjee, A.; Shah, J. K. Evaluation of the Predictive Capability of Ionic Liquid Force Fields for CH_4, CO_2, NH_3, and SO_2 Phase Equilibria. *Fluid Phase Equilib.* **2019**, *492*, 161−173.

(39) Shah, J. K.; Marin-Rimoldi, E.; Mullen, R. G.; Keene, B. P.; Khan, S.; Paluch, A. S.; Rai, N.; Romanielo, L. L.; Rosch, T. W.; Yoo, B.; et al. Cassandra: An Open Source Monte Carlo Package For Molecular Simulation. *J. Comput. Chem.* **2017**, *38*, 1727−1739.

(40) Shah, J. K.; Maginn, E. J. A General And Efficient Monte Carlo Method For Sampling Intramolecular Degrees of Freedom of Branched and Cyclic Molecules. *J. Chem. Phys.* **2011**, *135*, 134.

(41) Carvalho, P. J.; Álvarez, V. H.; Marrucho, I. M.; Aznar, M.; Coutinho, J. A. P. High Pressure Phase Behavior of Carbon Dioxide in 1-Butyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide and 1-Butyl-3-Methylimidazolium Dicyanamide Ionic Liquids. *J. Supercrit. Fluids* **2009**, *50*, 105−111.

(42) Jang, S.; Cho, D.-W.; Im, T.; Kim, H. High-Pressure Phase Behavior of CO_2 + 1-Butyl-3-Methylimidazolium Chloride System. *Fluid Phase Equilib.* **2010**, *299*, 216−221.

(43) Taguchi, R. Measurement and Calculation of High Pressure CO_2 Solubilities in Functional Ionic Liquids. *M.S. Thesis*, Graduate School of Environmental Studies, Tohoku University, 2009.

(44) Hiraga, Y.; Koyama, K.; Sato, Y.; Smith, R. L., Jr. Measurement and Modeling of CO_2 Solubility in [bmim]Cl − [bmim][Tf_2N] Mixed-Ionic Liquids For Design of Versatile Reaction Solvents. *J. Supercrit. Fluids* **2018**, *132*, 42−50.

(45) Zhao, Y.; Liu, X.; Lu, X.; Zhang, S.; Wang, J.; Wang, H.; Gurau, G.; Rogers, R. D.; Su, L.; Li, H. The Behavior of Ionic Liquids under

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

792 High Pressure: A Molecular Dynamics Simulation. *J. Phys. Chem. B*
793 **2012**, *116*, 10876−10884.
794 (46) Ramdin, M.; Amplianitis, A.; de Loos, T. W.; Vlugt, T. J. H.
795 Solubility of CO_2/CH_4 Gas Mixtures in Ionic Liquids. *Fluid Phase*
796 *Equilib.* **2014**, *375*, 134−142.

DOI: 10.1021/acs.iecr.9b03384
Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX