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Solubility of Natural Gas Species in Ionic Liquids and Commercial Solvents: Experiments and Monte Carlo Simulations

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ABSTRACT: A detailed comparison of the solubility of carbon dioxide (CO₂) and methane (CH₄) in ionic liquids (ILs) and in conventional solvents like Selexol, Purisol, propylene carbonate, and sulfolane is presented. The solubilities are compared on mole fraction, molality, and volume basis to demonstrate the effect caused by the high molecular weight of ILs. We found that conventional solvents are superior to existing ILs in terms of mass- or volume-based solubilities. Monte Carlo simulations have been used to quantitatively predict the solubility of CO₂, CH₄, and C₂H₆ in the solvents 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf₂N] and tetraethylene glycol dimethyl ether.

1. INTRODUCTION

Natural gas usually contains substantial amounts of carbon dioxide (CO₂) and hydrogen sulfide (H₂S), which should be removed to meet customer specifications and to prevent dry ice formation during liquefaction and transportation of the gas.¹ CO₂ is typically removed in an absorber-stripper configuration utilizing a physical solvent, a chemical solvent, or a mixture of both (hybrid) solvent types.² Selection of a proper solvent for CO₂ and H₂S removal is not a trivial task, since this selection depends on many factors (e.g., temperature, pressure, composition and type of impurities, and ultimately the product specifications). For example, monoethanolamine (MEA) should not be used in the presence of carbonyl sulfide (COS) in the feed, since COS irreversibly reacts with MEA resulting in degradation of the solvent.³ Heuristics for selecting solvents are given by Tennyson and Schaaf³ and Kohl and Nielsen.¹ Chemical solvents like amines have been used for many decades in the natural gas industry and have been shown to be effective in removing acid gases.⁴ However, the amine-process suffers a number of serious drawbacks including the high energy requirement for solvent regeneration, the corrosivity, and volatility of the used amines.^{5–7} Therefore, many alternative solvents/processes have been proposed to eliminate the problems associated with the amine-process.⁸ Recently, ionic liquids (ILs) have emerged as promising solvents for CO₂ capture from natural gas.⁹ The popularity of ILs can be attributed to their remarkable properties like negligible vapor pressures, high chemical and thermal stability,

and high CO₂ solubility.¹⁰ However, the key parameter for judging the separation performance of a solvent is its selectivity for a target component rather than the solubility.¹¹ An optimal process design requires not only solubility data of CO₂, but data of other major natural gas components (e.g., methane, ethane, etc.) is also essential. A huge amount of CO₂ solubility data in ILs have been reported in the literature, but CO₂/CH₄ selectivity data in ILs are relatively scarce.¹⁰ Camper et al.¹² and Scovazzo¹³ developed a model to predict CO₂/CH₄ selectivities in ILs. Sumon and Henni¹⁴ and Mortazavi-Manesh et al.¹⁵ used the COSMO-RS method to screen many different types of ILs for acid gas removal. Carvalho and Coutinho¹⁶ measured CO₂ and CH₄ solubilities in different types of ILs and related CO₂/CH₄ selectivities to the polarity of the ILs. Recently, we have measured CO₂ and CH₄ solubilities and selectivities in 10 different ILs composed of several classes of cations and anions using the Cailletet equipment (synthetic method).^{17–19} Reviews for CO₂ capture from natural gas are provided by Karadas et al.,² Ramdin et al.,¹¹ and Kumar et al.⁹

The aim of the present study is to assess the potential of ILs for CO₂ removal from natural gas. The performance of ILs in terms of CO₂ and CH₄ solubilities/selectivities are compared with respect to the commercial solvents Selexol, Purisol, propylene carbonate, and sulfolane. This comparison is not

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Figure 1. Solubility of CO₂ at 313.15 K on mole fraction basis in ILs and commercial solvents (gray symbols). ILs: trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate [thtdp][phos], open triangles; trihexyltetradecylphosphonium dicyanamide [thtdp][dca], open diamonds; 1-ethyl-3-methylimidazolium diethylphosphate [emim][dep], open squares; 1-allyl-3-methylimidazolium dicyanamide [amim][dca], open circles; 1-butyl-3-methylpyrrolidinium dicyanamide [bmpyr][dca], stars; 1,2,3-tris(diethylamino)cyclopropenylum dicyanamide [cprop][dca], pluses; methyltrioctylammonium bis(trifluoromethylsulfonyl)imide [toa][Tf₂N], black diamonds; 1-butyl-3-methyl-piperidinium bis(trifluoromethylsulfonyl)imide [bmpip][Tf₂N], black squares; 1,2,3-tris(diethylamino)cyclopropenylum bis(trifluoromethylsulfonyl)imide [cprop][Tf₂N], crosses; triethylsulfonium bis(trifluoromethylsulfonyl)imide [tes][Tf₂N], black triangles; trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide [thtdp][Tf₂N], open rectangles; and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [emim][FAP], black rectangles. Commercial solvents: Selexol (Genosorb 1753), gray circles; propylene carbonate, gray triangles; Purisol, gray diamonds; and sulfolane, gray rectangles. Lines are polynomial fits to guide the eye. Data for the ILs can be found in Ramdin et al.¹⁷ and the references cited therein. Data of commercial solvents can be found in refs 43 and 45–48.

straightforward since solubility data of CO₂ and CH₄ in the conventional solvents is despite their wide application interest scarcely reported in the literature. The solubilities of the gases are compared on mole fraction, molality, and volume basis to demonstrate the effect caused by the high molecular weight of the ILs. It is unfair to compare gas solubilities on a mole fraction basis in high molecular weight ILs with that of low molecular weight conventional solvents, because gas solubilities tend to increase with increasing molecular weight. It is more practical to compare gas solubilities in ILs on a mass or volume basis. The focus here is mainly on CO₂/CH₄ solubilities and selectivities, but data for other natural gas constituents are relevant as well. However, it is practically impossible to experimentally measure the solubility of all the natural gas components and their mixtures, because the number of components in natural gas can be quite large. Therefore, predictive methods are indispensable for a proper process design. Recently, we have used Monte Carlo simulations to predict the solubility of natural gas components in ILs.^{20,21} Here, Monte Carlo simulations have been used to quantitatively predict the solubilities of CO₂, CH₄, and C₂H₆ in the IL 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]). Furthermore, Monte Carlo simulations have been used to compute the solubilities of CO₂ and CH₄ in tetraethylene glycol dimethyl ether (TEGDME), which is the principal ingredient of Selexol.

2. SIMULATION DETAILS

The Continuous Fractional Component Monte Carlo (CFCMC) method in the osmotic ensemble has been used

to calculate the solubility isotherms of CO₂, CH₄, and C₂H₆ in the solvents [hmim][Tf₂N], and TEGDME.^{22–24} In this approach, the system is expanded with a “fractional” molecule that has a coupling parameter λ . The λ -parameter, which is bounded to the interval [0,1], is used to gradually increase or decrease the strength of the intermolecular interactions between the fractional molecule and the surrounding molecules in the system. The intermolecular (i.e., Lennard-Jones (LJ) and Coulombic) interactions are scaled to exhibit a correct behavior at the boundaries of $\lambda = 0$ (i.e., no interactions with the surroundings) and $\lambda = 1$ (i.e., full interactions with the surroundings). CFCMC uses, in addition to the conventional MC moves like translations and rotations, a λ trial-move, which changes the λ parameter with a value of $\Delta\lambda$; that is, $\lambda(n) = \lambda(o) + \Delta\lambda$. A successful λ change from the old state to the new state has now three possibilities: (1) λ remains between 0 and 1 leaving the number of particles, positions, and intramolecular energies of the system unchanged, (2) λ exceeds 1 ($\lambda = 1 + \epsilon$, $1 > \epsilon > 0$), implying that the current fractional molecule is made fully present and a new fractional particle with $\lambda = \epsilon$ is randomly inserted in the system, (3) and finally if λ drops below 0 ($\lambda = -\epsilon$, $1 > \epsilon > 0$), the current fractional molecule is deleted and a randomly selected molecule in the system is assigned as a new fractional molecule with a $\lambda = 1 - \epsilon$. The CFCMC approach is more efficient than conventional MC methods, since it allows higher insertion acceptance ratios, especially for dense systems.²⁵ More details on the CFCMC scheme can be found in the original publication by Shi and Maginn and the recent work of Torres-Knoop et al.^{22–25}

A classical force field including bonds, bends, torsions, Lennard-Jones (LJ) and electrostatic interactions were used to represent the atomic interactions of the solvents. The force field parameters for [hmim][Tf₂N] have been taken from Shi and Maginn.²³ The TraPPE united-atom (TraPPE-UA) models were used for CO₂, CH₄, and TEGDME.^{26,27} The Lorentz–Berthelot mixing rules were used for the LJ interactions between dissimilar sites. The Ewald method with a relative precision of 10^{−5} was used to account for the electrostatic interactions. LJ interactions were truncated and shifted at 12 Å, and tail corrections were not used. All simulations were executed in the osmotic ensemble, where the fugacity of the gas (*f*), the number of nonvolatile IL molecules (*N*), the hydrostatic pressure (*P*), and the temperature (*T*) were fixed. The volume of the system and the number of solute molecules in the liquid-phase were allowed to change to satisfy the imposed pressure and fugacity. Fugacities were calculated with the Peng–Robinson (PR) equation of state (EoS).²⁸ The λ moves were biased using the Wang–Landau²⁹ sampling scheme, which enforces the system to visit all the λ states and to achieve a uniform probability distribution of λ . The Configurational-bias Monte Carlo (CBMC) partial- and reinsertion moves were used to sample the internal degrees of freedom of the solvent molecules.^{30–32}

All CFCMC simulations were performed at a temperature of 313.15 K. An ensemble of 50 IL molecules, and 75 TEGDME molecules was simulated using the RASPA code.³³ The CFCMC simulation was started with an equilibration run of 50000 MC cycles, during this stage the weights of the various MC moves were adjusted to obtain approximately 50% acceptance rates. The number of MC steps in a cycle equals the total number of molecules in the simulation box. The production runs consisted of at least 0.5 million cycles, where the exact number was dictated by the convergence characteristics of the simulated system.

3. RESULTS AND DISCUSSION

3.1. CO₂ Solubility. The solubilities of CO₂ and CH₄ are compared on mole fraction, molality, and volume (molarity) basis to demonstrate the effect caused by the high molecular weight of ILs. Figure 1 shows the mole fraction-based solubility of CO₂ in several ILs in comparison with the widely used solvents Selexol, Purisol, propylene carbonate, and sulfolane. Clearly, some of the ILs (e.g., the alkyl-phosphonium-based ILs) have a higher CO₂ capacity on a mole fraction basis than the conventional solvents like Selexol, Purisol propylene carbonate, and sulfolane. However, a careful analysis of the data shows that the solubility increases with increasing molecular weight of the ILs.¹⁷ Therefore, the solubility should be compared on a molality or volume basis, which are more practical units from a process point of view. Figure 2 shows the same comparison, but now the solubility is expressed in moles per mass solvent or molality. Remarkably, the IL data tend to collapse on a universal solubility curve proposed by Carvalho and Coutinho.³⁴ The solubility data of CO₂ in conventional solvents do not obey the solubility curve. Clearly, the CO₂ solubility is strongly affected by the high molecular weight of the ILs. Although CO₂ is known to interact with the anions of the ILs, the dissolution of CO₂ in ILs is dominated by free volume effects. This effectively means that the CO₂ molecules are hosted in the cavities of the IL structure.^{35,36} It is, therefore, also interesting to compare the solubility on a volume basis. A comparison for the CO₂ solubility in ILs and in conventional

Figure 2. Solubility of CO₂ at 313.15 K on molality basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 1. Solid line is calculated using the correlation of Carvalho and Coutinho³⁴ at 313.15 K and dashed lines are polynomial fits to guide the eye. Data for the ILs can be found in Ramdin et al.¹⁷ and the references cited therein. Data of commercial solvents can be found in refs 43 and 45–48.

Figure 3. Solubility of CO₂ at 313.15 K on volume basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 1. Lines are polynomial fits to guide the eye. Data for the ILs can be found in Ramdin et al.¹⁷ and the references cited therein. Data of commercial solvents can be found in refs 43 and 45–48.

solvents on a molarity (i.e., kilomoles of solute per volume of solvent) basis is provided in Figure 3. The difference in solubility between the different ILs on a volume basis is also minimized. Figures 2 and 3 clearly show that conventional solvents are superior to ILs in terms of mass- or volume-based solubilities of CO₂.

3.2. CH₄ Solubility. The mole fraction-based solubility of CH₄ is shown in Figure 4 for several ILs and commercial solvents. The solubility trend for CH₄ is similar to that of CO₂: the solubility of CH₄ increases also with an increasing IL molecular weight. However, the molecular weight effects for CH₄ are different than those of CO₂. The molecular weight of the ILs is mainly increased by adding an alkyl-chain or extending the length of the alkyl-chains. The solubility of CH₄, which is nonpolar, increases as a consequence of this addition of nonpolar alkyl-chains. Moreover, the CO₂ solubility is mainly driven by free volume effects, while the solubility of CH₄ is dominated by nonpolar–nonpolar dispersive interactions. This conclusion is in agreement with the results shown in Figure 5: the molality-based solubility data of CH₄ do not collapse on a universal curve as in the case of CO₂. The volume-based

Figure 4. Solubility of CH_4 at 313.15 K on a mole fraction basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 1. Lines are polynomial fits to guide the eye. Data for the ILs can be found in Ramdin et al.¹⁷ and the references cited therein. Data of commercial solvents can be found in refs 44 and 48–51.

Figure 5. Solubility of CH_4 at 313.15 K on a molality basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 1. Lines are polynomial fits to guide the eye. Data for the ILs can be found in Ramdin et al.¹⁷ and the references cited therein. Data of commercial solvents can be found in refs 44 and 48–51.

solubility trend for CH_4 is not much different from the observed solubility trend on a molality basis, see Figure 6. Furthermore, solubility of CH_4 in conventional solvents are lower than those ILs previously characterized as promising for CO_2 capture. One exception is the 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [emim][FAP] IL, which has a comparable CO_2 and CH_4 solubility as Selexol on a mole fraction or volume scale. A good solvent for natural gas sweetening should not only have a high CO_2 solubility, but at the same time a low CH_4 solubility to avoid valuable product losses. The CO_2/CH_4 selectivity in ILs will be considered next.

3.3. Selectivity. As mentioned earlier, not the solubility, but rather the selectivity is the key parameter for judging the separation performance of an absorption process. Recently, we showed that the ideal CO_2/CH_4 selectivity in ILs is comparable to that of commercial solvents like Selexol, Purisol, propylene carbonate, and sulfolane.¹⁷ Furthermore, we showed that the ideal CO_2/CH_4 selectivity in ILs is approximately the same as the real selectivity.¹⁸ In other words, the solubility of CO_2 is not significantly influenced by the presence of CH_4 . The ideal selectivity was calculated as the ratio of the pure gas Henry

Figure 6. Solubility of CH_4 at 313.15 K on a volume basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 1. Lines are polynomial fits to guide the eye. Data for the ILs can be found in Ramdin et al.¹⁷ and the references cited therein. Data of commercial solvents can be found in refs 44 and 48–51.

constant of CH_4 over that of CO_2 . The selectivity was also shown to decrease dramatically with increasing temperature and IL molecular weight.¹⁷ A plot of the ideal CO_2/CH_4 selectivity as a function of the molar volume of all the ILs listed in Figure 1 is presented in Figure 7. The ideal CO_2/CH_4

Figure 7. Logarithm of the ideal CO_2/CH_4 selectivity as a function of the logarithm of the IL molar volume at a temperature of 313.15 K. Solid line is the universal model of Scovazzo,¹³ and dashed line is the model of Camper et al.¹² All selectivity data have been taken from Ramdin et al.¹⁷ and the references cited therein.

selectivity decreases with increasing molar volume and the trend is nicely captured by the correlations of Camper et al.¹² and Scovazzo.¹³ As a consequence, one should use an IL with a low molar volume in order to have a high CO_2/CH_4 selectivity. Unfortunately, the ILs with a low molar volume have a low CO_2 capacity.

In summary, the solubility of gases in ILs should be evaluated on a mass or volume basis in order to eliminate the effect caused by the high molecular weight of these solvents. Conventional solvents are superior to ILs when CO_2 and CH_4 solubilities are compared on a mass or volume basis. Although the CO_2/CH_4 selectivity in ILs is similar to that of commercial solvents, the high price and viscosity of ILs may limit their application in the natural gas sweetening process.

3.4. Simulations. In Tables 1 to 3 and Figure 8, the CFCMC simulation results for the solubility of CO_2 , CH_4 , and

Table 1. Solubility of CO₂ (1) in the IL [hmim][Tf₂N] (2) from Monte Carlo Simulations

T/K	p/MPa	x_1^a
333.15	0.400	0.067
333.15	0.800	0.132
333.15	1.715	0.264
333.15	4.800	0.474
333.15	8.360	0.590

^aUncertainty in x_1 is 0.004.**Table 2. Solubility of CH₄ (1) in the IL [hmim][Tf₂N] (2) from Monte Carlo Simulations**

T/K	p/MPa	x_1^a
333.15	1.440	0.032
333.15	2.671	0.056
333.15	3.946	0.079
333.15	5.518	0.110
333.15	7.217	0.129
333.15	9.207	0.156

^aUncertainty in x_1 is 0.002.**Table 3. Solubility of C₂H₆ (1) in the IL [hmim][Tf₂N] (2) from Monte Carlo Simulations**

T/K	p/MPa	x_1^a
333.15	0.586	0.048
333.15	1.220	0.104
333.15	2.832	0.219
333.15	5.806	0.342
333.15	10.965	0.390

^aUncertainty in x_1 is 0.003.

Figure 8. Solubility of CO₂ (black symbols), CH₄ (open symbols), and C₂H₆ (gray symbols) in [hmim][Tf₂N] at a temperature of 333.15 K. Experimental data of CO₂ from Aki et al.³⁷ (black diamonds) and Kumelan et al.³⁸ (black circles). Monte Carlo data of CO₂ from Shi and Maginn²³ (black squares) and this work (black triangles). Experimental data of CH₄ from Anderson et al.⁴⁰ (open diamonds) and Kumelan et al.⁴¹ (open circles). Monte Carlo data of CH₄ from this work (open triangles). Experimental data of C₂H₆ from Florusse et al.⁴² (gray triangles) and Monte Carlo data of C₂H₆ from this work (gray diamonds). The lines are calculated with the Peng–Robinson equation of state.²⁸

C₂H₆ in [hmim][Tf₂N] are reported. The MC results for CO₂ are compared with the experimental data of Aki et al.³⁷ and Kumelan et al.,³⁸ and simulation data of Shi and Maginn.²³ The

simulation data of this work is in good agreement with the experimental data and the simulation data of Shi and Maginn. The agreement is excellent in the low pressure regime, but the deviation slightly increases in the higher pressure range. The minor differences between the simulation results of this work and the results of Shi and Maginn may be due to differences in the simulation setup. Shi and Maginn used the Fennell and Gezelter³⁹ shifted force (FGSF) method for the electrostatic interactions. Here, the standard MC method with the more widely accepted Ewald summation method for electrostatic interactions is used. The simulation results for CH₄ are in good agreement with the experimental data of Anderson et al.⁴⁰ and Kumelan et al.⁴¹ at the low-pressure range, and a small deviation is observed in the higher pressure range. The simulation results of C₂H₆ are in excellent agreement with the experimental data of Florusse et al.⁴² even at high pressures.

In Table 4, the solubility of CO₂ and CH₄ in TEGDME computed from the MC simulations is reported. In Figure 9,

Table 4. Solubility of CO₂ and CH₄ in TEGDME from Monte Carlo Simulations

T/K	p/MPa	$x_{\text{CO}_2}^a$	$x_{\text{CH}_4}^b$
333.15	0.25	0.054	
333.15	0.50	0.114	0.013
333.15	1.00	0.187	0.025
333.15	2.50	0.292	0.060
333.15	5.00	0.483	0.108
333.15	7.50	0.571	0.128

^aUncertainty in x_{CO_2} is 0.004. ^bUncertainty in x_{CH_4} is 0.002.

Figure 9. Solubility of CO₂ (circles) and CH₄ (triangles) in TEGDME at a temperature of 333.15 K. Experimental data of CO₂ (filled circles) and CH₄ (filled triangles) in Genosorb 1753 from Rayer et al.^{43,44} Monte Carlo data of CO₂ (open circles) and CH₄ (open triangles) in TEGDME from this work. The lines are calculated with the Peng–Robinson equation of state.²⁸

the computed solubilities of CO₂ and CH₄ in TEGDME are compared with experimental data of CO₂ and CH₄ solubilities in Genosorb 1753, which is a similar solvent as Selexol.⁴³ The MC results for CO₂ are in good agreement with the experimental data of Rayer et al.⁴³ at low pressures, but significant deviations are observed at higher pressures. The MC results for CH₄ solubility in TEGDME are in good agreement

with the experimental data of Rayer et al.⁴⁴ Overall, the solubility of CO₂, CH₄, and C₂H₆ in [hmim][Tf₂N], and TEGDME computed from the MC simulations are in quantitative agreement with experimental data at low to moderate pressures. A possible explanation for the deviation at high pressures is that the system becomes more dense and inserting molecules becomes more difficult. Considering the free-volume mechanism, the solutes are hosted in the easily accessible cavities of the ILs at low pressures, but this hosting becomes more difficult at high pressures. However, as none of the force field parameters were fitted to experimental data in this study, the agreement can be considered as very good.

4. CONCLUSIONS

A detailed comparison for the solubility/selectivity of carbon dioxide (CO₂) and methane (CH₄) in ionic liquids (ILs) and commercial solvents Selexol, Purisol, propylene carbonate, and sulfolane is presented. The solubilities are compared on mole fraction, molality, and volume basis to demonstrate the effect caused by the high molecular weight of ILs. Conventional solvents are superior to ILs when CO₂ and CH₄ solubilities are compared on a mass or volume basis. Although the CO₂/CH₄ selectivity in ILs are similar to that of commercial solvents, the high price and viscosity of ILs may limit their application in the natural gas sweetening process. In addition, Monte Carlo simulations have been used to quantitatively predict the solubility of CO₂, CH₄, and C₂H₆ in the solvents 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf₂N], and tetraethylene glycol dimethyl ether (TEGDME). The agreement between the simulation results and the experiments is very good.

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