



Solubility of sulfur compounds in commercial physical solvents and an ionic liquid from Monte Carlo simulations



Seyed Hossein Jamali ^a, Mahinder Ramdin ^a, Tim M. Becker ^a, Ariana Torres-Knoop ^b, David Dubbeldam ^b, Wim Buijs ^a, Thijs J.H. Vlugt ^{a,*}

^a Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, Leeghwaterstraat 39, 2628CB, Delft, The Netherlands

^b Van 't Hoff Institute of Molecular Sciences, University of Amsterdam, Science Park 904, 1098XH, Amsterdam, The Netherlands

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ABSTRACT

Natural gas, synthesis gas, and flue gas typically contain a large number of impurities (e.g., acidic gases), which should be removed to avoid environmental and technological problems, and to meet customer specifications. One approach is to use physical solvents to remove the acidic gases. If no experimental data are available, the solubility data required for designing the sweetening process can be obtained from molecular simulations. Here, Monte Carlo (MC) simulations are used to compute the solubility of the gas molecules, i.e., carbonyl sulfide, carbon disulfide, sulfur dioxide, hydrogen sulfide, methyl mercaptan, carbon dioxide, and methane in the commercial solvents tetraethylene-glycol-dimethyl-ether (Selexol), n-methyl-2-pyrrolidone, propylene carbonate, methanol (Rectisol), and the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]). Henry coefficients of the gases in the investigated solvents are obtained from the computed solubilities. The ratio of Henry coefficients is used to compute ideal selectivities of the solvents. The solubilities and selectivities computed from MC simulations are compared with available experimental data. Some guidelines are provided to remove acidic gases using the investigated solvents. Rectisol is the best solvent for acid gas removal, but it should be used at low temperatures. Selexol and the ionic liquid have similar selectivity of sulfur compounds with respect to methane and may be used at elevated pressures and temperatures since both have low vapor pressures. The solubility of carbon disulfide, sulfur dioxide, and methyl mercaptan in these solvents is the highest. Hence, these components can be removed easily prior to hydrogen sulfide, carbonyl sulfide, and carbon dioxide in a pre-absorber.

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1. Introduction

Natural gas typically contains a wide range of light hydrocarbons, sulfur and nitrogen compounds, and other inorganic molecules [1]. The presence of acidic gases in natural gas, in particular sulfur compounds, is a major concern because of their corrosivity, toxicity, and ability to deactivate catalysts [2,3]. Therefore, it is essential to remove these components before the natural gas is further processed. Typical sulfur compounds in natural gas are hydrogen sulfide (H₂S), sulfur dioxide (SO₂), carbonyl sulfide (COS), carbon disulfide (CS₂), and organic sulfur compounds such as mercaptans (RSH) [1]. These components can be inherently present

in natural gas or can be produced during the processing of the gas or after burning sulfur-containing fuels. The aim of natural gas separation is to obtain pure light hydrocarbons [3]. This means that the acidic gases, i.e., CO₂ and sulfur compounds, have to be reduced substantially without removing valuable products such as methane.

Typically, these acidic components are removed using physical, chemical, or hybrid solvents [4] as well as other methods like membrane separation and cryogenic fractionation [5]. Chemical solvents react with solutes (CO₂, H₂S, etc.) and the solute-rich solvent is regenerated by applying heat. In contrast, physical solvents do not react, but physically absorb acidic gases. At high pressures, the acidic gases dissolve in the solvent, which is regenerated by reducing the pressure (flashing) or applying heat. Compression of the feed gas for acid gas removal is not economic unless the acidic gases have high partial pressures [4]. Therefore,

* Corresponding author.

E-mail address: t.j.h.vlugt@tudelft.nl (T.J.H. Vlugt).

physical solvents are attractive when acidic gases constitute a large fraction of the feed gas with high partial pressures (50–100 psi) whereas chemical solvents are appropriate for removing acidic gases with low partial pressures (10–15 psi) [4].

The main industrial chemical solvents for removing acidic gases cover a wide range of fluids such as amines (e.g., monoethanolamine (MEA), dimethylethanolamine (DMEA), and diisopropylamine (DIPA)), activated hot potassium carbonate [4]. The main industrial physical solvents considered for acid gas removal are propylene carbonate (PC, Fluor solvent process), N-methyl-2-pyrrolidone (NMP, Purisol process), methanol (Rectisol process), and polyethylene-glycol-dimethyl-ether (Selexol process) [1]. Hybrid processes utilize physical and chemical solvents to combine the advantages of both types. For instance, in the Sulfinol process, sulfolane is used as a physical solvent to remove the bulk of the acidic gases while DIPA chemically absorbs the remaining impurities.

A comprehensive discussion about commercial solvents, their processes along with their advantages and disadvantages is available in the book by Kohl and Nielsen [1]. Polyethylene-glycol-dimethyl-ether (DEPG) with the structural formula $\text{CH}_2\text{O}(-\text{C}_2\text{H}_4\text{O})_n\text{CH}_3$ (n between 3 and 9) is a solvent used in various commercial processes such as Selexol and Coastal AGR. Here, whenever the term Selexol is used, it refers to DEPG. Selexol has not only a high affinity for H_2S , but also absorbs CO_2 , mercaptans, COS, and other sulfur compounds [1,5]. Selexol has a high viscosity, so it is preferably used at high temperatures. The operating temperature of the process ranges from 0 °C up to 175 °C. In the Purisol process, NMP is used as a physical solvent to remove acidic gases. NMP has the highest $\text{H}_2\text{S}/\text{CO}_2$ selectivity among the commercial physical solvents [5]. Unfortunately, NMP has the highest vapor pressure at its working temperature compared to the other physical solvents, which is a major drawback. Therefore, NMP recovery may be necessary to prevent solvent losses through the process [5]. The working temperature of NMP ranges from –15 °C up to ambient temperatures. The processes known as “Rectisol”, “Ilfexol”, etc. use methanol as the physical solvent [1]. Hereafter, whenever the term Rectisol is used, it refers to methanol. Rectisol is mainly used for synthesis gas purification, and it can separate H_2S from CO_2 [1]. The vapor pressure of methanol at room temperature is high. Therefore, Rectisol is often applied at relatively low temperatures between –70 °C and 0 °C [5]. This requires a huge refrigeration load, which makes the process expensive. Unless a high H_2S selectivity is required, this process is not economically appealing because of its high capital and operational costs [5]. PC is the physical solvent of the Fluor solventSM process [1]. PC is an appropriate solvent if CO_2 is the main component to be removed and if little H_2S is present in the raw gas. PC has a higher vapor pressure than Selexol, but it is not necessary to utilize solvent recovery. Typical operating temperatures of this process are between –18 °C and 65 °C.

In recent years, ionic liquids (ILs) have been extensively investigated for natural gas or syngas sweetening purposes [6,7] as well as for carbon capture [6,8–13]. Most of the ILs have a very low vapor pressure, high chemical and thermal stability, low flammability, and relatively high acid gas capacities [6]. One of the prominent properties of ILs is their tunability that allows the design of application-specific ILs by changing the nature of the cations and anions. Here, we selected [bmim][TF_2N] as a reference IL and a comparison of its performance for acid gas removal with respect to the commercial solvents is provided.

The design of an acid gas removal process requires solubility data of all the components present in the natural gas or syngas for a wide range of temperatures and pressures. As stated in the book by Kohl and Nielsen [1]: “The key requirement is adequate liquid/

vapor equilibrium data covering all components and conditions encountered in the process.” However, for some of the components such as mercaptans, there is little or no experimental vapor-liquid equilibrium (VLE) data available. In general, it is difficult to experimentally measure the VLE of toxic and corrosive compounds (i.e., sulfur compounds) [6]. In these cases, computational methods, e.g., Monte Carlo simulations, play an important role in providing the required VLE data. This study is a supplement to our previous experimental and simulation work, focused mainly on CO_2/CH_4 solubilities and selectivities [6,8–13]. Here, we focus on the solubility and the selectivity of sulfur compounds. As it will be shown later, there is almost no experimental data for some of the sulfur compounds in conventional physical solvents. Obtaining solubility data for these compounds can be helpful for designing more accurate processes.

In this work, we investigate the solubility of sulfur compounds (H_2S , CS_2 , COS, SO_2 , and methyl mercaptan (CH_3SH)) as well as their ideal selectivities with respect to methane and CO_2 in physical solvents by Monte Carlo (MC) simulations using RASPA, a molecular simulation software package [14,15]. The commercial physical solvents considered in this study are PC, NMP, Selexol, and methanol. Since the main component of Selexol is tetraethylene-glycol-dimethyl-ether (TTEGDME, $n = 4$), simulations are carried out exclusively for this component. The results of MC simulations are compared with available experimental data and predictions from the Peng–Robinson equation of state (PR EoS).

This paper is organized as follows. In Section 2, we describe the details of the conducted MC simulations. In Section 3, the simulation results are presented and compared with available experimental data. The solubility data are used to compute the Henry coefficient of the gases in the solvents. Subsequently, the Henry coefficients are used to calculate ideal selectivities, which are required to assess the performance of a solvent. Based on the computed data, we provide some guidelines to remove acidic gases from natural gas or flue gas.

2. Simulation details

Monte Carlo simulations are performed in the osmotic ensemble where the number of solvent molecules, temperature, and pressure of the simulation box are kept constant [7,12,13,16–23]. The vapor pressure of the investigated solvents at their operating temperature is negligible which makes it possible to consider them as non-volatile liquids in simulations. The solute molecules can be exchanged with an open reservoir having the same pressure, temperature, and fugacity of the solute in the simulation box [16]. Three types of trial moves are considered for the solvent: translation, rotation, and partial reinsertion (to take into account the internal degrees of freedom of flexible molecules). There are three types of trial moves for the solute: translation, rotation, and exchange with the open reservoir. The exchange trial move is performed by the Continuous Fractional Component MC (CFCMC) method since the high density of the mixture makes it difficult for efficient insertion of new solute molecules [17–20,24]. When computing the loading, the fractional molecule is disregarded [25]. A volume change trial move is used to regulate the pressure of the system. For more details on the Monte Carlo simulation methodology, the reader is referred to the book by Frenkel and Smit [26].

The simulation temperature is fixed at 60 °C, except for Rectisol which is –25 °C due to its high vapor pressure at the ambient temperature. All simulations are started with an equilibration run to ensure that the number of solutes, the energy level, and other properties of the system fluctuate around their average values. After reaching equilibrium, the Wang-Landau scheme [27,28] is applied to obtain the biasing factors for the CFCMC method [17].

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