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DOI

[10.1080/08927022.2023.2228918](https://doi.org/10.1080/08927022.2023.2228918)

Publication date

2023

Document Version

Final published version

Published in

Molecular Simulation

Citation (APA)

Chen, Q., Ramdin, M., & Vlugt, T. J. H. (2023). Solubilities of CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in commercial physical solvents from Monte Carlo simulations. *Molecular Simulation*, 49(13-14), 1341-1349. <https://doi.org/10.1080/08927022.2023.2228918>

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To cite this article: Qu Chen, Mahinder Ramdin & Thijs J. H. Vlugt (2023) Solubilities of CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in commercial physical solvents from Monte Carlo simulations, *Molecular Simulation*, 49:13-14, 1341-1349, DOI: [10.1080/08927022.2023.2228918](https://doi.org/10.1080/08927022.2023.2228918)

To link to this article: <https://doi.org/10.1080/08927022.2023.2228918>



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Published online: 30 Jun 2023.



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ABSTRACT

The removal of acid gas impurities from synthesis gas or natural gas can be achieved using several physical solvents. Examples of solvents applied on a commercial scale include methanol (Rectisol), poly(ethylene glycol) dimethyl ethers (Selexol), *n*-methyl-2-pyrrolidone (Purisol), and propylene carbonate (Fluor solvent). Continuous Fractional Component Monte Carlo (CFCMC) simulations in the osmotic ensemble were used to compute the Henry coefficients of the pure gases CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in the aforementioned solvents. The predicted Henry coefficients are in good agreement with the experimental results. The Monte Carlo method correctly predicts the gas solubility trend in these physical solvents, which obeys the following order: H₂S > CO₂ > C₂H₆ > CH₄ > CO > N₂ > H₂. The gas separation selectivities for the precombustion process and the natural gas sweetening process are calculated from the pure gas Henry coefficients. The CO₂/N₂O analogy is verified for the solubility in these solvents.

ARTICLE HISTORY

Received 17 April 2023
Accepted 16 June 2023

KEYWORDS

osmotic ensemble; gas solubilities; separation selectivities; commercial physical solvents; CO₂/N₂O analogy

1. Introduction

Large amounts of carbon dioxide (CO₂) are produced when fossil fuels are burned to generate electricity in a power plant, which might cause serious climate change [1–3]. Carbon Capture and Storage (CCS) can be considered as one of the most direct and effective routes to reduce CO₂ emissions [4–6]. Currently, a power company can apply two main technologies (i.e. postcombustion and precombustion) to produce electricity [7, 8]. The selection of the type of solvents for CO₂ removal depends on the technology used for power generation [9, 10]. In the postcombustion process, the fuel is burned completely producing large volumes of CO₂ at a relatively low partial pressure (0.1 bar) [11, 12]. Hence, CO₂ capture at postcombustion conditions can only be achieved utilising a chemical solvent. Alkanolamines such as monoethanolamine (MEA) and *N*-methyl-diethanolamine (MDEA) have been used for many years in the gas-treating process to remove acid gases [13, 14]. However, this conventional amine scrubbing technology suffers from one major drawback. The process requires a large heat input to regenerate the solvent, and hence increases the gas-treating cost [15]. Besides the energy penalty, the amine solvents tend to be corrosive and therefore only a diluted solution, which typically contains 30% MEA, can be applied [14]. An alternative to postcombustion is the precombustion process associated with the integrated gasification combined cycle (IGCC). In the precombustion process, the fuel is first gasified and converted to syngas, which is a mixture of carbon monoxide (CO) and hydrogen (H₂). The syngas is then shifted with steam in the

Water-Gas-Shift (WGS) reactor to form CO₂ and more H₂ [16]. Once separated from the CO₂, the H₂ can be used for many applications [17]. The precombustion capture is characterised by relatively high partial pressures of CO₂ in the feed gas (>10 bar) after the WGS step [11, 12]. Physical solvents are therefore preferred to absorb CO₂, since the CO₂ can be stripped out of the solvents by merely reducing pressure rather than applying heat [9]. CO₂ capture is also applied in the natural gas sweetening process, where the separation of methane (CH₄) from the acid gas impurities (CO₂ and H₂S) is required [18]. For high pressure natural gas purification, physical solvents are also preferred. Examples of commercial solvents often in the precombustion process or natural gas industry include Rectisol, Selexol, Purisol and Fluor solvent [19, 20]. Although potential solvents or materials (e.g. the ionic liquids (ILs), metal-organic frameworks (MOFs) and membranes) seem attractive for CO₂ capture, they are still under development [11, 21–24].

The Rectisol process [25] (jointly developed by Lurgi GmbH and Linde AG) uses methanol (MeOH) as its solvent. This process operates at very low temperatures (–20°C to –70°C) when methanol has an exceptionally high capacity to selectively absorb both CO₂ and hydrogen sulfide (H₂S) [16, 26, 27]. Methanol has a relatively high vapour pressure at normal process condition, so deep refrigeration is required to prevent solvent losses. The Selexol process (now licensed by UOP) uses poly(ethylene glycol) dimethyl ethers (PEGDME, CH₃O[CH₂CH₂O]_{*n*}CH₃, where *n* is typically between 3 and 11 [28]) as solvent. This process, which normally performs

at 25°C, can effectively absorb CO₂ and H₂S from the syngas, or remove H₂S in the presence of CO₂ [29]. The Purisol process [25] (developed by Lurgi GmbH) uses *n*-methyl-2-pyrrolidone (NMP) as its solvent. Due to the exceptionally high selectivity of H₂S over CO₂ in NMP, the Purisol process operates at ambient temperature and is especially well suited for removing H₂S from the CO₂-rich syngas [19, 20]. The flour solvent process (licensed by Flour Daniel, Inc.) uses propylene carbonate (PC) as its solvent [30]. PC features a relatively lower selectivity of H₂S over CO₂, but a relatively higher selectivity of CO₂ to light hydrocarbon (e.g. CH₄) [20]. Therefore, the flour solvent process operates at normal temperature and has an advantage for CO₂ removal from the syngas in the absence of H₂S.

The present study focuses on the separation of CO₂ from syngas in the precombustion process or natural gas sweetening process using the four above-mentioned physical solvents. In the precombustion process, if natural gas is considered as fuel, which will be gasified in the presence of air and steam, the resulting separations will be CO₂/CH₄, CO₂/CO, CO₂/H₂ and CO₂/N₂. The separation selectivity of CO₂/H₂S will also be taken into account if the syngas is not desulfurized prior to CO₂ removal. In the gas sweetening process, the physical solvents tend to co-absorb both CH₄ and ethane (C₂H₆), so relevant separations are CO₂/CH₄ and CO₂/C₂H₆. The selectivity can be calculated from the solubility data of corresponding gases in the physical solvents. Although these physical solvents have been used in gas-treating process for decades, the solubility data of sparingly soluble gases (e.g. H₂ and N₂) and toxic gases (e.g. CO) in methanol at low temperature and in Selexol, NMP and PC at normal temperature are scarcely reported in the literature. Alternatively, the molecular simulation method has already proven to be effective in predicting the solubility data [31]. Shi and Maginn accurately computed the isotherms, Henry coefficients, and partial molar enthalpies of CO₂ and H₂O absorption in the ionic liquid [hmim][Tf₂N] using atomistic Monte Carlo simulations [32]. Ramdin et al. successfully predicted the solubility and selectivity of precombustion gases in the ionic liquid [bmim][Tf₂N] using the Monte Carlo method [16]. Recently, Salehi et al. used Monte Carlo simulations to compute gas solubilities in choline chloride urea and choline chloride ethylene glycol deep eutectic solvents, and yielded reasonable results compared to experimental data [33]. Indeed, the molecular simulation method has been extensively used to predict gas solubilities in ionic liquids [34–36], deep eutectic solvents [37, 38], and other physical solvents [39, 40]. In this work, Monte Carlo simulations have been performed to compute the solubility of CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in the physical solvents methanol, Selexol, NMP, and PC, respectively.

The solubility of CO₂ is often compared to that of N₂O in either chemical or physical solvents, since both gases have similar molecular weights and structures. This empirical method, referred to as “the CO₂/N₂O analogy” [41, 42], is often applied to predict the CO₂ solubility in amine solutions where physical properties of CO₂ in amine solutions are otherwise hindered by the presence of the chemical reaction between CO₂ and amines [43]. This analogy has recently

been verified by means of molecular simulations for a 30% aqueous MEA solution at 303 K [44, 45]. The CO₂/N₂O analogy therefore provides an alternative to predict the CO₂ solubility in solvents. According to early studies, the solubilities of CO₂ and N₂O in less polarised solvents (e.g. *n*-heptane) are very similar; whereas the solubilities of CO₂ and N₂O in more polarised solvents (e.g. water) are different [44, 46]. The physical solvents methanol, Selexol, NMP, and PC can be considered as polar solvents, so it is of great interest to estimate the solubility ratios of CO₂ to N₂O in these solvents.

This paper is organised as follows. Section 2 outlines the simulation details including all the force fields and the simulation method. In Section 3, the simulation results on the gas solubilities, selectivities and the solubility ratios of CO₂ to N₂O in the physical solvents methanol, PEGDME, NMP, and PC are presented and discussed thoroughly. Our findings are summarised in Section 4.

2. Simulation details

Continuous Fractional Component Monte Carlo (CFCMC) method [47] in the osmotic ensemble was used to compute the Henry coefficients of the precombustion gases in the physical solvents methanol, PEGDME, NMP, and PC. The reason to use the CFCMC scheme is that the conventional MC methods usually fail in molecule insertion/deletion for open systems at high density. An open system refers to a system where the number of molecules varies and in this work almost all the systems belong to open systems. To overcome this difficulty, the CFCMC method was developed. This method has been originally proposed by Shi and Maginn [48–50] and further developed in several other groups of Torres-Knoop [51], Dubbledam [52] and Vlucht [53, 54]. The method has been extensively used by Chen and Ramdin [16, 44, 55–58] to compute the solubility of gases in physical solvents. It is worth mentioning that the modified Widom test particle insertion method [59, 60] can also accurately and conveniently compute the Henry coefficients at high densities, giving results which are consistent with the Henry coefficients predicted by the CFCMC method [60]. However, one of the advantages of the CFCMC method is that it can be used to compute the full gas absorption isotherm, which allows for a direct comparison with experiments.

All the MC simulations were conducted using the molecular simulation package RASPA [52, 61]. For CFCMC simulations in the osmotic ensemble [16, 44], the number of (nonvolatile) solvent molecules (*N*), the fugacity of the gas (*f*), the total hydrostatic pressure (*P*), and the temperature (*T*) are all fixed. The simulations were performed at a temperature of 248 K for solvent methanol and 298 K for solvents PEGDME, NMP, and PC. A series of pressures were selected to make sure that the Henry coefficients of the solute gases were computed in the linear regime of Henry's law. Ensembles of 250 methanol molecules, 50 PEGDME molecules, 150 NMP molecules, and 150 PC molecules were respectively used in the simulations for different systems. For solvent molecules, the standard TraPPE model was adopted for methanol [62] and PEGDME [63]. The generalised Amber force field (GAFF) was used for NMP [64]; the OPLS all-atom force field was

used for PC [65]. Note that in RASPA, the rings in NMP and PC molecules can only be treated as rigid. For gas solutes, the force fields for CO₂ and N₂ were taken from the standard TraPPE models [66]. The force fields for CH₄ and C₂H₆ were also derived from the TraPPE models [66] with Lennard-Jones parameters modified by Dubbeldam et al. [67]. The CO model was developed by Martín-Calvo et al. [68], the N₂O model by Lachet et al. [69] and the H₂ model by Cracknell et al. [70]. For H₂S, the five-site model (5S) of Gutiérrez-Sevillano et al. was applied [71]. It is worth mentioning that several models for H₂S have been developed including the three-site model (3S) [72], four-site model (4S) [73] and 5S. Ramdin et al. have examined the solubility of H₂S in the ionic liquid [bmim][Tf₂N] using these three models of H₂S and found no significant difference in computing the Henry coefficient of H₂S [16]. All the force field parameters are listed in the Supporting Information. The Lennard-Jones parameters for the cross interactions were obtained from the Lorentz-Berthelot mixing rules [74]. The Ewald sum method [75] with a relative precision of 10⁻⁵ was employed to calculate the long range electrostatic interactions. The LJ interactions were truncated and shifted at 1.2 nm and no tail corrections were applied. The fugacity of the gases was obtained from the Peng-Robinson (PR) equation of state (EoS) [76].

For methanol, NMP and PC, all the CFCMC simulations were started with an equilibration run of 50000 MC cycles, with a subsequent production run of at least 200000 MC cycles (for methanol at least 500000 MC cycles), where the number of MC steps in a cycle equals the total number of molecules in the simulation box. For long-chained molecule PEGDME, at least 1 million MC cycles are for the equilibration and at least 1 million MC cycles for the subsequent production runs. The average number of (integral and fractional) solute molecules was sampled to calculate the solubility. The reported data were calculated from the block averages [51], and the standard deviation was used to calculate the uncertainty. In each MC cycle, several types of trial moves are considered with their fixed probabilities. For the solutes, 24.94% are translation moves, 24.94% rotation moves, 24.94% reinsertion moves, 24.94% λ -moves, and 0.24% volume change moves. For the solvents, translation, rotation, reinsertion, and volume change moves are 33.22%, 33.22%, 33.22%, and 0.34%, respectively. For more information about these types of trial moves, the reader is referred to the original works of the CFCMC method [47, 51].

3. Results and discussion

The solubilities of gases are reported in terms of Henry coefficient. The Henry coefficient of a given solute i in the solvent j can be computed from

$$H_{ij} = \lim_{x_i \rightarrow 0} \frac{f_i^G}{x_i^L} \quad (1)$$

where f_i^G denotes the fugacity of the solute i in the gas phase and x_i^L represents the mole fraction of the solute i in the liquid phase. The fugacities and Henry coefficients are reported in units of MPa. The solvent densities of methanol, PEGDME,

Table 1. The densities of solvents methanol, PEGDME, NMP, and PC at a pressure of 1 bar and a temperature of 298 K. The MD simulation results were compared with the experimental values.

Solvents	Sim (g/cm ³)	Exp (g/cm ³)	Diff%
methanol	0.788 ± 0.002	0.787 [77]	+0.127
PEGDME($n = 4$)	1.031 ± 0.002	1.007 [78]	+2.383
PEGDME($n = 6$)	1.055 ± 0.002	n/a	n/a
PEGDME($n = 4, 6$)	1.042 ± 0.003	n/a	n/a
NMP	1.036 ± 0.007	1.028 [79]	+0.778
PC	1.230 ± 0.003	1.200 [80]	+2.500

NMP, and PC were first tested in the NPT ensemble at a pressure of 1 bar and a temperature of 298 K by molecular dynamics (MD) simulation [31]. For PEGDME, tetra(ethylene glycol) dimethyl ether (TEGDME) ($n = 4$), hexa(ethylene glycol) dimethyl ether (HEGDME) ($n = 6$), and a mixture of 50% TEGDME and 50% HEGDME were used. It is indicated in Table 1 that the simulation models of the four physical solvents can correctly reproduce the experimental liquid density [77–80] at 1 bar and 298 K. The Henry coefficients of the solutes CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in the solvents methanol, PEGDME, NMP, and PC were obtained from MC simulations in the osmotic ensemble at a temperature of 248 K for methanol and 298 K for PEGDME, NMP, and PC. For PEGDME, three systems are chosen for comparison including pure TEGDME, pure HEGDME, and a mixture of 50% TEGDME + 50% HEGDME, since there is limited information in the literature regarding the exact components comprising Selexol. The simulated Henry coefficients in these systems are presented in Tables 2–5. All the fitted raw data are included in the Supporting Information. Typical examples of the systems including CO₂ and the solvents methanol, TEGDME, NMP, and PC are illustrated in Figure 1. Figure 2 shows a typical example of the fugacity of CO₂ in the gas phase plotted as a function of the solute mole fraction of solvents methanol at 248 K, and TEGDME, NMP, and PC at 298 K, while Figure 3 shows another typical example of the fugacity of the solutes CO₂, CH₄, C₂H₆, CO, H₂, N₂, and H₂S in the gas phase plotted as a function of the solute mole fraction of methanol at 248 K.

For methanol, the Henry coefficients of CO₂ and N₂ at 248 K are in excellent agreement with the experimental data of Weber et al. [81]. To the best of our knowledge, no experimental data of Henry coefficients for CH₄, C₂H₆, CO, H₂, N₂O, and H₂S in methanol at 248 K were reported in the literature. Methanol has a relatively high vapour pressure, and it is therefore very important to test whether or not the osmotic ensemble is valid by disallowing the methanol molecules in the gas phase. As a result, CFCMC simulations in the Gibbs ensemble [82–85] were performed for CO₂ solubility in methanol at 248

Table 2. The computed Henry coefficients of CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in methanol at a temperature of 248 K.

Solutes	H_{sim} [MPa]	H_{exp} [MPa]	Diff%
CO ₂	5.00 ± 0.17	4.49 [81]	+11.4
CH ₄	91.8 ± 2.2	n/a	n/a
C ₂ H ₆	10.25 ± 0.20	n/a	n/a
CO	239 ± 5	n/a	n/a
H ₂	626 ± 10	n/a	n/a
N ₂	364 ± 9	373 [81]	−2.41
N ₂ O	5.26 ± 0.18	n/a	n/a
H ₂ S	1.47 ± 0.02	n/a	n/a

Table 3. The computed Henry coefficients of CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in PEGDME at a temperature of 298 K.

Solutes	Solvents	H_{sim} [MPa]	H_{exp} [MPa]	Diff%	H_{sim} [mol/(L-MPa)]
CO ₂	PEGDME ($n=4$)	1.05 ± 0.01	3.0 [29]	-66.7	4.41 ± 0.01
CH ₄	PEGDME ($n=4$)	18.1 ± 0.5	38.1 [87]	-52.5	0.256 ± 0.028
C ₂ H ₆	PEGDME ($n=4$)	4.32 ± 0.11	5.9 [87]	-26.8	1.07 ± 0.02
CO	PEGDME ($n=4$)	30.9 ± 1.5	n/a	n/a	0.150 ± 0.048
H ₂	PEGDME ($n=4$)	76.6 ± 2.6	n/a	n/a	0.060 ± 0.034
N ₂	PEGDME ($n=4$)	54.6 ± 1.7	n/a	n/a	0.0850 ± 0.0312
N ₂ O	PEGDME ($n=4$)	0.975 ± 0.020	n/a	n/a	4.76 ± 0.02
H ₂ S	PEGDME ($n=4$)	0.492 ± 0.010	n/a	n/a	9.43 ± 0.02
CO ₂	PEGDME ($n=6$)	0.298 ± 0.010	n/a	n/a	11.4 ± 0.0
CH ₄	PEGDME ($n=6$)	5.38 ± 0.17	n/a	n/a	0.632 ± 0.032
C ₂ H ₆	PEGDME ($n=6$)	1.09 ± 0.03	n/a	n/a	3.12 ± 0.03
CO	PEGDME ($n=6$)	9.82 ± 0.45	n/a	n/a	0.346 ± 0.046
H ₂	PEGDME ($n=6$)	28.2 ± 0.8	n/a	n/a	0.120 ± 0.028
N ₂	PEGDME ($n=6$)	12.4 ± 0.2	n/a	n/a	0.274 ± 0.016
N ₂ O	PEGDME ($n=6$)	0.282 ± 0.019	n/a	n/a	12.0 ± 0.1
H ₂ S	PEGDME ($n=6$)	0.138 ± 0.008	n/a	n/a	24.6 ± 0.1
CO ₂	PEGDME ($n=4,6$)	0.416 ± 0.007	n/a	n/a	9.40 ± 0.02
CH ₄	PEGDME ($n=4,6$)	8.18 ± 0.33	n/a	n/a	0.478 ± 0.040
C ₂ H ₆	PEGDME ($n=4,6$)	1.72 ± 0.06	n/a	n/a	2.27 ± 0.04
CO	PEGDME ($n=4,6$)	15.1 ± 0.4	n/a	n/a	0.259 ± 0.027
H ₂	PEGDME ($n=4,6$)	41.6 ± 1.5	n/a	n/a	0.0940 ± 0.0362
N ₂	PEGDME ($n=4,6$)	19.6 ± 0.9	n/a	n/a	0.200 ± 0.046
N ₂ O	PEGDME ($n=4,6$)	0.366 ± 0.008	n/a	n/a	10.7 ± 0.0
H ₂ S	PEGDME ($n=4,6$)	0.214 ± 0.002	n/a	n/a	18.3 ± 0.0

Table 4. The computed Henry coefficients of CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in NMP at a temperature of 298 K.

Solutes	H_{sim} [MPa]	H_{exp} [MPa]	Diff%
CO ₂	6.52 ± 0.16	6.38 [90]	+2.19
CH ₄	78.3 ± 2.0	104 [87]	-24.7
C ₂ H ₆	11.9 ± 0.2	21.4 [87]	-44.4
CO	292 ± 4	n/a	n/a
H ₂	832 ± 11	n/a	n/a
N ₂	633 ± 12	n/a	n/a
N ₂ O	7.43 ± 0.25	n/a	n/a
H ₂ S	0.879 ± 0.017	0.740 [91]	+18.8

K. The Henry coefficient of CO₂ in methanol is 5.14 ± 0.14 MPa in the Gibbs ensemble at 248 K, which is very close to 5.00 ± 0.17 MPa in the osmotic ensemble at the same temperature. The mole fractions of methanol in CO₂ in the gas phase are about 0.005–0.006 at pressures from 0.01 to 0.05 MPa, suggesting that 248 K is an ideal working temperature for methanol. Moreover, to test the effect of hydroxyl group in solvent molecules for absorption, the solubilities of CO₂ in methanol (with one hydroxyl group) and ethylene glycol (with two hydroxyl group) at a temperature of 298 K have been compared. The simulated Henry coefficients of CO₂ in methanol and glycol at 298 K are 16.9 ± 0.2 MPa and 42.3 ± 0.3 MPa respectively, which are in quantitative agreement with the experimental results of Gui et al [86]. This indicates

that hydroxyl group could hinder the CO₂ absorption in solvents.

For PEGDME, the computed Henry coefficients of CO₂, CH₄, and C₂H₆ in TEGDME (PEGDME, $n=4$) and HEGDME (PEGDME, $n=6$) at 298 K are consistent with the simulation results of Ramdin et al [56], but tend to

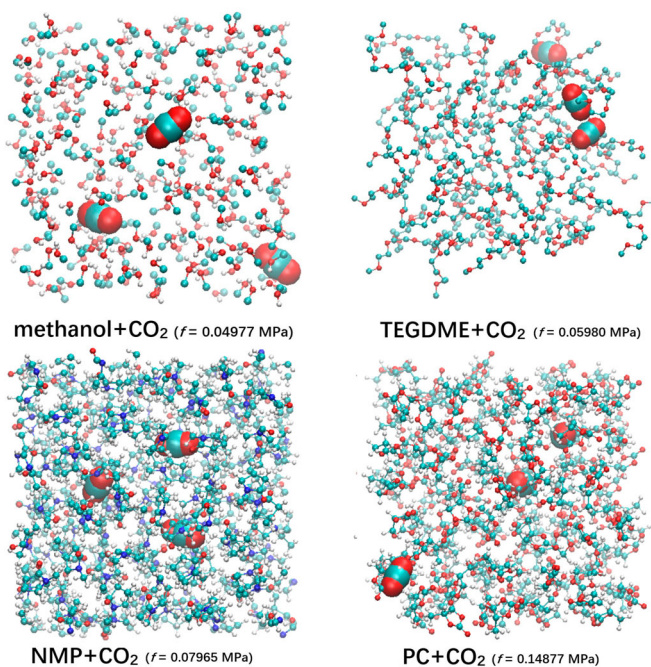


Figure 1. (Colour online) Typical snapshots of CO₂ and solvents methanol, TEGDME, NMP, and PC. The atoms in CO₂ molecules are represented in solid van der Waal (VDW) spheres while the atoms in all four solvents are represented in scaled VDW spheres. For CO₂, carbon(C) is marked cyan, and oxygen(O) red. For methanol and TEGDME, the alkyl groups CH₃ and CH₂ are both marked cyan, O red, and hydrogen(H) white. For NMP and PC, C is marked cyan, O red, H white, and nitrogen(N) blue. The fugacities of CO₂ in the gas phase for methanol, TEGDME, NMP, and PC are 0.04977 MPa, 0.05980 MPa, 0.07965 MPa, and 0.14877 MPa, respectively.

Table 5. The computed Henry coefficients of CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in PC at a temperature of 298 K.

Solutes	H_{sim} [MPa]	H_{exp} [MPa]	Diff%
CO ₂	7.41 ± 0.14	7.88 [91]	-5.96
CH ₄	57.3 ± 0.7	114.0 [92]	-49.7
C ₂ H ₆	12.7 ± 0.2	23.2 [92]	-45.2
CO	261 ± 5	n/a	n/a
H ₂	654 ± 11	n/a	n/a
N ₂	381 ± 6	n/a	n/a
N ₂ O	8.11 ± 0.08	n/a	n/a
H ₂ S	1.61 ± 0.03	2.22 [90]	-27.5

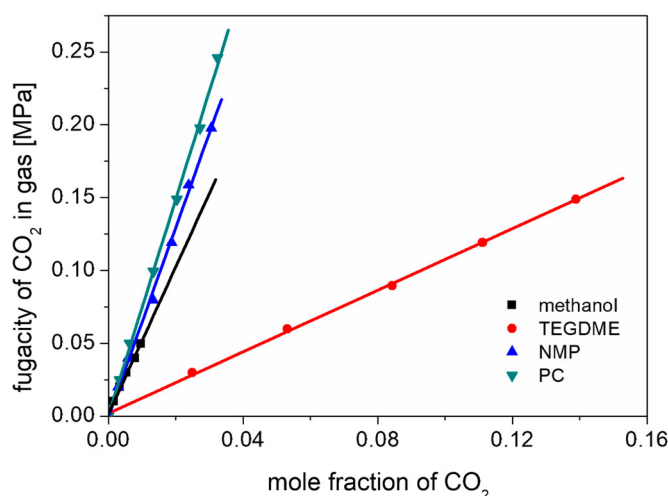


Figure 2. (Colour online) Solubility of CO₂ in methanol at 248 K, and in TEGDME, NMP, and PC at 298 K.

underestimate the available experiment results [29, 87]. The solubility of all the gases studied is increased when the value n of PEGDME is increased. Moreover, the Henry coefficients are also reported in another unit mol/(L·MPa) for PEGDME. This volume-based gas solubility independent of solvent densities can directly show the intrinsic solute-solvent interaction [57, 88, 89], which is useful to compare different compositions of PEGDME. In three different compositions of PEGDME studied, the solute-solvent interaction is increased with the increased value n of PEGDME. Note that a higher Henry coefficient in the unit of MPa indicates a lower solubility, while a higher Henry coefficient in the unit of mol/(L·MPa) indicates a higher solubility. For NMP and PC, most of the computed Henry coefficients are in quantitative agreement with the experimental values [87, 90–92], but certain deviations from the experimental results can be found. These differences between experiments and simulations may be ascribed to the Lorentz-Berthelot mixing rules [74]. Even though all the solute models employed in this study can reproduce experimental phase equilibrium

data, and all the solvent models used can reproduce experimental liquid density as shown in Table 1, the Lorentz-Berthelot mixing rules may not be adequate to accurately describe the cross interactions between solutes and solvents for some systems, which can also be observed in previous works [93]. However, the differences between experiments and simulations in this study are generally acceptable, since our work correctly predicts the solubility trend reported in the literature [20] of the investigated gases in the following order: H₂S > CO₂ > C₂H₆ > CH₄ > CO > N₂ > H₂. All the investigated solvents exhibit higher affinity with H₂S than with CO₂, while CO₂ is more soluble than C₂H₆ and CH₄ in all the solvents. CO, N₂, and H₂ constitute the least soluble gases in syngas. These findings derived from molecular simulations also confirm the basis for acid gas removal in the investigated physical solvents. It can also be found in our simulations that the solubilities of almost all the gases are much higher in PEGDME than in methanol, NMP, and PC. In particular, the solubilities of all the gases studied are nearly an order of magnitude higher in HEGDME (PEGDME, $n=6$) than in methanol, NMP, and PC. However, one cannot conclude that the Selexol solvent at 298 K can absorb more investigated gases than methanol at 248 K and NMP and PC at 298 K, since the principal ingredients of Selexol solvents are much more complicated than the components used in this study. Nevertheless, the Selexol solvent does have a major drawback: it tends to absorb more hydrocarbons such as CH₄ and C₂H₆, which necessitates an additional separation step to be carried out downstream of the natural gas sweetening process.

The ideal selectivity can be calculated from the computed Henry coefficients using

$$S_{1,2}^{\text{ideal}} = \frac{H_1}{H_2} \quad (2)$$

All the ideal selectivities of H₂S, C₂H₆, CH₄, CO, N₂, and H₂ with respect to CO₂ are listed in Table 6. Our simulation results show that the four commercial solvents all exhibit

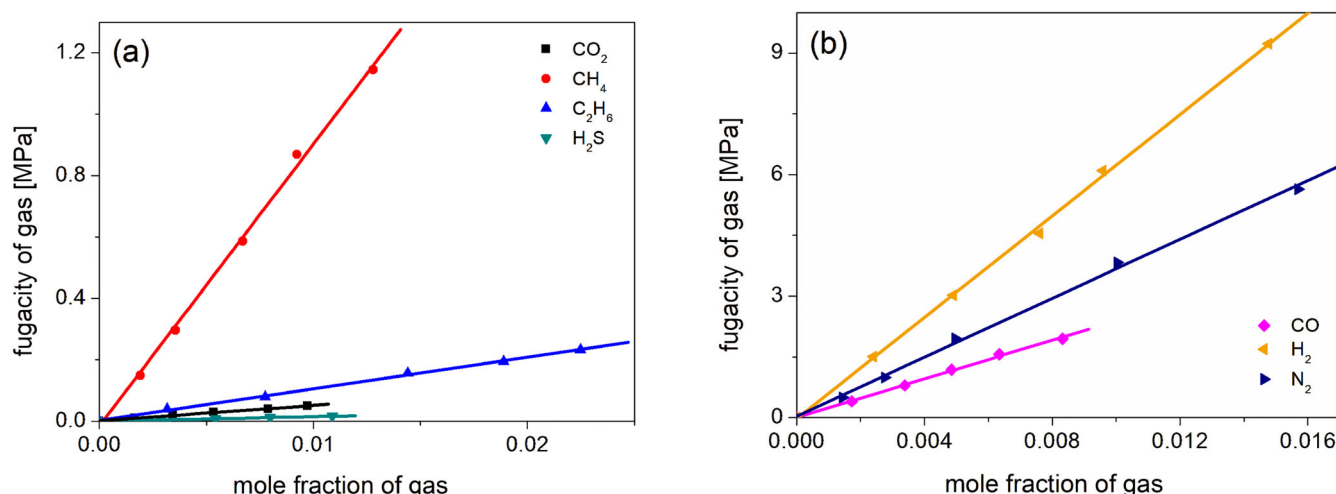


Figure 3. (Colour online) (a) Solubility of CO₂, CH₄, C₂H₆, and H₂S in methanol at 248 K. (b) Solubility of CO, H₂, and N₂ in methanol at 248 K.

Table 6. Selectivities of CO₂ over CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in methanol at a temperature of 248 K, and in PEGDME, NMP and PC at a temperature of 298 K.

Separation	Methanol	PEGDME (<i>n</i> =4)	PEGDME (<i>n</i> =6)	PEGDME (<i>n</i> =4, 6)	NMP	PC
CH ₄ /CO ₂	18.4	17.2	18.0	19.7	12.0	7.73 ± 0.04
C ₂ H ₆ /CO ₂	2.05 ± 0.04	4.11 ± 0.03	3.66 ± 0.04	4.13 ± 0.05	1.82 ± 0.04	1.70 ± 0.04
CO/CO ₂	47.8	29.4	33.0	36.3	44.8	35.2
H ₂ /CO ₂	125	73.0	94.6	100	128	88.2
N ₂ /CO ₂	72.8	52.0	41.6	47.1	97.1	51.4
CO ₂ /H ₂ S	3.40 ± 0.04	2.13 ± 0.02	2.16 ± 0.07	1.94 ± 0.03	7.41 ± 0.04	4.60 ± 0.04

good performance in selective CO₂ removal from syngas consisting of CH₄, CO, H₂, and N₂ in the precombustion process. In the natural gas sweetening process, the CO₂/C₂H₄ and CO₂/C₂H₆ separation are also feasible in all the four commercial solvents studied. In addition, a screening of the four solvents indicates that NMP has superior CO₂/H₂S selectivity over methanol, PEGDME, and PC, which is a well-known advantage of the NMP solvent. Although the ideal selectivities calculated from the computed Henry coefficients in this work are generally consistent with those calculated from experimental solubility data from the literature [20], the real selectivities are expected to deviate from the ideal selectivities. For binary gas mixtures in the feed, there are interaction and competition between different solutes during the physisorption process. Specifically, the presence of CO₂ may negatively influence the solubilities of CO, N₂, H₂, CH₄ and C₂H₆ in the physical solvents, so the real relevant selectivities are expected to be lower. Similarly, since H₂S is much soluble than CO₂ in the investigated physical solvents, the absorption of CO₂ could be significantly hindered by the presence of H₂S. As a result, the real selectivity for H₂S/CO₂ may become much lower. However, it should be noted that Ramdin et al. have found that the presence of CO₂ does not greatly impact the solubilities of N₂ or CH₄ in several ionic liquids (ILs) regardless of the feed gas composition [11, 94], but whether the situation in ILs with exceptionally high viscosity can be applied to the four commercial solvents in this work remains to be studied.

The ratios of Henry coefficients of CO₂ to N₂O are calculated to verify the CO₂/N₂O analogy in these polar physical solvents. As listed in Table 7, the CO₂/N₂O ratios are below unity in methanol, NMP, and PC, while the CO₂/N₂O ratios are above unity in all three PEGDME solvents. Similar to our previous findings [44], solvents with larger dipole moments (e.g. NMP) are likely to absorb more CO₂, while solvents with smaller dipole moments (e.g. PEGDME) are likely to absorb more N₂O. The CO₂/N₂O solubility ratios in these solvents range from 0.878 to 1.13, indicating that the CO₂/

N₂O analogy holds for the solubility in methanol at 248 K, and PEGDME, NMP, and PC at 298 K.

4. Conclusions

This work intends to use CFCMC simulations in the osmotic ensemble to compute the Henry coefficients of the pure gases CO₂, CH₄, C₂H₆, CO, H₂, N₂, N₂O, and H₂S in four commercial physical solvents including methanol, PEGDME, NMP, and PC. The computed Henry coefficients are overall in good agreement with the experimental results. The following gas solubility trend can be observed in our simulations for all the solvents: H₂S > CO₂ > C₂H₆ > CH₄ > CO > N₂ > H₂. Furthermore, the gas separation selectivities for CH₄, C₂H₆, CO, H₂, N₂, and H₂S over CO₂ are calculated from the pure gas Henry coefficients. The results indicate that CO₂ can be selectively removed from syngas consisting of CH₄, CO, H₂, and N₂ in the precombustion process, and from CH₄ and C₂H₆ in the natural gas sweetening process. Finally, the ratios of the Henry coefficients of CO₂ to N₂O which are close to unity validate the CO₂/N₂O analogy for the solubility in these physical solvents. Our research shows that molecular simulation is a powerful tool to predict the gas solubility in solvents especially in the absence of experimental data.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was sponsored by NWO Exacte Wetenschappen (Physical Sciences) for the use of computer facilities, with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for Scientific Research, NWO).

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Table 7. Ratios of Henry Coefficients of CO₂ to N₂O in methanol, PEGDME, NMP, and PC at a temperature of 248 K for methanol and a temperature of 298 K for PEGDME, NMP, and PC.

Solvent	[H(CO ₂)/H(N ₂ O)] _{sim}
methanol	0.950 ± 0.048
PEGDME(<i>n</i> =4)	1.08 ± 0.02
PEGDME(<i>n</i> =6)	1.06 ± 0.08
PEGDME(<i>n</i> =4,6)	1.13 ± 0.04
NMP	0.878 ± 0.048
PC	0.915 ± 0.035

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