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ABSTRACT

Computing bubble-points of multicomponent mixtures using Monte Carlo simulations is a non-trivial task. A new method is used to compute gas compositions from a known temperature, bubble-point pressure, and liquid composition. Monte Carlo simulations are used to calculate the bubble-points of carbon dioxide (CO_2) and methane (CH_4) mixtures in the ionic liquids (ILs) 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf_2N] and 1-ethyl-3-methylimidazolium diethylphosphate [emim][dep]. The Continuous Fractional Component Monte Carlo (CFCMC) method in the osmotic ensemble has been used to compute the solubility of CO_2/CH_4 gas mixtures at different temperatures (T), pressures (P), and gas compositions (y_i). The effect of T, P, and y_i on the real CO_2/CH_4 selectivity (i.e., the selectivity of CO_2 in the presence of CH_4) is investigated. The real selectivity will differ from the ideal selectivity, which is defined as the ratio of the Henry's constants, if the solubility of CO_2 is influenced by the presence of CH_4. The computed real selectivities are compared with the experimentally obtained real and ideal selectivities. The real CO_2/CH_4 selectivity decreases with increasing temperature and pressure, while the gas phase composition has a minor effect. The real selectivity is approximately identical to the ideal selectivity for relatively low pressures and low solute concentrations in the liquid phase. The real selectivity deviates from the ideal selectivity as the solute concentration in the liquid phase increases.

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1. Introduction

Industrial processes often involve multicomponent gas mixtures, which have to be separated or purified to obtain the final product [1]. Solubility and selectivity data of the components in the mixture are required to properly design and operate separation processes [2]. Moreover, the gases dissolved in the solvent may not necessarily form an ideal mixture, since the presence of one gas species may influence the solubility of the other [3]. Therefore, accurate solubility data of gas mixtures are essential to describe this non-ideal behavior [4]. Recently, we investigated the potential of ionic liquids (ILs) for CO_2 capture from natural gas using

experiments and Monte Carlo simulations [2,5–10]. Bubble-point pressures of carbon dioxide (CO_2) and methane (CH_4) mixtures were measured in different ionic liquids using the Cailletet apparatus, which operates according to the visual synthetic method [6]. In this method, known amounts of gases and ionic liquid are introduced in a capillary using mercury as a sealing and pressurizing fluid. The bubble-point is measured at a fixed temperature by gradually increasing the pressure until the gas bubble is completely dissolved in the liquid (i.e., the bubble-point pressure) [11]. Note that in the Cailletet setup phase transitions are observed visually and sampling of the phases is not possible. Therefore, the composition of the gas phase at the bubble point is unknown. The aim of this work was to investigate the effect of the presence of CH_4 (CO_2) on the solubility of CO_2 (CH_4) as both are simultaneously dissolved in an IL. This effect can be quantified by the so-called real CO_2/CH_4

selectivity:

$$S_{CO_2/CH_4}^R = \left(\frac{y_{CH_4}/x_{CH_4}}{y_{CO_2}/x_{CO_2}}\right)_{p,T} \quad (1)$$

in which y_i and x_i are the mole fractions of solute i in the gas phase and liquid phase, respectively. The ideal selectivity can be defined in several ways, but for convenience the ratio of Henry's constants (H_i) is used here [7]:

$$S_{CO_2/CH_4}^I = \left(\frac{H_{CH_4}}{H_{CO_2}}\right)_T \quad (2)$$

The Henry's constants, H_{ij}, of solute i in solvent j are calculated as [4]:

$$H_{ij} = \lim_{x_i \to 0} \frac{f_i^L}{x_i} \quad (3)$$

where the fugacity of the solute i (f_i) is calculated from a suitable equation of state. In principle, the real selectivity will differ from the ideal selectivity and the deviation is governed by the degree of non-ideality caused by the simultaneous dissolution of CO_2 and CH_4. From the data of the Cailletet experiments, it is not possible to calculate the real selectivity S_{CO_2/CH_4}^R, since only the bubble-point pressures of the CO_2–CH_4 mixtures were measured and the gas phase compositions, y_i, were unknown. This is, as stated before, because the composition of the phases cannot be sampled. The Peng–Robinson (PR) equation of state (EoS) may be used to calculate the gas phase compositions and therefore one can estimate the real selectivity [6]. However, the PR EoS is known to yield less accurate results for the gas phase composition for multicomponent mixtures, even when the liquid phase properties are predicted correctly [12]. We note that bubble-point calculations are extremely important for industrial separation processes [13]. For example, one may want to evaluate the performance of a separation column and hence the quality of the separated product at a certain operating temperature and pressure. This evaluation requires the knowledge of bubble-point pressures of the mixture and the compositions of each phase.

In this study, we aim to compute the gas phase compositions (y_i) of a CO_2 + CH_4 + IL mixture at a given temperature, liquid phase composition or bubble-point pressure, using molecular simulation. Several molecular simulation techniques (e.g., Gibbs ensemble Monte Carlo, Grand Equilibrium method, COSMO-RS, and fluctuation solution theory) have been used in the 'third industrial fluid properties simulation challenge' to compute bubble-points of HFC/ethanol mixtures [14–20]. Unfortunately, not all (classical) molecular simulation techniques are suitable to compute bubble points of multicomponent mixtures. The Gibbs ensemble Monte Carlo (GEMC) method can be used to compute phase equilibrium at specified temperature, global composition, and volume or pressure. However, standard GEMC simulations are not suitable to directly compute bubble points of multicomponent systems. A suitable ensemble to compute bubble points requires the temperature and liquid phase compositions to be specified, while the pressure and the gas phase compositions need to be calculated. The pseudo bubble point ensemble introduced by Ungerer et al. [21] and the Grand Equilibrium (GE) method proposed by Vrabec and Hasse [22] can be used to compute bubble points of multicomponent mixtures. The method of Ungerer et al. uses a liquid and a vapor box, like in the GEMC method, in which the temperature, the liquid compositions, and the total volume are fixed. The composition of the gas phase and the volume of the phases are allowed to change. The GE method of Vrabec and Hasse is related to the method of

Ungerer et al., but avoids direct coupling between the gas phase and the liquid phase. In this method, Taylor expansions of the chemical potentials as a function of pressure in the liquid phase are used to set the chemical potentials of the vapor phase in a pseudo grand-canonical ensemble simulation. The methods of Ungerer et al. [21], and Vrabec and Hasse [22], both require the calculation of the liquid phase chemical potentials using Widom's test particle method or an equivalent method. Here, a different approach is used to compute bubble points of multicomponent mixtures avoiding the computationally demanding chemical potential evaluations. It is important to note that chemical potentials obtained from Widom's test particle method are usually subjected to large uncertainties [23]. Simulations using the Continuous Fractional Component Monte Carlo (CFCMC) technique in the osmotic ensemble have been used to compute the solubilities of CO_2 and CH_4 gas mixtures in the ILs 1-n-butyl-3-methylimidazolium bis(-trifluoromethylsulfonyl)imide [bmim][Tf$_2$N] and 1-ethyl-3-methylimidazolium diethylphosphate [emim][dep]. The composition of the gas is calculated iteratively from the liquid composition by performing two separate simulations in the osmotic ensemble at the same hydrostatic pressure, but for different gas compositions. The composition of the gas that is in equilibrium with the experimental liquid composition is then approximated by a first-order Taylor expansion. The gas phase compositions and CO_2/CH_4 selectivities obtained from the MC simulations are compared with the PR EoS modeling results.

The paper is organized as follows. In the next section, a theoretical approach is presented to calculate the bubble-point pressure of a (multicomponent) gas-mixture from the knowledge of only pure component solubility data assuming ideal mixing. In a following section, the details of the MC simulations (i.e., ensemble, force field, and simulation parameters) and the method to compute bubble-points are outlined. Subsequently, the results for the gas solubilities and selectivities are presented and discussed. In the final section, conclusions are presented regarding the real CO_2/CH_4 selectivities in ILs.

2. Theory

It is of practical interest to predict the bubble-point pressure of a (multicomponent) gas-mixture from the knowledge of only pure component solubility data, since measuring solubilities of gas mixtures requires an increased experimental effort [24]. Here, we consider the solubility of a (multicomponent) gas-mixture in a single solvent. The equilibrium relations for the solvent and solutes are given by Ref. [4]:

$$y_s P \phi_s = x_s \gamma_s P_s^{sat} \quad (4)$$

$$y_i P \phi_i = x_i \gamma_i H_i \quad (5)$$

Here, P is the pressure, ϕ the fugacity coefficient, y the gas phase composition, x the liquid phase composition, H the Henry's constant, P_s^{sat} the saturation pressure of the solvent, and γ the activity coefficient. The subscripts s and i denote the solvent and solute, respectively. The pressure, P, can be obtained from Equations (4) and (5). Since ILs have a negligible vapor pressure [25], Equation (4) cancels and after rearranging Equation (5) one obtains the bubble-point pressure of a n-solute (i.e., n is the number of components in the gas phase excluding the IL since it is considered non-volatile) system:

$$P = \frac{\sum_{i=1}^n x_i \gamma_i H_i}{\sum_{i=1}^n y_i \phi_i} \quad (6)$$

For a ternary system (e.g., CO_2 + CH_4 + IL) in which the IL is nonvolatile, Equation (6) reduces to:

$$P = \frac{x_{CO_2}\gamma_{CO_2}H_{CO_2} + x_{CH_4}\gamma_{CH_4}H_{CH_4}}{y_{CO_2}\phi_{CO_2} + y_{CH_4}\phi_{CH_4}} \tag{7}$$

For sufficiently low pressures and solubilities (i.e., $\phi_{CO_2} \approx \phi_{CH_4} \approx 1$ and $\gamma_{CO_2} \approx \gamma_{CH_4} \approx 1$), Equation (7) reduces to the following well-known equation [4]:

$$P = x_{CO_2}H_{CO_2} + x_{CH_4}H_{CH_4} \tag{8}$$

Equation (8) allows us to calculate the bubble-point pressure of a binary gas-mixture from the knowledge of pure component Henry's constants assuming ideal mixing.

3. Simulation details

We recall that the aim is to compute the gas composition (y_i) of a CO_2 + CH_4 + IL mixture at a given temperature (T), liquid composition (x_i) or bubble-point pressure (P) using Monte Carlo (MC) simulations. The "or" in the previous sentence denotes a strict constraint, since the number of degrees of freedom for a ternary system containing two phases is three. Therefore, an ensemble with a fixed temperature, liquid composition and pressure would violate the Gibbs phase rule. As explained earlier, standard ensembles (e.g., Gibbs, osmotic, etc.) commonly used for phase equilibria computations cannot be applied directly to compute bubble-point pressures and compositions of multicomponent mixtures. These ensembles require the specification of the pressure and/or the gas composition, which are a priori unknown and should be computed from the simulations. Several iterative methods have been proposed in the literature to compute bubble-point pressures of multicomponent mixtures using a pseudo-ensemble [21,22,26—30]. All of them requires the computation of the liquid phase chemical potentials (e.g., using Widom test particle method or an equivalent method [23]), which are typically subjected to large uncertainties for complex dense liquid systems [23]. We have used the following approach to avoid the computationally demanding chemical potential evaluations. We are interested in the change of the solute composition in the liquid phase (x_i) caused by a change in the gas fugacity ($f_i(P,T,y_i)$):

$$\left(\frac{\partial x_i}{\partial y_i}\right)_{T,P,\Sigma} = \frac{(\partial f_i/\partial y_i)_{T,P,\Sigma}}{(\partial f_i/\partial x_i)_{T,P,\Sigma}} \tag{9}$$

The differentiation in the left hand side of Equation (9) is performed at constant temperature and pressure using the constraints $\sum_{i=1}^{n} y_i = 1$ and $\sum_{i=1}^{n} x_i = 1$, which is indicated by the symbol Σ. Note that in the simulations the IL ion-pairs are considered nonvolatile, hence $y_{CH_4} = (1 - y_{CO_2})$. The numerator in Equation (9), $(\partial f_i/\partial y_i)$, can be calculated with an equation of state for the gas phase. The Peng—Robinson (PR) equation of state (EoS) with a binary interaction parameter between CO_2 and CH_4 of 0.1 (i.e., $k_{ij} = 0.1$ [31]) is used to calculate the fugacities as a function of pressure and gas composition [32]. We note that one could alternatively compute the gas fugacities from molecular simulations. In this way, the computed fugacities would be fully consistent with the force field used for the gases. However, the computational models for CO_2 and CH_4 are well established and tuned to reproduce the vapor—liquid properties of the fluids. They reproduce the experimental densities, vapor pressures, and fugacities very well, and therefore explicit fugacity computations using a PR EoS give almost identical results [33,34]. Therefore, the gas fugacities computed with molecular simulations or the PR EoS will be almost identical. The denominator in Equation (9), $(\partial f_i/\partial x_i)$, is calculated

from two independent simulations in the osmotic ensemble. In this ensemble, the temperature (T), the hydrostatic pressure (P_{hydro}) which is equal to the pressure of the gas phase (P), the solute fugacities (f_i), and the number of solvent molecules (N) are fixed. The volume of the system (V) and the number of solute molecules in the liquid phase will change to satisfy the equilibrium conditions $f_i^l = f_i^g$. The fugacity (f_i) and the hydrostatic pressure are related through the PR EoS for the gas phase. The two simulations in the osmotic ensemble are performed at the same hydrostatic pressure, which is equal to the experimental bubble-point pressure, but at different gas compositions. The difficulty now is to choose the gas compositions at which the two simulations should be performed. Fortunately, the PR EoS can be used to fit the experimental bubble-point pressure of the ternary system CO_2—CH_4-IL to obtain an initial guess for the gas composition. The gas compositions for the two simulations are chosen in the vicinity of this initial gas composition. The gas composition that will yield the experimental liquid composition can then be obtained from a first-order Taylor expansion:

$$y_i = y_{i0} + \left(\frac{\partial y_i}{\partial x_i}\right)_{T,P,\Sigma}(x_i - x_{i0}) \tag{10}$$

Here, y_i and x_i are respectively the gas phase and liquid phase composition of solute i, and y_{i0} and x_{i0} denote the reference gas phase and the experimental liquid phase composition of solute i, respectively. In Fig. 1, the procedure described above is explained graphically. Once the gas phase compositions are known from Equation (10), Equation (1) can be applied to calculate the real selectivities.

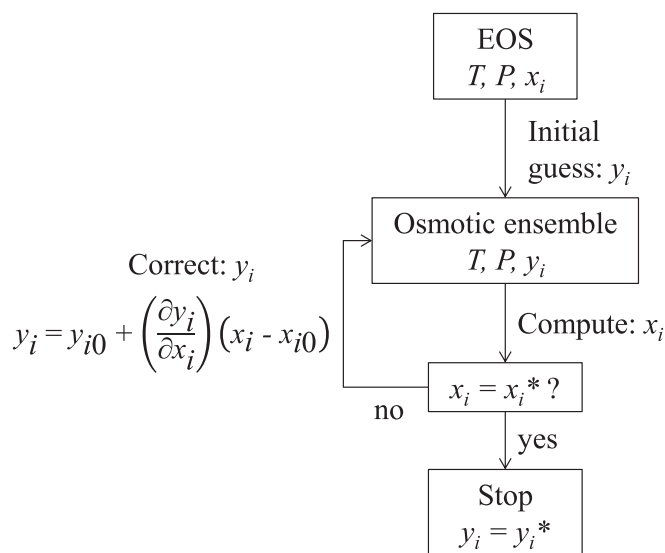The molecular simulation software RASPA [35] was used to

Fig. 1. Graphical explanation of the procedure used for computing the bubble point of CO_2/CH_4 gas mixtures in ILs. The Peng—Robinson (PR) equation of state (EoS) is used to obtain an initial guess for the gas composition, y_i, by fitting the experimental bubble-point pressure of the CO_2—CH_4-IL system. This initial gas composition is used in the MC simulations in the osmotic ensemble to compute the solubility of the gases (x_i) in the ILs. In a following step, the computed solubility (x_i) is compared with the required (experimental) solubility (x_i^*). The simulation is stopped once $x_i \approx x_i^*$ with a tolerance of 0.003, otherwise an additional simulation is performed at constant pressure with a corrected gas composition obtained from Equation (10). Using this procedure, one can obtain the gas composition (y_i^*) that coexist with the experimental liquid composition (x_i^*). The PR EoS for the ternary CO_2-CH_4-IL system is only used to obtain a reasonable initial guess for y_i, but in principal any value of y_i can be used in the simulations at an expense of more iterations.

perform the molecular simulations. The Continuous Fractional Component Monte Carlo (CFCMC) method in the osmotic ensemble was used to compute the solubility of the gases. In this approach, molecules are gradually or fractionally inserted utilizing a coupling parameter λ. The intermolecular (i.e., Lennard-Jones (LJ) and Coulombic) interactions between the "fractional" molecule and the surrounding molecules are scaled with λ. The scaling is such that there is no interaction for $\lambda = 0$, and for $\lambda = 1$ the conventional LJ and Coulombic interaction potentials are recovered. Slowly inflating the fractional molecule allows the system to rearrange, which decreases the probability for atomic overlaps and thus increases the efficiency of the simulation [36]. The method has been described in detail by Shi and Maginn [37,36], and by Dubbeldam et al. [38] and Torres-Knoop et al. [39]. The method has been applied by Shi and Maginn [40–42] and Ramdin et al. [8–10,43] to compute the solubility of several gases in ILs and conventional solvents. An ensemble of 50 and 70 IL ion-pairs was respectively used in the simulations for [bmim][Tf₂N] and [emim][dep]. These specific numbers of IL ion-pairs were chosen to keep the simulation box always larger than twice the cutoff distance, to dissolve at least one (integer) solute molecule, and to avoid excessively long simulation times that are required for larger systems. A classical force field was used in the simulations for the ILs, which included bond-stretching, bond-bending, torsion, Lennard-Jones and electrostatic interactions. All force field parameters of [bmim][Tf₂N] and [emim][dep] were taken from Maginn et al. [44,45]. The TraPPE models were used for CO_2 and CH_4 [33,34]. The Lennard-Jones (LJ) interactions between different atoms were described by the Lorentz-Berthelot combining rules [23]. The electrostatic interactions were taken into account by the Ewald sum method using a relative precision of 10^{-5} [46]. The LJ interactions were always truncated and shifted at 12 Å and tail corrections were not taken into account. The Configurational-Bias Monte Carlo (CBMC) scheme was used to sample the internal degrees of freedom of the IL ion-pairs [23,47–50]. The Wang-Landau sampling scheme was used to bias the λ trial moves, which prevents the system from being stuck in a certain λ state [51]. The CFCMC simulations were started with an equilibration run of 50000 MC cycles, followed by a production run of 0.5–1 million MC cycles. In RASPA, the number of MC steps in a cycle is defined as the total current number of molecules in the system. The simulation is divided into five blocks and the error in the computed properties is obtained from the standard deviation of the block averages. The uncertainty in the solute mole fraction is lower than 0.002, which is lower than the typical uncertainties in experimental data.

4. Results and discussion

The CFCMC method in the osmotic ensemble was used to compute the bubble-point of CO_2/CH_4 gas mixtures in [bmim][Tf₂N] and [emim][dep] at 313.15 K and 333.15 K. In our previous study, the solubility of the pure gases CO_2 and CH_4 in [bmim][Tf₂N] and [emim][dep] at 313.15 K and 333.15 K was computed from Monte Carlo simulations [9,43]. The computed isotherms of the pure gases were in quantitative agreement with experimental data measured using the Cailletet technique, see Fig. 2. Therefore, the MC simulations are expected to yield reasonable results for CO_2/CH_4 gas mixtures as well. In Table 1, the MC simulation results are compared with the experimental data and PR EoS modeling results reported in Ramdin et al. [6]. In the Cailletet experiments, three different gas mixtures initially containing 25% CO_2 - 75% CH_4 (25–75 mixture), 50% CO_2 - 50% CH_4 (50-50 mixture), and 75% CO_2 - 25% CH_4 (75-25 mixture) were investigated [6]. The given compositions (i.e., 25–75, 50–50, and 75–25) denote only the gas composition at the start of the Cailletet experiment, which
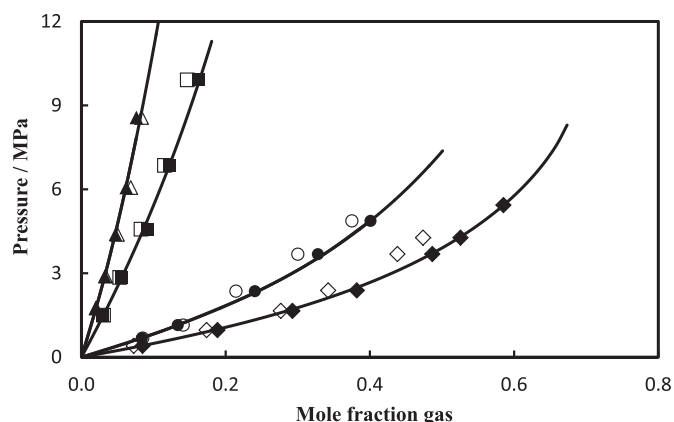

Fig. 2. Solubility of pure CO_2 and CH_4 in [bmim][Tf₂N] and [emim][dep] at 313.15 K from experiments (closed symbols) and Monte Carlo simulations (open symbols). CO_2 (diamonds) and CH_4 (squares) in [bmim][Tf₂N]. CO_2 (circles) and CH_4 (triangles) in [emim][dep]. Lines are Peng-Robinson equation of state modeling results [7,9]. Data taken from Ramdin et al. [8,43].

changes during the bubble-point measurements due to the operating principle of the Cailletet setup. In our previous experimental study, the gas composition at the bubble-point, $y_{CO_2}^{PR}$ in Table 1, was estimated from the PR EoS by fitting the experimental bubble-point pressure [6]. In our MC simulations, the composition of the gas phase is obtained iteratively by substitution of Equation (9) into Equation (10). The method is illustrated in Fig. 3 at a pressure of 1.97 MPa and 313.15 K, for the first data point in Table 1, using three different gas compositions. Similar diagrams can be constructed for the other solutes in a multicomponent system. Note that for the ternary system CO_2–CH_4-IL, it is not necessary to draw a diagram for CH_4, since the gas-phase composition of CH_4 can be obtained from the constraint $y_{CH_4} = (1 - y_{CO_2})$. In this way, the gas composition can be determined from a given bubble-point pressure and liquid composition. Clearly, the gas composition obtained from the MC simulations ($y_{CO_2}^{sim.}$) and the PR EoS modeling ($y_{CO_2}^{PR}$) are very similar for the 25–75, and 50-50 gas mixture, while a slight deviation is observed for the 75-25 gas mixture. The fit of the bubble-point pressure of the 75-25 gas mixture by the PR EoS was not perfect, see Ramdin et al. [6] for the modeling results. Therefore, the gas composition obtained from the PR EoS is unreliable for the 75-25 gas mixture. Subsequently, the real CO_2/CH_4 selectivity is calculated from Equation (1). The ideal selectivity, which is defined in Equation (2) as the ratio of the Henry's constants, is also reported in Table 1. The real selectivity is approximately the same as the ideal selectivity, which suggests that there is no enhancement of the solubility of one gas due to the presence of the other gas species. In Table 1, the bubble-point pressure of the system $CO_2 + CH_4$ + [bmim][Tf₂N] predicted by Equation (8) is presented. The predicted bubble-point pressures are in excellent agreement with the experimental data for pressures up to 30 bar. At higher pressures, the predictions are less accurate, which is a consequence of neglecting nonidealities in Equation (8). As it becomes evident from Equation (7), the deviation is caused either by nonidealities in the gas phase (i.e., $\phi_i \neq 1$) or by nonidealities in the liquid phase (i.e., $\gamma_i \neq 1$). The deviation is likely caused by non-idealities in the gas phase, since the liquid phase mole fractions of CO_2 and CH_4 are rather low. The concentration of CO_2 in our experiments was kept relatively low in order to dissolve a certain predefined amount of CH_4 in the IL (i.e., the CH_4/IL molar ratio was fixed), see Ramdin et al. [6] for the experimental details.

Table 1
Bubble-point compositions of the system $CO_2 + CH_4 +$ [bmim][Tf$_2$N] obtained from MC simulations (sim.) and Peng–Robinson (PR) equation of state at a given temperature (T) and bubble-point pressure ($P^{exp.}$). $P^{pred.}$ is the bubble-point pressure predicted by Equation (8). The gas composition (y_i), which is in equilibrium with the experimental liquid composition (x_i), is obtained from Equation (10). Real and ideal selectivities are obtained from Equation (1) and Equation (2), respectively. The Henry's constants of CO_2 in [bmim][Tf$_2$N] at 313.15 K and 333.15 K computed from the MC data are 5.4 MPa and 7.1 MPa, respectively [43]. The Henry's constants of CH_4 in [bmim][Tf$_2$N] at 313.15 K and 333.15 K computed from the MC data are 50.7 MPa and 53.7 MPa, respectively [43]. The experimental Henry's constants of CO_2 (CH_4) in [bmim][Tf$_2$N] at 313.15 K and 333.15 K are 4.9 MPa (49.3 MPa), and 6.6 MPa (52.4 MPa), respectively [56,55].

T/K	x_{CO_2}	x_{CH_4}	$P^{exp.}$/MPa	$P^{pred.}$/MPa	$y_{CO_2}^{PR}$	$y_{CO_2}^{sim.}$	S_{CO_2/CH_4}^{R}	S_{CO_2/CH_4}^{I}
313.15[a]	0.014	0.04	1.970	2.040	0.034	0.035	9.5	9.4
313.15[a]	0.037	0.11	6.322	5.603	0.036	0.037	8.8	9.4
313.15[b]	0.04	0.039	2.088	2.117	0.092	0.099	9.3	9.4
313.15[b]	0.103	0.102	6.560	5.529	0.097	0.108	8.4	9.4
313.15[c]	0.108	0.037	2.408	2.349	0.217	0.250	8.7	9.4
313.15[c]	0.189	0.064	4.855	4.073	0.221	0.266	8.2	9.4
333.15[a]	0.014	0.04	2.147	2.189	0.043	0.047	7.1	7.6
333.15[a]	0.037	0.11	6.847	6.011	0.044	0.048	6.7	7.6
333.15[b]	0.04	0.039	2.302	2.308	0.114	0.127	7.0	7.6
333.15[b]	0.103	0.102	7.220	6.025	0.119	0.134	6.5	7.6
333.15[c]	0.108	0.037	2.755	2.649	0.263	0.306	6.6	7.6
333.15[c]	0.189	0.064	5.578	4.596	0.269	0.316	6.4	7.6

[a] 25–75 gas mixture was used in the Cailletet experiments.
[b] 50-50 gas mixture was used in the Cailletet experiments.
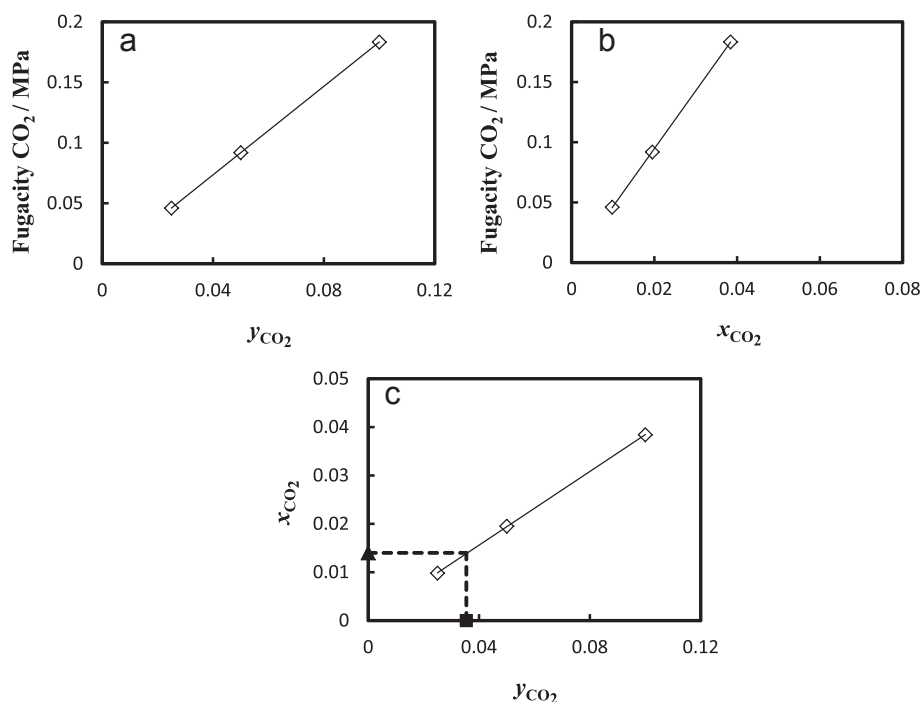[c] 75-25 gas mixture was used in the Cailletet experiments.

Fig. 3. (a) Fugacity of CO_2 as a function of CO_2 composition at a constant pressure of 1.970 MPa and 313.15 K calculated with the PR EoS. (b) The solubility of CO_2 in [bmim][Tf$_2$N] computed with MC simulations in the osmotic ensemble at CO_2 fugacities corresponding to Fig. 3(a). (c) Combination of Fig. 3(a) and (b) results in a $x - y$ plot (diamonds), which allows the determination of the gas phase composition (y_{CO_2}, square) at a given liquid composition (x_{CO_2}, triangle) using Equation (10).

It is, therefore, possible that ideal CO_2/CH_4 selectivities are observed due to the low CO_2 concentrations in the liquid phase. We have used MC simulations in the osmotic ensemble to investigate the effect of CO_2 concentration in the liquid phase on the CO_2/CH_4 selectivity, see Table 2 and Fig. 4. The following can be concluded from Tables 1 and 2 and Fig. 4: (1) the selectivity decreases with increasing temperature and pressure, (2) the gas composition has only a minor effect on the selectivity, (3) the ideal selectivity is observed for relatively low pressures and low CO_2 concentrations in the liquid phase, (4) the real selectivity deviates from the ideal selectivity for relatively high CO_2 concentrations in the liquid phase. Recently, Budhathoki et al. [52] used Gibbs

ensemble Monte Carlo simulations to compute CO_2/CH_4 selectivities in [bmim][Tf$_2$N]. These authors also observed ideal selectivity for low CO_2 concentrations in the liquid phase, but the selectivity was shown to decrease for relatively high CO_2 concentrations. This is in agreement with our simulation results.

In Table 3, the MC results for the system CO_2–CH_4-[emim][dep] are presented. Similar conclusions can be drawn for this system, i.e., the real selectivity decreases with increasing temperature and pressure, but the pressure effects are quite small. The real selectivity is approximately the same as the ideal selectivity for low pressures and low solute concentrations in the liquid phase. At higher CO_2 concentrations, the real selectivity starts to deviate from

Table 2
CO_2/CH_4 solubilities and selectivities in [bmim][Tf_2N] from MC simulations in the osmotic ensemble at a given T, P, and y_i. The experimental Henry's constants of CO_2 and CH_4 in [bmim][Tf_2N] at 313.15 K are 4.9 MPa and 49.3 MPa, respectively [56,55]. The Henry's constants of CO_2 and CH_4 in [bmim][Tf_2N] at 313.15 K computed from the MC data are 5.4 MPa and 50.7 MPa, respectively [8,43]. The ideal CO_2/CH_4 selectivities computed from the experiments and MC data as a ratio of the Henry's constants are 10.1 and 9.5, respectively.

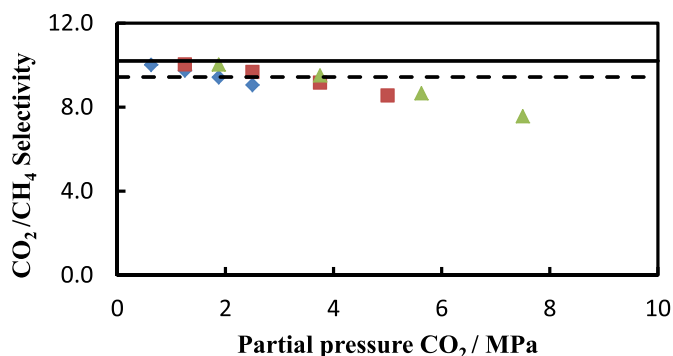| T/K	P/MPa	y_{CO_2}	y_{CH_4}	x_{CO_2}	x_{CH_4}	$S^R_{CO_2/CH_4}$
313.15	2.5	0.25	0.75	0.111	0.033	10.0
313.15	5.0	0.25	0.75	0.183	0.056	9.7
313.15	7.5	0.25	0.75	0.230	0.073	9.4
313.15	10.0	0.25	0.75	0.263	0.087	9.1
313.15	2.5	0.50	0.50	0.204	0.020	10.0
313.15	5.0	0.50	0.50	0.317	0.033	9.7
313.15	7.5	0.50	0.50	0.384	0.042	9.2
313.15	10.0	0.50	0.50	0.425	0.050	8.6
313.15	2.5	0.75	0.25	0.284	0.009	10.0
313.15	5.0	0.75	0.25	0.421	0.015	9.5
313.15	7.5	0.75	0.25	0.495	0.019	8.7
313.15	10.0	0.75	0.25	0.534	0.024	7.6

Fig. 4. Effect of the CO_2 partial pressure on the real CO_2/CH_4 selectivity in [bmim][Tf_2N] at 313.15 K. 25—75 gas mixture (diamonds), 50-50 gas mixture (squares), and 75-25 gas mixture (triangles). The ideal selectivity computed from MC data (dashed line) and from experiments (solid line) are included.

Table 3
CO_2/CH_4 solubilities and selectivities in [emim][dep] from MC simulations in the osmotic ensemble at a given T, P, and y_i. The Henry's constants of CO_2 in [emim][dep] at 313.15 K and 333.15 K computed from the MC data are 7.7 MPa and 11.7 MPa, respectively [43]. The Henry's constants of CH_4 in [emim][dep] at 313.15 K and 333.15 K computed from the MC data are 81.6 MPa and 103.0 MPa, respectively [43].

T/K	P/MPa	y_{CO_2}	y_{CH_4}	x_{CO_2}	x_{CH_4}	$S^R_{CO_2/CH_4}$
313.15	2.5	0.25	0.75	0.079	0.021	11.1
313.15	5.0	0.25	0.75	0.123	0.038	9.8
313.15	7.5	0.25	0.75	0.152	0.051	8.9
333.15	2.5	0.25	0.75	0.051	0.018	8.7
333.15	5.0	0.25	0.75	0.091	0.031	8.7
333.15	7.5	0.25	0.75	0.121	0.042	8.6
313.15	2.5	0.5	0.5	0.135	0.014	9.8
313.15	5.0	0.5	0.5	0.203	0.024	8.5
313.15	7.5	0.5	0.5	0.254	0.032	8.0
333.15	2.5	0.5	0.5	0.099	0.011	8.6
333.15	5.0	0.5	0.5	0.169	0.020	8.4
333.15	7.5	0.5	0.5	0.219	0.027	8.2
313.15	2.5	0.75	0.25	0.180	0.007	9.0
313.15	5.0	0.75	0.25	0.295	0.011	8.8
313.15	7.5	0.75	0.25	0.367	0.015	8.2
333.15	2.5	0.75	0.25	0.143	0.006	8.5
333.15	5.0	0.75	0.25	0.237	0.010	8.2
333.15	7.5	0.75	0.25	0.300	0.013	7.7

the ideal selectivity. This is not unexpected, because the definition of the ideal selectivity (Equation (2)) does not account for the nonidealities in the mixture. Hert et al. [53] measured the

simultaneous solubility of CO_2 and CH_4 in the IL 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf_2N]. These authors observed an enhancement of CH_4 solubility in the presence of CO_2 by more than 200%, relative to the pure gas solubility at similar conditions. Nonidealities of this proportion are very unlikely to occur, since the experiments of Hert et al. were performed at relatively low pressures (up to 17 bar) and the liquid phase mole fractions of CO_2 and CH_4 were lower than 0.1. Therefore, the data of Hert et al. should be treated with caution until substantiated further [54].

The above outlined method to compute bubble-points at a given temperature and liquid composition deserves some discussion. For example, two simulations were used to evaluate $(\partial f_i/\partial x_i)$ in Equation (9). However, providing a poor initial guess for the gas composition will require more than two independent simulations in order to accurately evaluate Equation (10). An educated guess for the gas composition can always be obtained from an equation of state provided that the bubble-point pressure of the mixture is known. In practice, bubble-point pressure measurements of multicomponent mixtures are much easier to perform compared to the more elaborate sampling experiments. Typically, the gas composition is then obtained by fitting the bubble-point pressure with a suitable equation of state. Alternatively, Monte Carlo simulations as outlined here can be used to compute gas compositions from a known bubble-point pressure.

5. Conclusion

Practical processes often require separation of multicomponent mixtures to obtain the final product. Solubility and selectivity data are required to evaluate the separation performance of a process and to design proper separation units. The real selectivity of a solvent for a specific solute in a multicomponent mixture can be obtained by sampling the composition of the phases in an experiment. However, sampling and subsequent analysis of the phases is an elaborate task. Therefore, one often prefers to measure the bubble-point pressure of the multicomponent mixture and apply an equation of state to compute the gas phase compositions required for the selectivity analysis. Here, we outline a method to compute the gas composition from a known bubble-point pressure using Monte Carlo simulations. MC simulations in the osmotic ensemble are used to compute the solubility of CO_2–CH_4 gas mixtures in the ILs [bmim][Tf_2N] and [emim][dep]. The composition of the gas is derived iteratively from the liquid composition by performing two separate simulations in the osmotic ensemble at the same pressure, but different gas compositions. The composition of the gas that is in equilibrium with the experimental liquid composition is then approximated by a first-order Taylor expansion. The method is applied to compute the gas composition of the ternary system CO_2 + CH_4 + [bmim][Tf_2N] using the experimental bubble-point pressure. The gas compositions obtained from the Monte Carlo simulation are compared with gas compositions predicted by the Peng-Robinson equation of state modeling. Both methods yield similar gas compositions. Subsequently, the real CO_2/CH_4 selectivity in [bmim][Tf_2N] and [emim][dep] is computed and compared with the ideal selectivity, which is defined as the ratio of the Henry's constant of CH_4 over that of CO_2. The real selectivity is approximately the same as the ideal selectivity for pressures up to 30 bar and for liquid phase solute mole fractions up to 0.3. At higher pressures and higher solute concentrations the real selectivity starts to deviate from the ideal selectivity. The gas composition has only a minor effect on the real selectivity.

Acknowledgments

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