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DOI
10.1016/j.jocs.2015.09.002

Publication date
2016

Document Version
Accepted author manuscript

Published in
Journal of Computational Science

Available online at www.sciencedirect.com

ScienceDirect

Journal of Computational Science 00 (2016) 1–20

J. Comput. Sci.

Solubilities of CO_2, CH_4, C_2H_6, and SO_2 in Ionic Liquids and Selexol from Monte Carlo Simulations

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Abstract

Monte Carlo simulations are used to calculate the solubility of natural gas components in ionic liquids (ILs) and Selexol, which is a mixture of poly(ethylene glycol) dimethyl ethers. The solubility of the pure gases carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), and sulfur dioxide (SO_2) in the ILs 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([$C_n$mim][Tf_2N], n = 4, 6), 1-ethyl-3-methylimidazolium diethylphosphate ([emim][dep]), and Selexol ($CH_3O[CH_2CH_2O]_nCH_3$, n = 4, 6) have been computed at 313.15 K and several pressures. The gas solubility trend observed in the experiments and simulations is: $SO_2 > CO_2 > C_2H_6 > CH_4$. Overall, the Monte Carlo simulation results are in quantitative agreement with existing experimental data. Molecular simulation is an excellent tool to predict gas solubilities in solvents and may be used as a screening tool to navigate through the large number of theoretically possible ILs.

Keywords: Gas Absorption, Molecular Simulation, Carbon Dioxide Capture, Natural Gas Sweetening

1. Introduction

The global natural gas demand is expected to increase with 1.9 % per year the coming two decades [1]. This requires and stimulates exploitation of unconventional and sub-economical low quality reservoirs, which are usually contaminated with large amounts of acid gases [2]. Therefore, it is desirable to develop technologies that increase the energy efficiency and reduce the environmental footprint of natural gas processing. Physical, chemical, or hybrid solvents are extensively used in the natural gas industry to remove acid gases like carbon dioxide (CO_2) and hydrogen sulfide (H_2S) [3, 4]. Examples of commercial processes utilizing physical solvents include Purisol, Rectisol and Selexol, whereas the Fluor Econamine FG and the Shell Sulfinol process uses a chemical and hybrid solvent, respectively [5]. The selection of a proper solvent depends on many factors (e.g., temperature, pressure, type and concentration of impurities, and customer specifications). For example, the use of physical solvents is preferred at high acid-gas partial pressures, while chemical/hybrid solvents are more suitable at low acid-gas partial pressures or when a deep removal of the acid gases up to few ppm levels is required [6]. Guidelines for choosing a solvent for acid-gas removal are

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provided by Kohl and Nielsen, and Tennyson and Schaaf [7, 8]. Although the existing solvents/processes are successfully applied, they all suffer from one of the following: a high energy requirement, a high solvent volatility, or a low capacity/selectivity [9]. Recently, ionic liquids (ILs) have gained interest, mainly due to their very low vapor pressure and high acid-gas capacity, as new potential solvents for natural gas sweetening [10–12]. However, the performance of ILs with respect to existing solvents (e.g., Selexol) is still under debate [13]. A key parameter to gauge the performance of a separation process is the selectivity of a solvent for a target component relative to the other components in the mixture. For example, the natural gas sweetening process requires a solvent that is highly selective towards the acid gases to prevent product losses and additional separation steps [14]. The calculation of the selectivity requires solubility data of all the major components participating in the mixture. Natural gas typically contains a large number of components (e.g., CO_2, CH_4, H_2S, N_2 and higher alkanes) [12]. It is, therefore, practically impossible to experimentally determine the solubility of all these natural gas constituents for a large number of solvents. Furthermore, the number of theoretically possible ILs is extremely large and predictive tools like equation of states and molecular simulations are essential for selecting a proper IL.

In the present work, Monte Carlo simulations are used to compute the solubility of natural gas components in ILs and Selexol, which is a mixture of of poly(ethylene glycol) dimethyl ethers (PEGDME, $CH_3O[CH_2CH_2O]_nCH_3$, where n is typically between 3 and 11) [15]. Simulations of gas solubilities in Selexol are performed, because despite its wide application, gas solubility data in Selexol is scarcely reported in the literature and often limited to Henry constants. The recently developed Continuous Fractional Component Monte Carlo (CFCMC) method [16, 17] is used in the osmotic ensemble to calculate the solubility of the pure gases carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), and sulfur dioxide (SO_2) in the ILs 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_n\text{mim}][Tf_2N]$, $n = 4, 6$), 1-ethyl-3-methylimidazolium diethylphosphate ([emim][dep]) and Selexol ($CH_3O[CH_2CH_2O]_nCH_3$, $n = 4, 6$) at 313.15 K and several pressures. The solubility of the gases obtained from the MC simulations are compared with available experimental data.
The paper is organized as follows. In the next section, the simulation details (i.e., simulation settings and force fields) are outlined and in a subsequent section the results on gas solubilities and selectivities in ILs and Selexol are presented and discussed. In the final section, conclusions are presented regarding the performance of ILs with respect to Selexol.

2. Simulation Details

Phase equilibria calculations using Monte Carlo simulations rely on insertions and deletions of molecules to and from a system [18]. Standard Monte Carlo methods are inefficient due to the low insertion and deletion probabilities especially for systems with a high density [19]. Therefore, advanced biasing/sampling methods have been devised (e.g., Configurational-bias Monte Carlo (CBMC) and gradual insertions) that can (partially) overcome this problem [20–22]. An example of such a method is the Continuous Fractional Component Monte Carlo (CFCMC) scheme developed by Shi and Maginn [16, 17]. In this approach, the ensemble is expanded with a "fractional" molecule, which is coupled to the system through a parameter λ. The λ-parameter is confined on the interval [0, 1] and is used to gradually increase or decrease the strength of the interactions between the fractional molecule and the surrounding "whole" molecules in the system. In this way, the system can rearrange as the fractional molecule is slowly inflated, which decreases the probability for atomic overlaps. The Lennard-Jones (LJ) and Coulombic interactions between the fractional molecule and the surrounding molecules are scaled such that the conventional intermolecular potentials are recovered for $\lambda = 1$ and no interactions in the limit as $\lambda \to 0$. The CFCMC scheme performs λ-moves in addition to the standard MC moves like translation, rotation and volume change [23, 24]. A λ change will result in the following three possibilities. (1) λ stays between 0 and 1, $0 < \lambda < 1$, the number of absorbed molecules, atomic positions and intramolecular energies remain unaltered. (2) λ exceeds 1, $\lambda = 1 + \epsilon$ with $0 < \epsilon < 1$, which results in a transformation of the current fractional molecule into a "whole" molecule and a new fractional molecule with $\lambda = \epsilon$ is randomly added to the system. (3) λ drops below 0, $\lambda = -\epsilon$, which implies that the current fractional molecule is deleted and a new fractional molecule with $\lambda = 1 - \epsilon$ is randomly added to the system. The Wang-Landau (WL) sampling scheme is used to bias the λ moves, which is necessary to prevent the system from being stuck in a certain λ state [25]. This biasing factor is calibrated during the equilibration run to achieve a flat histogram for λ. The λ-range is divided into 21 bins and measured histograms are considered sufficiently flat when all bins are visited at least 30% of the most visited bin. Figure 1, shows an example of a λ histogram and the associated biasing factors for the system CO_2-$[C_6\text{mim}][Tf_2N]$ at

313.15 K. The CFCMC scheme is more efficient than conventional MC and CBMC methods in particular for systems with a high density [26]. Details of the CFCMC method can be found in the original papers by Shi and Maginn [16, 17, 27–29], the excellent review by Dubbeldam et al. [20] and the recent publication by Torres-Knoop et al. [26]. A classical force field including bond-stretching, bond-bending, torsions, Lennard-Jones (LJ) and electrostatic interactions was used for the solvent molecules. The force field parameters of the ILs were taken from Maginn et al. [17, 30, 31]. The TraPPE united-atom (TraPPE-UA) models were used for CO_2, CH_4, C_2H_6, SO_2 and Selexol [32–35]. The solute molecules were considered rigid in the simulations. The Lorentz-Berthelot combining rules were used for the LJ interactions between dissimilar atoms [36]. Long-range electrostatic interactions were taken into account by the Ewald method using a relative precision of 10^{-5} [22]. The LJ interactions were truncated and shifted at 12 Å and no tail corrections were used. The internal degrees of freedom of the solvent molecules were sampled using the CBMC scheme [22, 37–39]. The MC simulations were executed in the osmotic ensemble, which means that the temperature (T), the hydrostatic pressure (P), the fugacity of the solute (f), and the number of solvent molecules (N) were all fixed. In this ensemble, the volume of the system and the number of solute molecules will change as a response to the imposed hydrostatic pressure and gas fugacity. Note that the fugacity of the gas is related to the pressure of the gas, which exactly equals the hydrostatic pressure of the liquid. The Peng-Robinson (PR) equation of state (EoS) was used to compute the fugacity of the gases as a function of the pressure [40].
The CFCMC simulations were performed at 313.15 K and pressures up to 12 MPa using the molecular simulation software RASPA [41]. The following number of solvent molecules, 50, 50, 70, 75, and 70, were used in the simulations for [C_4mim][Tf_2N], [C_6mim][Tf_2N], [emim][dep], $CH_3O[CH_2CH_2O]_4CH_3$ and $CH_3O[CH_2CH_2O]_6CH_3$, respectively. The rationale behind choosing these specific numbers of molecules is to keep the simulation box always larger than twice the cutoff distance, to dissolve at least one (integer) solute molecule, and to avoid excessive computations that are required for larger systems. To save computational time, the MC simulations were preceded by a molecular dynamics (MD) simulation, where the liquid structure was equilibrated for 10 ns in the isobaric-isothermal (NPT) ensemble. The equilibrated ensemble of the MD run was then used to initiate the MC simulations. The CFCMC simulations in the osmotic ensemble were started with an equilibration run of 10^5 MC cycles followed by a production run of 0.5 to 2 million cycles. The actual number of simulation cycles were governed by the convergence characteristics of the systems. The IL systems typically required 0.5 to 1 million cycles, while the Selexol systems were run for 1 to 2 million cycles. Note that in RASPA the number of MC steps in a cycle is defined as the total current number of molecules in the system with a minimum of 20. For example, the system CO_2-[C_4mim][Tf_2N] was run for 0.5 million MC cycles, which corresponds to a computational time of 3 weeks on a Xeon-E52620 machine. It is clear that using more solvent molecules in the simulations would lead to very long simulation times, since the computational cost scales as N^2, where N is the number of particles. Once we verified that the system has attained its equilibrium state, the solubility data is obtained from block averages and the uncertainty is calculated from the standard deviation. Typically, four to five times longer simulations were required to reduce the error bar in the solute mole fraction from 0.005 to 0.002, which is lower than the typical uncertainties in the experimental data.

3. Results and Discussion

Monte Carlo simulations in the osmotic ensemble were used to compute the solubility of the pure gases CO_2, CH_4, C_2H_6, and SO_2 in the ILs ([$C_n$mim][Tf_2N], n = 4, 6), [emim][dep], and poly(ethylene glycol) dimethyl ethers (PEGDME, $CH_3O[CH_2CH_2O]_nCH_3$, n = 4, 6), which are the principle ingredients of Selexol. The Selexol solvent is a mixture of PEGDME with n ranging from 3 to 11 [15]. Unfortunately, the exact composition of Selexol is rarely reported in the experimental literature, which makes a direct comparison with the simulations cumbersome. The solubility of the gases in the solvents has been computed at 313.15 K and pressures corresponding to the conditions of the natural gas sweetening process. A snapshot of the MC simulations for the system CO_2-[C_6mim][Tf_2N] is shown in Figure 2. In Figure 3, the solubility of CO_2 obtained from the simulations is compared with experimental absorption data. For the system CO_2-$CH_3O[CH_2CH_2O]_6CH_3$ only MC data is shown in Figure 3, since experimental data of this system is lacking in the literature. Clearly, the CO_2 solubility in the ILs is lower than the PEGDME solvents. Furthermore, the CO_2 solubility data obtained from the MC simulations are in quantitative agreement with the experimental results. In Figure 4, the solubility of CH_4 in all the investigated solvents is compared with experiments. Solvents that exhibit a high CO_2 solubility also have a high CH_4 solubility. The MC data are in excellent agreement with the experimental data at low pressures, but the deviation increases at higher pressures. High pressure VLE data for the

system CH_4-PEGDME is not available in the literature. However, the Henry constant of CH_4 (i.e., the limiting slope of the fugacity vs. the mole fraction (x_{CH_4}) curve as $x_{CH_4} \to 0$) in $CH_3O[CH_2CH_2O]_4CH_3$ at 313.15 K obtained from the simulations is 37.9 MPa, which is in close agreement with the experimental value of 38.2 MPa [42]. Figure 4 also shows that $CH_3O[CH_2CH_2O]_6CH_3$ has a high affinity for CH_4, which will cause product losses in the natural gas sweetening process. In Figure 5, the solubility of C_2H_6 obtained from the MC simulations is compared with the experimental data. No experimental data have been reported for the PEGDME systems, but the simulation results show that the PEGDME solvents posses a high C_2H_6 solubility. The solubility of hydrocarbons is increased as the nonpolar domains of the solvents are increased, which is due to nonpolar-nonpolar interactions [6]. The high hydrocarbon solubility is a major drawback of the Selexol solvents, which will require an additional separation step downstream of the natural gas sweetening process. The solubility of SO_2 is only computed for the solvents $[C_6mim][Tf_2N]$ and $CH_3O[CH_2CH_2O]_4CH_3$, see Figure 6. The results show that SO_2 has an extremely high solubility in both the solvents, which means that SO_2 can selectively be removed in the presence of CO_2. A first estimate of the ideal SO_2/CO_2 selectivity can be obtained from the ratio of the Henry constant of CO_2 over that of SO_2. In Table 1, the Henry constants of the gases in the investigated solvents, computed from the Monte Carlo data, are reported. Note that a lower Henry constant implies a higher solubility. The experimental (computed) Henry constants of CO_2 and SO_2 in $[C_6mim][Tf_2N]$ at 313.15 K are respectively 4.3 (3.44) MPa and 0.23 (0.28) MPa, which yields an experimental (computed) ideal SO_2/CO_2 selectivity of 19 (12) [43, 44]. The experimental (computed) Henry constants of CO_2 and SO_2 in $CH_3O[CH_2CH_2O]_4CH_3$ at 313.15 K are respectively 4.3 (2.87) MPa and 0.037 (0.04) MPa, which yields an experimental (computed) ideal SO_2/CO_2 selectivity of 116 (71) [45, 46]. Clearly, $CH_3O[CH_2CH_2O]_4CH_3$ is more selective towards SO_2 than $[C_6mim][Tf_2N]$. Furthermore, the MC data is in quantitative agreement with the experiments at low SO_2 loadings, but at high loading the deviation is significant. In Figure 7, the solubility of the gases in $[C_6mim][Tf_2N]$ obtained from the MC simulations are compared. The following solubility trend, $SO_2 > CO_2 > C_2H_6 > CH_4$, is observed for all the investigated solvents. These results show that molecular simulation is an excellent tool to compute gas solubilities in complex solvents in the absence of experimental data. Molecular simulation can also provide some useful information on the molecular level. In Figures 8 and 9, the radial distribution functions (RDFs) of CO_2, and the cation and anion of the IL $[C_4mim][Tf_2N]$ are shown. These RDFs provide a qualitative picture of the dissolution of CO_2 into the IL. For example, Figure 9 shows that CO_2 is predominantly residing close to the O and F atom of $[Tf_2N]$. This also suggests that the interaction between CO_2 is stronger with the anion than the cation of the IL.

In summary, the solubility of the gases in the investigated solvents follow the trend: $SO_2 > CO_2 > C_2H_6 > CH_4$. The solubility of CH_4 and C_2H_6 in the Selexol solvents are much higher than the ILs, which is a major drawback in their application for natural gas sweetening. SO_2 can be removed selectively in the presence of CO_2 using both solvents, but the PEGDME solvents are more selective towards SO_2 than the investigated ILs. Overall, the price/performance ratio of the investigated ILs is still not sufficient to compete with the Selexol process.

4. Conclusions

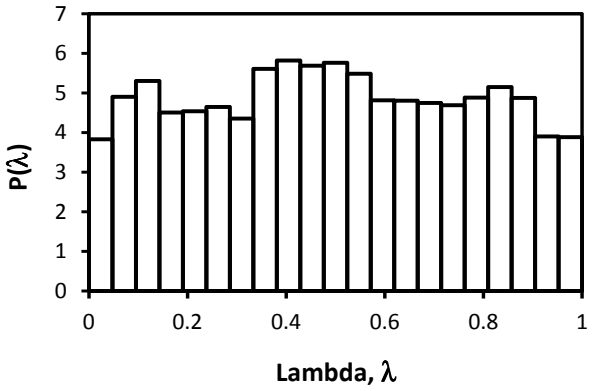
The Continuous Fractional Component Monte Carlo method has been used to compute the solubility of the gases CO_2, CH_4, C_2H_6, and SO_2 in the ILs ($[C_nmim][Tf_2N]$, $n = 4, 6$), [emim][dep], and poly(ethylene glycol) dimethyl ethers (PEGDME, $CH_3O[CH_2CH_2O]_nCH_3$, $n = 4, 6$). The following gas solubility trend is observed in the experiments and simulations for all the solvents: $SO_2 > CO_2 > C_2H_6 > CH_4$. The solubility of SO_2 is substantially higher than that of CO_2, which indicates that SO_2 can be removed selectively in the presence of CO_2. However, the PEGDME solvents are roughly a factor 5 more selective towards SO_2 than the ILs. Furthermore, the solubility of CH_4 and C_2H_6 is higher in PEGDME than in the ILs, which is a well-known drawback of these Selexol solvents. The price/performance ratio is in favor of the Selexol solvents considering the high cost and viscosity of the investigated ILs. The solubility of the gases obtained from the MC simulations are in quantitative agreement with available experimental data. The results show that molecular simulation is a promising tool to predict gas solubilities in solvents and that it may be used as a screening tool to select ILs for specific applications.

Acknowledgments

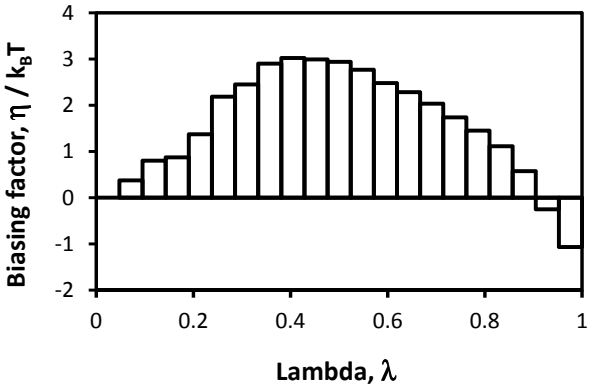
Financial support by the ADEM, A green Deal in Energy Materials, program of the Dutch Ministry of Economic Affairs, Agriculture and Innovation and the Stichting Nationale Computerfaciliteiten (National Computing Facilities Foundation, NCF) for the use of supercomputing facilities. It is also performed as part of the CATO-2 program, the Dutch National R&D program on CO_2 capture, transport and storage funded by the Dutch Ministry of Economic Affairs (Sayee Prasaad Balaji), and by the Netherlands Research Council for Chemical Sciences (NWO/CW) through a VIDI grant (David Dubbeldam).

Table 1. Henry constants of CO_2, CH_4, C_2H_6, and SO_2 at 313.15 K in the investigated solvents computed from the Monte Carlo simulations.

System	Henry constant / MPa			
	CO_2	CH_4	C_2H_6	SO_2
$[C_6mim][Tf_2N]$	3.44	32.29	8.14	0.28
$[C_4mim][Tf_2N]$	5.36	50.74	8.91	-
[emim][dep]	7.72	81.67	-	-
$CH_3O[CH_2CH_2O]_4CH_3$	2.87	37.90	6.48	0.04
$CH_3O[CH_2CH_2O]_6CH_3$	0.87	8.17	2.95	-



(a)



(b)

Figure 1. (a) Probability distribution of λ for the system CO_2-[C_6mim][Tf_2N] at 313.15 K. (b) The biasing factor η for a given value of λ.

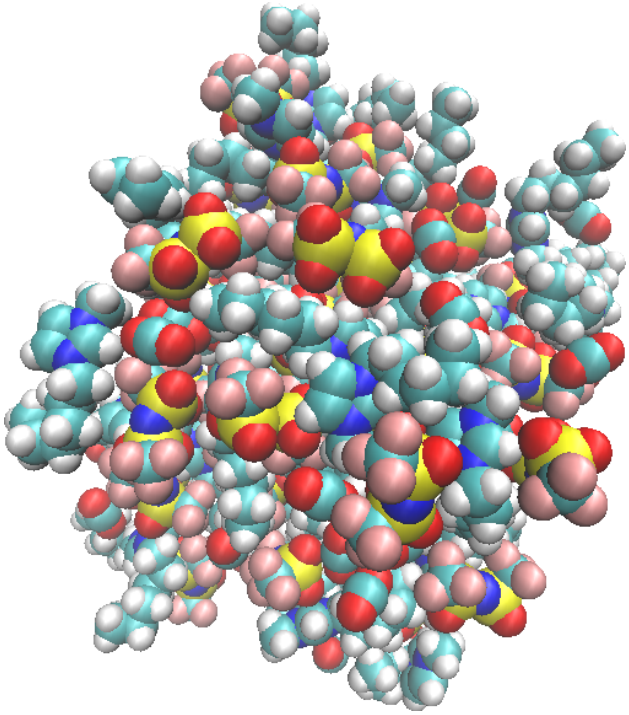


Figure 2. Typical snapshot of the system CO_2 + [C_6mim][Tf_2N] at 313.15 K.

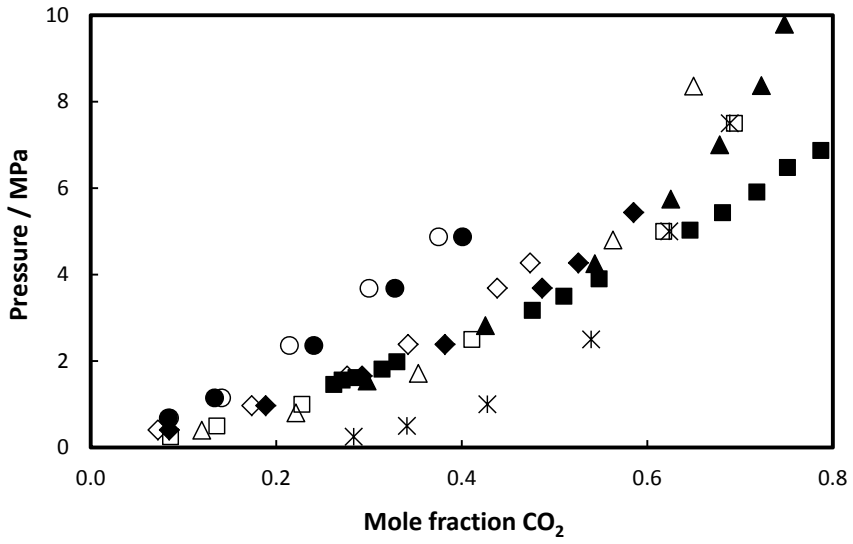


Figure 3. Solubility of CO_2 at 313.15 K in ILs and Selexol from experiments (closed symbols) and Monte Carlo simulations (open symbols). [C_6mim][Tf_2N], triangles; [C_4mim][Tf_2N], diamonds; [emim][dep], circles; $CH_3O[CH_2CH_2O]_4CH_3$, squares; and only MC data for $CH_3O[CH_2CH_2O]_6CH_3$, stars. Experimental data taken from Refs. [6, 47–49].

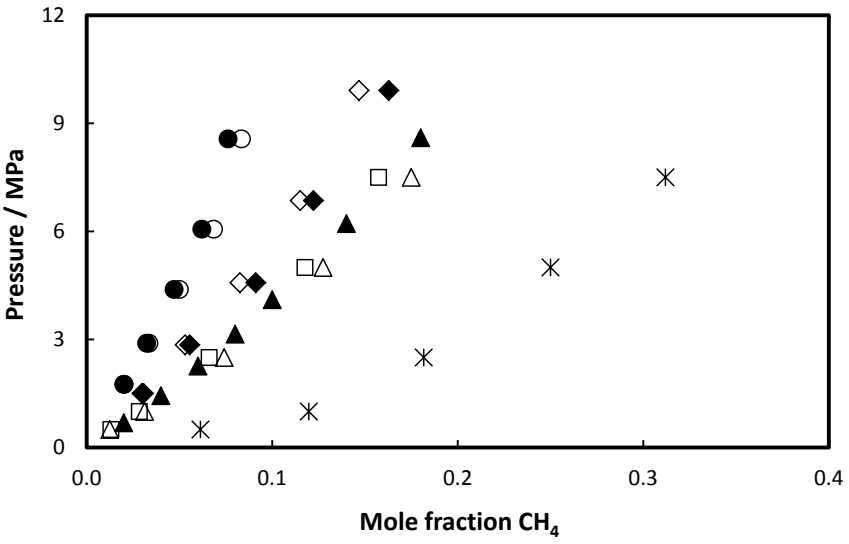


Figure 4. Solubility of CH_4 at 313.15 K in ILs and Selexol from experiments (closed symbols) and Monte Carlo simulations (open symbols). [C_6mim][Tf_2N], triangles; [C_4mim][Tf_2N], diamonds; [emim][dep], circles; $CH_3O[CH_2CH_2O]_4CH_3$, squares; and only MC data for $CH_3O[CH_2CH_2O]_6CH_3$, stars. Experimental data taken from Refs. [6, 50, 51].

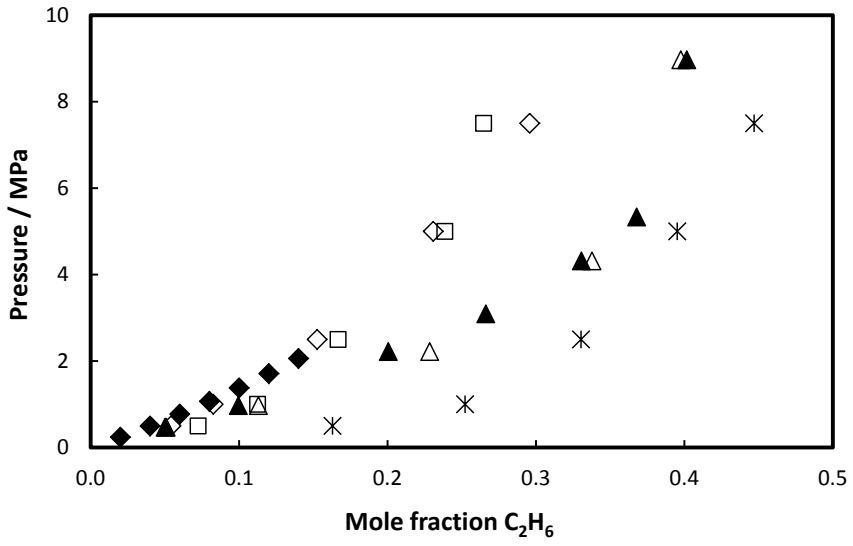


Figure 5. Solubility of C_2H_6 at 313.15 K in ILs and Selexol from experiments (closed symbols) and Monte Carlo simulations (open symbols). $[C_6mim][Tf_2N]$, triangles; $[C_4mim][Tf_2N]$, diamonds; $CH_3O[CH_2CH_2O]_4CH_3$, squares; and only MC data for $CH_3O[CH_2CH_2O]_6CH_3$, stars. Experimental data taken from Refs. [52, 53].

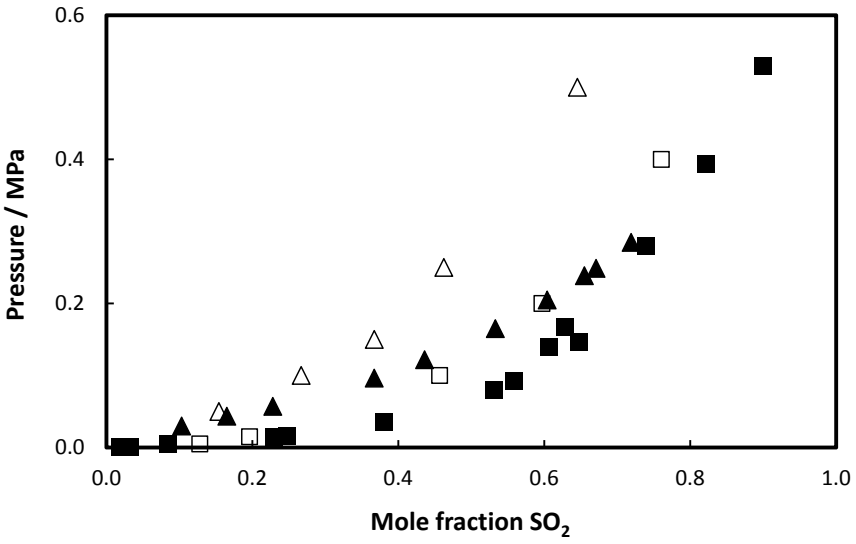


Figure 6. Solubility of SO_2 at 313.15 K in ILs and Selexol from experiments (closed symbols) and Monte Carlo simulations (open symbols). $[C_6mim][Tf_2N]$, triangles and $CH_3O[CH_2CH_2O]_4CH_3$, squares. Experimental data taken from Refs. [44, 46].

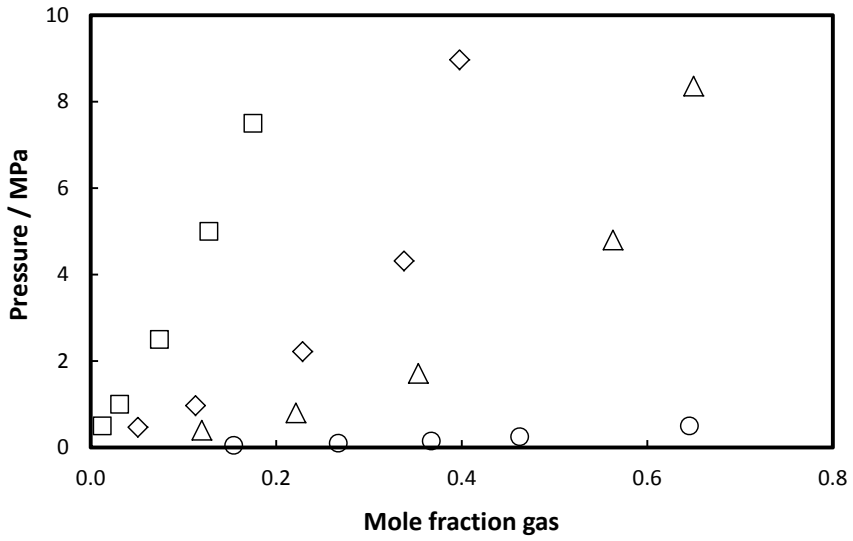


Figure 7. Solubility of the gases in $[C_6mim][Tf_2N]$ at 313.15 K obtained from MC simulations. SO_2, circles; CO_2, triangles; C_2H_6, diamonds; and CH_4, squares.

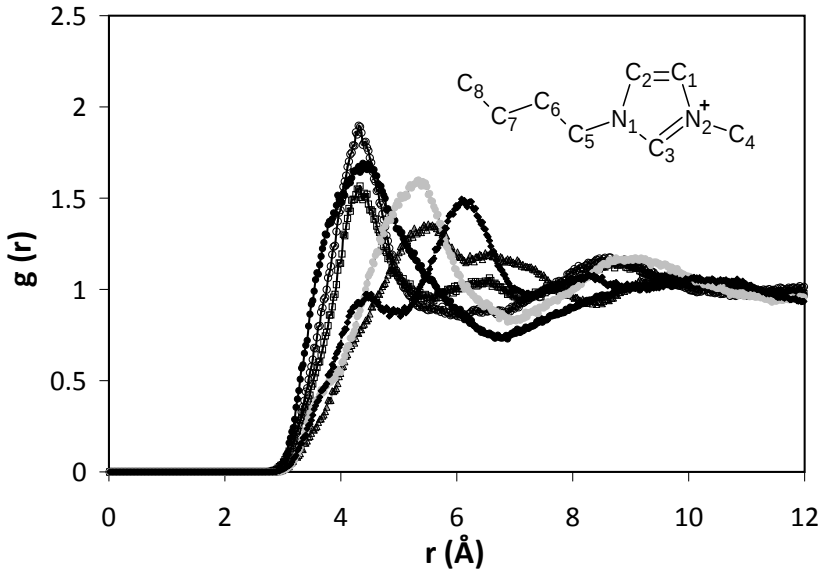


Figure 8. Radial distribution functions of the C-atom in CO_2 and the C_1 (open squares), C_3 (black diamonds), C_4 (open circles), C_8 (black circles), N_1 (open triangles), and N_2 (gray circles) atoms of the cation [C_4mim] at a temperature of 313.15 K and x_{CO_2} = 0.47. Inset shows the atom definition of [C_4mim].

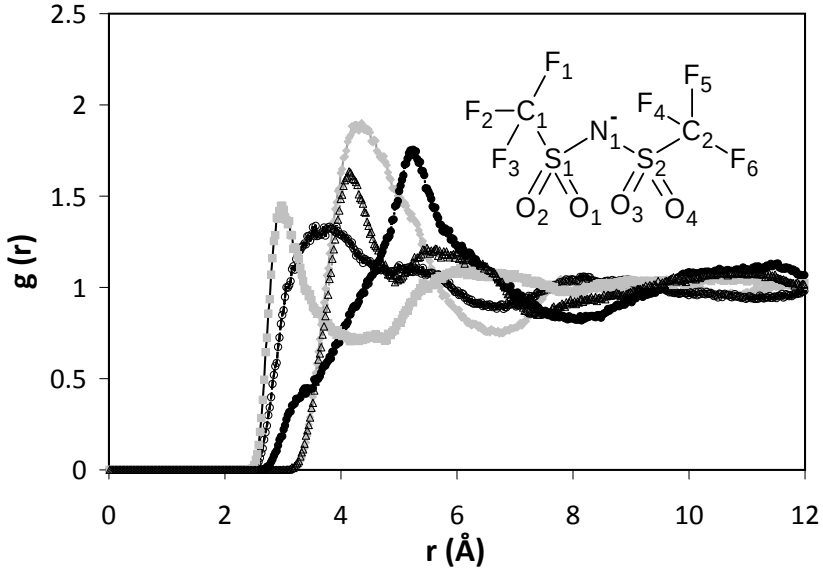


Figure 9. Radial distribution functions of the C-atom in CO_2 and the N_1 (black circles), S_1 (open triangles), O_1 (gray squares), C_1 (gray diamonds), and F_1 (open circles) atoms of the anion [Tf_2N] at a temperature of 313.15 K and $x_{CO_2} = 0.47$. Inset shows the atom definition of [Tf_2N].

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