

Mahinder Ramdin

CO₂ Capture with Ionic Liquids:

Experiments and Molecular
Simulations

Delft University of Technology

CO₂ Capture with Ionic Liquids: Experiments and Molecular Simulations

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Mahinder RAMDIN
Scheikundig ingenieur
geboren te Nickerie, Suriname.

This dissertation has been approved by the
promotor: Prof. dr. ir. T.J.H. Vlugt
copromotor: Dr. ir. T.W. de Loos

Composition of the doctoral committee:

Rector Magnificus	Chairman
Prof. dr. ir. T.J.H. Vlugt	Promotor, Delft University of Technology
Dr. ir. T.W. de Loos	Copromotor, Delft University of Technology

Independent members:

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Dr. B.P. Tighe	Delft University of Technology



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Dedicated to my beloved grandfather

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Chapter 1

A Brief Introduction to CO₂ Capture

Carbon dioxide (CO₂) is considered as one of the major greenhouse gases responsible for climate change [1, 2]. In the process of burning fossil fuels to produce electricity and heat (i.e., the post-combustion process), large amounts of CO₂ are emitted into the atmosphere. In order to prevent irreversible climate change, it is crucial to reduce the CO₂ emissions and one of the options to achieve this is by the carbon capture and storage (CCS) route [3]. In this route, CO₂ is captured from flue gas and subsequently stored in deep underground geological formations. CO₂ capture is not only relevant from an environmental perspective, but it has also industrial significance in the ammonia production process, hydrogen production process, and the natural gas sweetening process [4]. Alternatives for the post-combustion process are the pre-combustion and the oxyfuel combustion process, which is still in the development phase [5]. In the pre-combustion process, a fuel is gasified to produce syngas, which is a mixture of carbon monoxide (CO) and hydrogen (H₂) [6]. The syngas is shifted in a reactor to produce more hydrogen, but CO₂ is also produced in this step [7]. The CO₂ should be separated from H₂, which then can be used for several applications. Natural gas is typically contaminated with the sour gases CO₂ and hydrogen sulfide

(H₂S), which should be removed to meet customer specifications and to avoid technological problems during transportation of the gas [8].

The choice of technology to capture CO₂ at post-combustion, pre-combustion or natural sweetening conditions depends on the operating conditions of these processes [9]. Chemical solvents like monoethanolamine (MEA) are preferred for post-combustion CO₂ capture, because the low partial pressure of CO₂ in the flue gas eliminates the use physical solvents [10, 11]. Application of the amine process for CO₂ capture from flue gas at post-combustion (i.e., low pressure) conditions is mainly hindered by the high energy consumption and the immense scale of the problem [12]. To give an impression of the scale of flue gas production relative to the scale of natural gas processing, consider the following example. The global CO₂ emission and the global natural gas production in 2012 was 34.5 billion tonnes (~ 17580 billion cubic meters (bcm)) and 3364 bcm, respectively [13, 14]. Assuming that the flue gas and the raw natural gas contained 10% CO₂, one can calculate the actual volume of flue gas or natural gas that had to be processed at the power plant (175800 bcm) or at the well (3738 bcm), respectively. This simple example shows that the global scale of flue gas production is ~ 50 times larger than the global scale of natural gas production. Moreover, the estimated energy penalty of a coal-fired power plant using MEA for CO₂ capture is in the range of 25 to 45% [15]. A huge amount of steam/energy is required in the desorber for solvent regeneration and concurrent liberation of the chemically complexed CO₂ [9].

The main focus of this study is CO₂ capture at pre-combustion and natural gas sweetening conditions. The relatively high operating pressure of these processes allows the use of physical solvents or adsorbents. The physical solvents Selexol, Rectisol, and Purisol are frequently used in the natural gas industry. However, chemical/hybrid solvents (e.g., MEA/Sulfinol) are preferred over physical solvents when a deep removal of the acid gases up to few ppm levels is required. 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 [15]. 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 [9, 16, 17]. However, the performance of ILs with respect to existing solvents (e.g., Selexol, Rectisol, Purisol, etc.) is still under debate [18].

CO₂ capture at post-combustion conditions requires new solvents which are more energy efficient, less toxic and corrosive, and cheaper than existing solvents. However, designing solvents with these specific characteristics is a challenging task. Moreover, experimentally screening a large number of molecules is a costly and time consuming operation. Here, we develop and apply molecular simulation techniques to screen solvents for CO₂ capture at post- and pre-combustion conditions.

In this thesis, we investigated the potential of physical ILs for CO₂ capture at pre-combustion and natural gas sweetening conditions. The performance of ILs with respect to conventional solvents is assessed in terms of gas solubilities and selectivities. The work discussed in this thesis consists of two parts. The first part deals with experimental determination of gas solubilities in ILs, while in the second part molecular simulations are used to predict gas solubilities in physical solvents. In Chapter 2, a comprehensive review of CO₂ capture with ILs is presented. In Chapter 3, the experimental results of pure CO₂ and CH₄ solubilities in many different kinds of ILs are reported. Ideal CO₂/CH₄ selectivities are derived from the experimental data and a comparison with conventional solvents is provided. In Chapter 4, the experimental results on the solubility of CO₂/CH₄ gas mixtures in ILs is discussed. Real CO₂/CH₄ selectivities are derived from this mixed-gas solubility data. In Chapter 5, Monte Carlo (MC) molecular simulations are used to predict the solubility of natural gas components in ILs and Selexol. In Chapter 6, MC simulations are used to compute the bubble points of CO₂/CH₄ gas mixtures in ILs. In Chapter 7, MC simulations are used to compute the solubility of the pre-combustion gases CO₂, CH₄, CO, H₂, N₂ and H₂S in an IL. Separation selectivities relevant for the pre-combustion process are derived from the MC data and a comparison with experimental data is provided. In Chapter 8, a novel Monte Carlo method is developed to study the reactions of CO₂ with aqueous monoethanolamine (MEA). The so-called Reaction Ensemble Monte Carlo method in combination with the Continuous Fractional Component technique (RxMC/CFC) [19] is used to

compute the equilibrium speciation of all relevant species formed during the chemisorption process of CO₂ with aqueous MEA solutions. The computed speciation results are compared with available experimental data. Finally, Chapter 9 provides a detailed comparison of gas solubilities in ILs with respect to the conventional solvents Selexol, Purisol, Rectisol, propylene carbonate, and sulfolane.

In this work, we demonstrate that, (1) ideal CO₂/CH₄ selectivities are approximately the same as real CO₂/CH₄ selectivities, (2) gas solubilities in IL should be compared on mass or volume basis, (3) MC simulations can be used to quantitatively predict gas solubilities and equilibrium speciation in complex (reacting) solvents, (4) conventional solvents are superior to ILs in terms of gas solubilities.

Chapter 2

CO₂ Capture with Ionic Liquids: A Review

This chapter is based on the paper: M. Ramdin, T. W. de Loos and T. J. H. Vlucht. State-of-the-Art of CO₂ Capture with Ionic Liquids. Ind. Eng. Chem. Res., 51 (2012) 8149-8177.

2.1 Introduction

The suspected correlation between the increased CO₂ concentration in the atmosphere and the green-house effect has initiated a worldwide debate aimed at emission reduction of CO₂ and other green-house gases [1, 2]. CO₂ emissions have increased since the dawn of the industrial revolution. This resulted in an increase of CO₂ concentration in the atmosphere from about 280 ppm before the industrialization to 390 ppm nowadays [20]. The global CO₂ emission in 2008 was about 29.4 gigatons (Gt), which is an increase of around 40% relative to the 1990 emission of 20.9 Gt [20]. Currently the power sector is responsible for 41% of all the energy-related CO₂ emissions, followed by the transport sector (23%), industry sector (20%), buildings sector (10%) and others [21]. The high share of the CO₂ emission in the

power sector is related to fuel combustion to generate electricity or heat. The share of coal in the total CO₂ emission from fuel combustion in 2008 was 43%, while the contribution of oil and gas was 37% and 20%, respectively [20]. Under the Baseline Scenario or Reference Scenario [22], the CO₂ emission will continue to increase and will most likely double, relative to the 2007 emission of 28.8 Gt, by 2050 [21]. Under this scenario the anticipated growth in future energy demand will be met using predominantly fossil fuels. This energy path is not consistent with the required deep cuts in global greenhouse-gas emissions by 2050 to limit the long-term global average temperature rise below 2 °C relative to pre-industrial levels [23]. The 2 °C target, which is believed to be the point where dramatic climate change will set in [24], was set during the UN conference on climate change in December 2009 in Copenhagen. In the long-term, a transition in energy path, from fossil fuels to low-carbon-technologies, will be required to meet the 2 °C goal. McKinsey & Company investigated several readily available or developing low-carbon-technologies, which could be used to mitigate CO₂ emissions [25–28]. However, in the foreseeable future, fossil fuel, in particular coal [29, 30], will continue to be a substantial fraction of the energy portfolio [20]. In this regard CO₂ capture and storage (CCS) will be essential [3], although it should be considered as a temporary solution to the problem. Both, the capture of CO₂ and the storage are technical challenging and many hurdles have to be overcome to commercialize these processes [3, 31, 32].

The major barrier to commercialize the CO₂ capture and storage process at large scale is the energy/cost associated with the separation method. Currently available technology for CO₂ capture is based on amine-solvents, for example monoethanolamine (MEA) [33]. The capture of CO₂ with amines involves a chemical reaction with a large enthalpy of reaction [34]. Consequently, a large amount of heat is required to release the captured CO₂ in the regeneration step. Retrofitting a CCS unit to an existing power plant, using conventional-amine solvents for CO₂ scrubbing, would lower the energy output of the plant by 25-40% [3]. Accordingly, the price of electricity would rise by 0.01-0.07 \$/kWh relative to a plant without a CCS system [1, 35]. The energy consumption for removing one ton of CO₂, by employing a 30 wt% MEA (aqueous) solution and assuming 90%

CO₂ removal, is estimated to be in the range of 2.5-3.6 Gigajoule (GJ). The theoretical minimum work for CO₂ separation and compression to the required pressure of 150 bar is 0.42 GJ/ton CO₂, indicating the potential for process improvements [33, 36]. About half of this energy is required in the stripper to regenerate the CO₂ and the other half is used to compress the CO₂ to about 150 bar for subsequent sequestration [33]. Currently, not a single large scale plant with CCS is known to be operational. The primary reason for this is the high CO₂ removal cost ranging from 50 to 150 \$/ton CO₂ removed, although recently much lower costs (30-35 \$/ton CO₂) were reported [37]. Even a lower and debatable cost of 15 \$/ton CO₂ was reported by Inventys [38], but their technology is based on an adsorbent material instead of amines. However, the existing methodologies for CO₂ capture are energy intensive and far from cost effective, hence unattractive for large scale applications [1]. Therefore, much research has been devoted to find or design new solvents/materials for CO₂ capture. This includes CO₂ separation by chemical/physical absorption, chemical/physical adsorption, membranes, solid adsorbents and biomimetic approaches [5, 12, 15, 39, 40]. Recently D'Alessandro *et al.* [15] reviewed new and emerging materials for CO₂ capture, with particular attention for Metal-Organic Frameworks (MOFs). A special class of absorption materials, namely ionic liquids (ILs), have been proposed as an alternative to the volatile, corrosive and degradation sensitive amine-solvents [41, 42].

Ionic liquids are salts, which consist exclusively of ions, with a melting point lower than 100 °C [43]. The use of ionic liquids, although discovered a long time ago, was very limited until the late 1990s to few examples in electrochemistry and organic chemistry. This changed unexpectedly as a result of an article published by Freemantle [44] in 1998, describing the potential applications of ionic liquids as novel solvents for green chemistry [45–47]. Since then, ionic liquids have been the interest of many researchers, resulting in an expansion of the application field. So far, (potential) applications of ionic liquids have been reported in analytical chemistry [48], biochemistry [43], catalysis [49–51], electrochemistry [52, 53], separation technology [54–57], fluid engineering [58] and others [59, 60]. ILs are nowadays applied at industrial scale in the BASIL™ process of BASF for pro-

ducing alkoxyphenylphosphines and the Degussa process for pigment paste production [61]. We note that the IL in the BASIL process does not serve as a solvent, but it is produced during the reaction step. ILs owe their unexpected popularity to their remarkable properties, such as: (nearly) negligible volatility, high thermal stability, non-flammability, tunability, solvation properties and high CO₂ solubility. The major driving force for research on ILs is their potential to replace traditional industrial solvents, which are often volatile organic compounds (VOCs). Substitution of the conventional volatile solvents by the relatively non-volatile ionic liquids would prevent environmental pollution due to emission of VOCs into the atmosphere. Furthermore, the tunability property of ILs provide an extra degree of freedom for designing solvents with certain specific characteristics [62].

This introduction provides an indication of the scale of the problem and the urgency to take action in order to prevent irreversible climate change. CCS is one of the remedies to the problem and in the following we will focus on the special application interest of ionic liquids as a CO₂ capture medium. Blanchard *et al.* [41] were the first to observe that significant amounts of CO₂ could be dissolved in imidazolium-based ionic liquids to facilitate an extraction of a dissolved product, without contaminating that product with the ionic liquid, since the ionic liquid was insoluble in CO₂. This study initiated an explosion of scientific research on CO₂ absorption with ionic liquids, leading to a rapid growth of the literature on this specific topic [63]. Therefore, the aim of the present chapter is to give an extensive review of the achievements and recent developments in the search for a suitable ionic liquid for CO₂ capture from flue-gas streams and other point-sources. This review provides a different perspective on CO₂ capture with ILs than those published in other recent reviews [17, 55, 64–68]. That is, we focus on the potential application of ILs for CO₂ capture at the post-, pre-combustion and natural gas sweetening process. More importantly, a comparison of the CO₂ capture performance (i.e. solubility, selectivity, viscosity, price, etc.) of ILs with the commercially available solvents is presented. The review is started with an analysis of the relevant CO₂ capture processes (i.e. post-combustion, pre-combustion, oxyfuel combustion and natural gas

sweetening) and the conventional amine technology. Subsequently, a comprehensive overview of the main literature on CO₂ capture with ionic liquids is given. More specifically, attention is paid to the trends observed regarding CO₂ solubilities and selectivities in different ionic liquids, effect of anions, cations and functional groups on physical properties, biodegradability and toxicity of ionic liquids. The CO₂ capture performance of ILs is then compared with existing solvents (e.g. Selexol, Purisol, Sulfinol, etc.). The trends highlighted here may eventually help solvent designers to navigate through the massive number (about 10¹⁸) of theoretically possible ternary IL systems [62, 69]. Recent developments on task specific or functionalized ionic liquids and supported ionic liquid membranes are also discussed. Finally, the remaining challenges and future research possibilities are outlined.

2.2 CO₂ Capture Processes

The conditions for CO₂ capture, hence also the economics, are determined by the technology used for the production of electricity (or heat) from fossil fuels [70]. Today, a power company planning to build a new power station utilizing fossil fuels, can choose from two technologies, and a third one, which is in the development phase [71]. The characteristics of all the three processes (i.e. post-combustion, pre-combustion and oxyfuel combustion) are different, yielding different conditions for CO₂ capture.

2.2.1 Post-combustion Capture

The first option is the post-combustion process [72], which is widely used at traditional fossil-fuel-fired power stations to produce electricity. Under post-combustion conditions the fuel is burned fully in one step in air, see Figure 2.1. The released heat is used to produce high-pressure steam, which drives a steam turbine to generate electricity. The flue-gas leaving the boiler contains substantial amounts of particulate matter, which is filtered out in the soot removal step. Subsequently, the sulphur in the flue-gas is scrubbed by a limestone slurry to produce gypsum. The cleaned flue-gas, which now contains 10-16% CO₂, would be released into the atmosphere in the absence

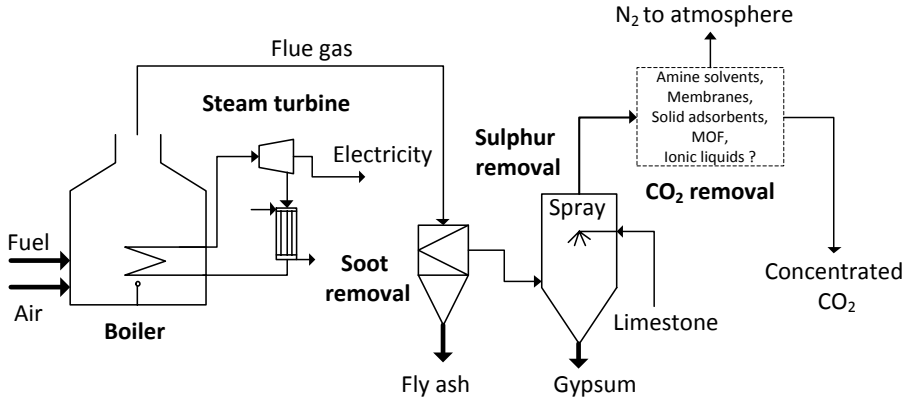


Figure 2.1: Schematic representation of a simplified post-combustion CO₂ capture system [72]. In this process, the fuel is directly burned in air to produce large volumes of fluegas with low partial pressures of CO₂. The CO₂ can in principle be captured with amines, but this process turns out to be expensive [15].

of a CO₂ capture system. However, as explained in the introduction, the role of CO₂ in the global warming requires it to be captured and stored safely underground for some time. The following can be stated by analyzing the data shown in Table 2.1 for the post-combustion process; (1) the relevant separation is CO₂/N₂, hence any separation process should be CO₂ selective and (2) the process outputs large volumes of flue-gas with low CO₂ partial pressures, accordingly the separation process should be able to cope with these conditions. We will see later that a low CO₂ partial pressure, which is typical for post-combustion processes, is not very advantageous for (physical) CO₂ capture. However, the advantage of the post-combustion process is that the CCS unit can be retrofitted without major modifications to an existing power plant.

Table 2.1: Typical conditions for post-combustion [15, 66] capture, pre-combustion [15, 73] capture and the natural gas sweetening [6, 17, 74] process.

	Post-combustion	Pre-combustion ^a	Natural gas sweetening
Gas composition	by mole	by mole	by mole
CO ₂	10-15%	37.7%	0.1-8%
H ₂ O	5-10%	0.14%	
H ₂		55.5%	
O ₂	3-4%		
CO	20 ppm	1.7%	
N ₂	70-75%	3.9%	0-0.2%
NO _x	<800 ppm		
SO _x	<500 ppm		
H ₂ S		0.4%	0-15%
CH ₄			70-95%
C2+			0-15%
Conditions			
Temperature (°C)	40-75	40	30-40
Pressure (bar)	1	30	5-120

^a After the water-gas-shift reaction

2.2.2 Pre-combustion Capture

The second option is the pre-combustion process [75], which is associated with the integrated gasification combined cycle (IGCC) and is more complex as shown in Figure 2.2. In this approach the fuel (coal, oil, etc.) is gasified, rather than burning it completely like in the post-combustion process, in presence of pure oxygen and steam to produce syngas. The syngas, which is a mixture of carbon monoxide (CO) and hydrogen (H₂), is purified and fed to the water-gas-shift (WGS) reactor. In this reactor, steam is added to convert the CO, according to the water-gas-shift reaction, to H₂ and CO₂. The gas can be desulfurized either before or after the WGS reactor, but preferentially before since any sulphur may be poisonous to the catalyst

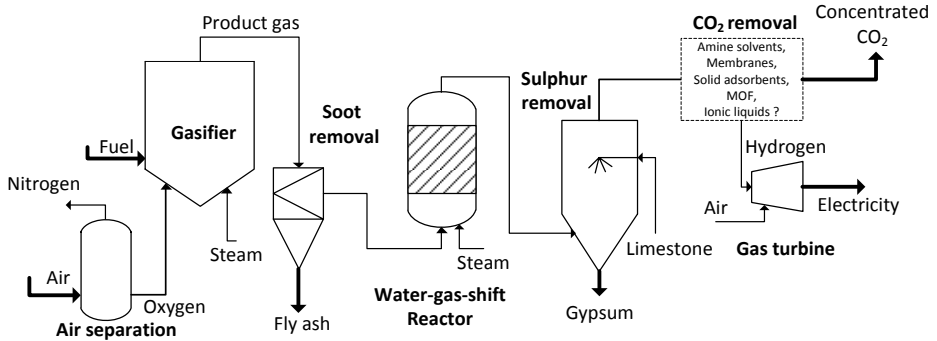


Figure 2.2: Schematic representation of a simplified pre-combustion CO₂ capture system [75]. In this process, the fuel is first gasified to produce syngas, which is converted to CO₂ and H₂ in the WGS reactor. Since this process operates at high pressures, the CO₂ can in principle be captured by several techniques.

used in the WGS reactor [6]. At this stage the gas consist primarily of CO₂ and H₂. Subsequently, the CO₂ is captured and the H₂ is combusted in a gas turbine to produce electricity and heat. The heat produced during the combustion can be recovered by a heat recovery system (not shown in Figure 2.2) to generate more electricity. The typical conditions, after the WGS reactor, for pre-combustion CO₂ capture are given in Table 2.1, from which we can deduce that the relevant separation is CO₂/H₂. Furthermore, the pre-combustion process yields a gas mixture with high CO₂ partial pressures, which is favorable for CO₂ separation.

2.2.3 Oxyfuel Combustion Capture

The third option is the oxyfuel combustion [76] process, which is a promising concept but still under development. A simplified schematic representation of this process is given in Figure 2.3. In this approach concentrated oxygen, instead of air, is used to burn the fuel. The released heat is used to produce high-pressure steam, which turns a steam turbine to generate electricity. The flue-gas, which mainly consists of H₂O and CO₂, is stripped of the soot

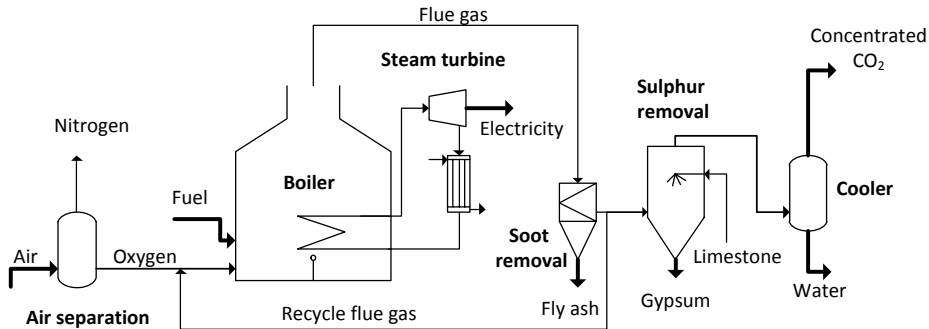


Figure 2.3: Schematic representation of a simplified oxyfuel-combustion CO₂ capture system [76]. In this process, pure oxygen instead of air is used to burn the fuel, thereby eliminating nitrogen in the downstream separation.

particles and partly recycled to the boiler to control the temperature. The remaining flue-gas stream is desulphurized and cooled down to condense the water. The result is a concentrated stream of CO₂, which is ready to be stored underground. The fundamental difference between this process and the other two processes is that no CO₂ capture is involved; instead N₂/O₂ is the relevant separation in this process. The concentrated CO₂ stream is a result of excluding nitrogen in the burning step.

Detailed economic evaluation of the three processes is provided by the US Department of Energy [77–84]. These cost estimation studies suggest that pre-combustion CO₂ capture is the least expensive option for CO₂ capture, but the investment for this process is higher than for the post-combustion and oxyfuel combustion process. In fact, pre-combustion and oxyfuel combustion technology can only be applied at new power plants, since existing power plants operate and will continue to operate at least a decade according to the post-combustion scheme [77]. Currently, no commercial power plant (either post- or pre-combustion) with CCS is in operation, hence cost estimates are highly uncertain [28]. Nevertheless, the factors determining the cost for the different CO₂ capture processes can

readily be identified. The most expensive component at post-combustion conditions in the CCS chain process is the CO₂ absorption/desorption, in particular the solvent regeneration step. In addition, the post-combustion capture process produces CO₂ at low pressures compared to sequestration requirements, adding significant expenses for pressurization. On the other hand, the advantage of the post-combustion process is that the CCS unit can be retrofitted directly, without major modifications, to an existing power plant. The pre-combustion process benefit from the high operating pressures, since (1) CO₂ is produced at high pressures reducing cost for pressurization, and (2) the higher pressures allows application of less energy intensive separation technologies. However, these cost savings may be offset as the capital cost might be higher due to the complexity of the process. The utilization of an expensive high-pressure WGS reactor and a costly air separation unit may bring extra cost. The major disadvantage of the pre-combustion capture process is that it can be applied only at new power plants, since the majority of the existing power plants operate according to the post-combustion method. The oxyfuel combustion process eliminates the expensive CO₂ capture step, but on the other hand the process requires a costly air separation step. The boiler of the oxyfuel combustion process requires special construction materials to withstand the high temperatures, which is a consequence of using pure oxygen [5]. Other concern of the oxyfuel combustion process is the high SO₂ concentration in the flue gas causing tube corrosion [85]. It is evident that CCS will bring extra cost and that the cost will be governed by the process type utilized for power generation.

2.2.4 Natural Gas Sweetening

CO₂ capture is not only important from an environmental perspective, but is also of industrial relevance in the natural gas sweetening process. The global natural gas demand is expected to increase with 1.4% per year the coming two to three decades [86]. Hence it would be beneficial to find an efficient and cost effective method for CO₂ removal from natural gas. Natural gas contains large amounts of methane (CH₄), but also all kind

of impurities resulting in a classification as 'sour' for high content of sour gases (e.g. H₂S and CO₂) or 'sweet' for low content of H₂S and CO₂. The composition of natural gas is highly dependent on the location of the gas field, which is reflected in the large variation of the natural gas components shown in Table 2.1. The relevant separation in this process is CO₂/CH₄, but an additional separation may be required if other (e.g. H₂S) sour gases are involved. However, the acid gases in the natural gas should be removed at the well to avoid technological problems during gas transportation and to comply with environmental regulations [17]. Accordingly, the CO₂ should be removed to prevent dry ice or gas hydrate formation, which can clog the system during liquefaction of the natural gas. Furthermore, the corrosiveness of H₂S and CO₂ in the presence of water, the toxicity of H₂S and the lack of heating value of CO₂ requires sweetening of the sour natural gas [87]. The most popular technology, comprising for over 95% of the units in the field in the United States [17], to capture H₂S and CO₂ is amine-based, although the high pressure at the gas well (see Table 2.1) allows the use of physical absorbents, solid adsorbents and membranes [15]. In fact, physical solvents like Rectisol, Purisol and Selexol are preferred over chemical solvents for high pressure gas purification processes [10].

2.2.5 Conventional Amine Technology

Many CO₂ capture technologies are under investigation, but presently amine scrubbing is probably the only feasible technology to capture CO₂ from a large scale fossil-fuel-fired power plant [33]. Amine scrubbing for CO₂ removal is a mature technology used in the ammonia process, steam reforming process and the natural gas sweetening process [34]. Many alkanolamines, like primary amines monoethanolamine (MEA) and diglycolamine (DEA), secondary amines like diethanolamine (DEA) and diisopropanolamine (DIPA) and tertiary amines like methyldiethanolamine (MDEA) and triethanolamine (TEA) and sterically hindered amines have been considered for CO₂ capture [34]. However, due to its high reactivity with CO₂, MEA is predominantly used for CO₂ capture. A typical process configuration for post-combustion CO₂ capture from flue-gas streams

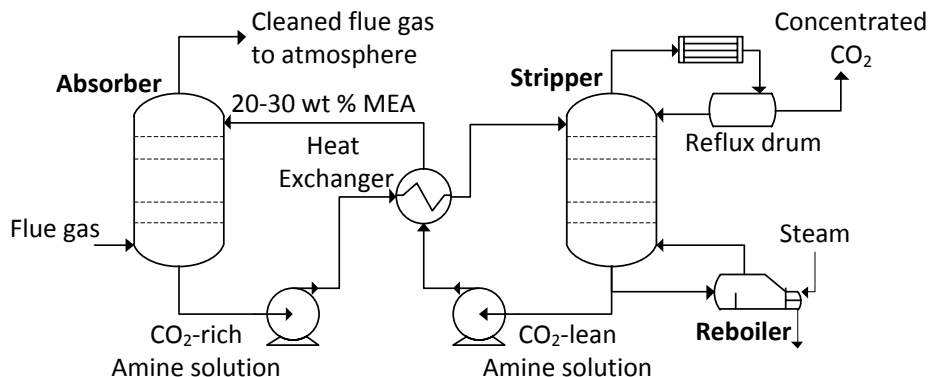


Figure 2.4: Schematic representation of a simplified process for CO₂ absorption with amines [33]. CO₂ is captured in the absorber by a reaction with monoethanolamine (MEA) and subsequently released in the stripper by heating.

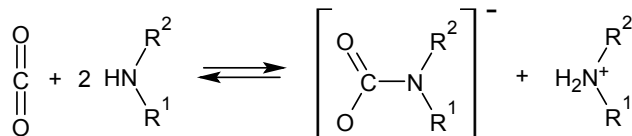


Figure 2.5: Absorption of CO₂ with primary amines. CO₂ reacts in a 1:2 stoichiometry with a primary amine forming a carbamate salt.

is shown in Figure 2.4. The flue-gas, which is typically at 40-60 °C, is introduced at the bottom of an absorption tower, while a 20-30 wt% MEA solution is continuously added at the top. The CO₂ in the flue gas is selectively and chemically absorbed by a primary amine (e.g. MEA) through a zwitterion mechanism [34] to form carbamates, see Figure 2.5. Subsequently, the CO₂-rich amine solution is drained off from the bottom of the absorber and introduced at the top of the stripper where the bounded CO₂ is released upon heating with steam. The regeneration of the amine solvent

and concurrently liberation of the CO₂ takes place at elevated temperatures, typically at 100-140 °C, and at near atmospheric (1-2 bar) pressures. The regenerated amine solvent is recycled back to the absorption tower for continuing the cycle. The concentrated CO₂ stream leaving the stripper is ready to be stored underground after pressurization.

The major drawback of this process is the high energy requirement for solvent regeneration, which is a consequence of the high reactivity of MEA leading to a large enthalpy of reaction associated with the carbamate production. Beside this energy penalty, MEA suffer a number of other drawbacks making it unattractive for large scale applications. These include the corrosiveness of MEA, this in fact is the reason for using dilute solutions, degradation of the solvent in the presence of oxygen, and the volatility of the solvent, which causes environmental pollution [15]. Furthermore, the theoretical maximum CO₂ loading of MEA for the carbamate formation scheme is approximately 0.5 mol CO₂ per mol of MEA, as can be deduced from Figure 2.5 [34]. Clearly, MEA is not a very energy efficient and environment friendly solvent for CO₂ capture. Hence, much research focused on developing solvents with improved characteristics with respect to the following: energy requirements for solvent regeneration, CO₂ loading, kinetics, volatility, chemical degradation and corrosivity [88]. Improved amines, such as the secondary amines (e.g. DEA) and tertiary amines (e.g. MDEA) have been considered as an alternative for MEA. The reaction of CO₂ with secondary amines is also described by the zwitterion mechanism, but the enthalpy of reaction is lower due to the lower stability of the carbamate formed during the reaction [15]. Since tertiary amines do not have any hydrogen atom attached to the nitrogen atom, the carbamation reaction cannot take place. Instead, bicarbonate formation takes place according to a base-catalyzed hydration mechanism [34]. The enthalpy of reaction for the bicarbonate formation is lower than for the carbamate formation, resulting in a lower energy penalty for solvent regeneration. In addition, tertiary amines have a theoretical CO₂ loading capacity of 1 mole of CO₂ per mole of amine, although the reactivity of tertiary amines with respect to CO₂ is lower [34]. This is inherent to the thermodynamics of the reaction, since the enthalpy of reaction is related to the CO₂ capacity as $\ln K = -\Delta_r G^0 / RT$,

with K the equilibrium constant of the reaction, $\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$ the standard Gibbs reaction energy, $\Delta_r H^0$ the standard enthalpy of reaction and $\Delta_r S^0$ the standard entropy of the reaction. Clearly, there is a trade-off between aiming a high CO₂ capacity at a certain temperature and wanting to keep the enthalpy of reaction low at the same time [66].

Given the many disadvantages of the amine-process, it is highly desirable to develop solvents that perform substantially better than conventional amines with respect to energy requirement for solvent regeneration, corrosivity, chemical degradation, thermal stability and volatility. The last decade, ionic liquids (ILs) have emerged as a promising alternative to the amines due to their remarkable properties, such as negligible volatility, high chemical/thermal stability and tunability. The latter is probably the most important property of ionic liquids, since it allows design of task-specific ionic liquids (TSILs). In the following we analyze the data reported in the literature on CO₂ capture with ionic liquids.

2.3 CO₂ Capture with Ionic Liquids

The number of possible ILs is very large. Few examples of commonly used cations and anions of ILs are shown in Figure 2.6, where the R_{*i*} groups are often alkyl groups. Among these ILs, the imidazolium class is most widely investigated and reported in the literature. Initial research on CO₂ capture with ILs focused primarily on the phase behavior of CO₂ with different physical (non-functionalized) ionic liquids. As shown in Figure 2.7, the phase behavior of IL-CO₂ systems is remarkable compared to conventional organic solvents (e.g. n-hexane, toluene). Firstly, a relatively large amount of CO₂ can be dissolved in a typical ionic liquid, like [emim][Tf₂N]. Secondly, conventional molecular solvent-CO₂ systems show a simple two-phase envelope with a mixture critical point at moderate pressures [89]. Clearly, this is not the case for a CO₂-IL system, instead CO₂ dissolves well at low pressures, but at higher mole fractions of CO₂ the bubble-point pressure sharply increases to very high pressures, without showing a critical point at moderate pressures. This unusual behavior is common for CO₂-IL systems

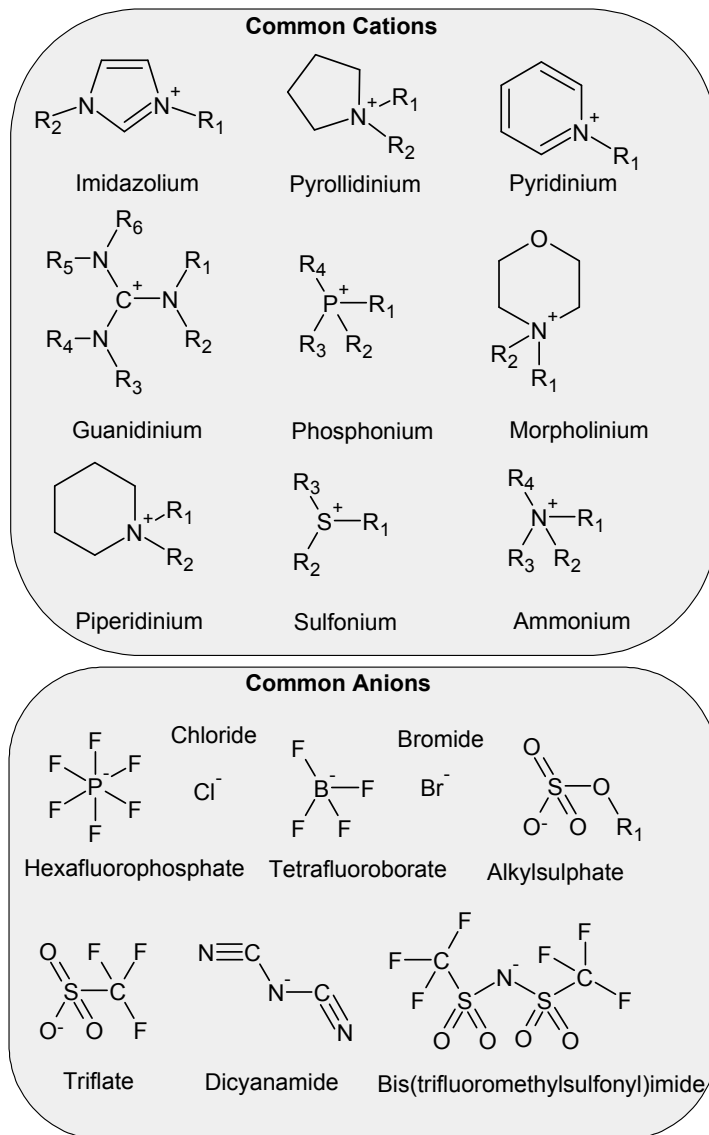


Figure 2.6: Commonly used anions and cations of ionic liquids.

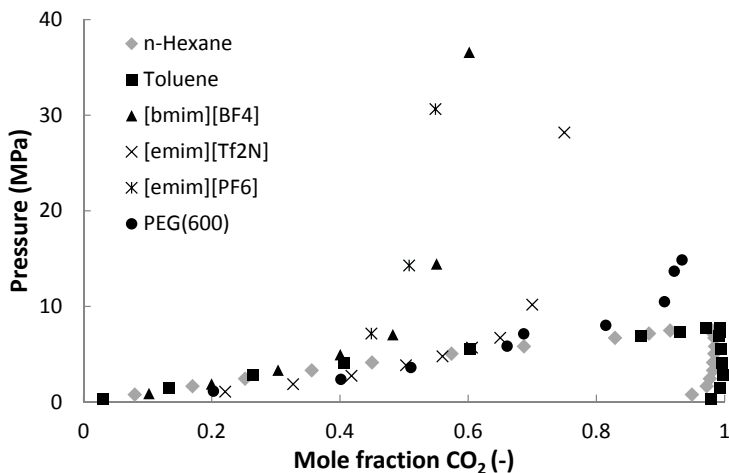


Figure 2.7: Comparison of the VLE phase behavior of CO₂-conventional solvents systems with CO₂-ILs systems. Conventional solvents show a critical point at moderate pressures, whereas ILs systems do not show this behavior. The behavior of CO₂-IL systems is comparable with high molecular weight liquid polymers, for example PEG(600)-CO₂ system. Data at 313 K taken from Refs [90–95].

and can be classified as type III fluid-phase behavior according the classification of van Konynenburg and Scott [92, 96]. We note, however, that it is not fair to compare high molecular weight and almost nonvolatile ILs with low molecular weight volatile compounds. A more justifiable comparison of CO₂-IL systems would be that with high molecular weight liquid polymers. As shown in Figure 2.7, the PEG(600)-CO₂ system shows a behavior comparable to that of CO₂-IL systems. In the following a more systematic approach is used to show trends regarding CO₂ capture with ILs.

2.3.1 Physical Ionic Liquids

In this section we will only concentrate on CO₂ absorption by conventional ILs based on a physical mechanism (i.e. upon absorption of CO₂, no chemical reaction takes place). CO₂ solubility, selectivity, ionic liquid viscosity and volatility are considered.

CO₂ Solubility

The anion is believed to play a key role in the dissolution of CO₂, whereas the cation is supposed to have a secondary role [97]. This finding is supported by molecular simulation studies and experimental data [98, 99]. To help understanding the high solubility in imidazolium ILs, Cadena *et al.* [99] used molecular simulations. These authors found that the CO₂ primarily associates with the [PF₆] anion, regardless of the cation. The in situ ATR-IR spectroscopy data of Kazarian *et al.* [100] again reveals the favorable interaction between the anions ([BF₄] and [PF₆]) and CO₂. The spectroscopic data suggested that the interaction is a Lewis acid-base type where the anion serve as a Lewis base, while CO₂ act as a Lewis acid. Furthermore, the spectroscopic data provide strong evidence that the interaction between CO₂ and [BF₄] anion should be stronger than for the [PF₆] anion, since [BF₄] is a stronger base. However, experimental solubility data show a higher CO₂ solubility in [bmim][PF₆] rather than [bmim][BF₄]. Thus, the solubility cannot solely be explained by anion-CO₂ interactions and a free volume mechanism is also expected to play a significant role in dissolving CO₂ [100]. A free volume mechanism where CO₂ molecules are hosted in the free spaces (cavities) of the liquid is not unlikely, since the liquid volume of ILs do not change significantly upon dissolution of large amounts of CO₂ [89, 97, 99]. In addition, Kanakubo *et al.* [101] performed X-Ray diffraction measurements on the [bmim][PF₆]-CO₂ system and showed that CO₂ preferentially organizes around the [PF₆] anion. The effect of the anion has been studied experimentally by pairing the [bmim] cation with several anions as shown in Figure 2.8. This figure show data at 333 K with CO₂ solubilities increasing in order of the anions: [NO₃] < [SCN] < [MeSO₄] < [BF₄] < [DCA]

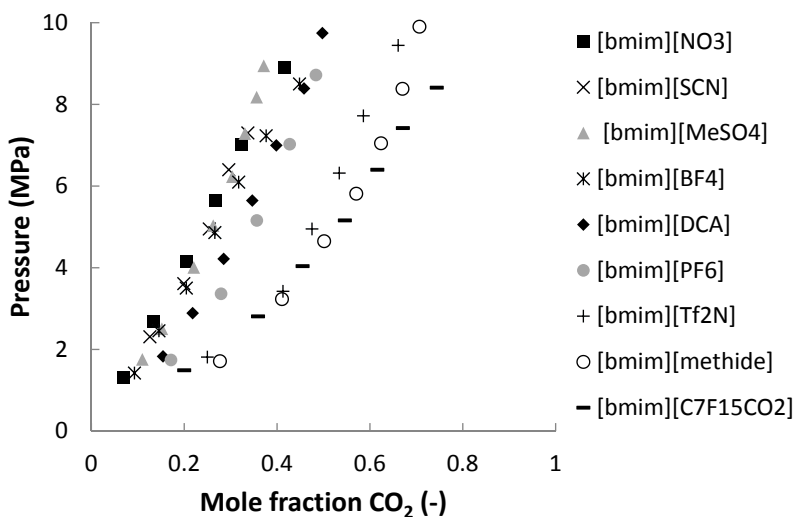


Figure 2.8: Effect of anion on CO₂ solubility. Fluorinated anions show higher CO₂ solubilities than unfluorinated ones. Data at 333 K taken from Refs [97, 102, 103].

$< [\text{PF}_6] < [\text{Tf}_2\text{N}] < [\text{Methide}] < [\text{C}_7\text{F}_{15}\text{CO}_2]$. This trend was successfully reproduced by Maiti [104] and Sistla [105] using the COSMO-RS model (Conductor-like Screening Model for Real Solvent) where guanidinium and phosphonium based ILs were supposed to be promising for higher CO₂ solubility than the corresponding imidazolium-ILs. Generally, fluor containing ILs have higher CO₂ solubilities compared to ILs without a fluor group. The effect of anion-fluorination is shown in Figure 2.9 for ILs with a common [bmim] cation. CO₂ solubility increases as the number of fluor groups in the anion increases. The solubility increases in the following anion order: $[\text{BF}_4] < [\text{TfO}] < [\text{TfA}] < [\text{PF}_6] < [\text{Tf}_2\text{N}] < [\text{methide}] < [\text{C}_7\text{F}_{15}\text{CO}_2] < [\text{eFAP}] < [\text{bFAP}]$. Consistently, in a screening study Zhang *et al.* [106] used COSMO-RS to demonstrate that using a longer fluoroalkyl chain in the anion (e.g. [FAP] anion) corresponds to higher CO₂ solubilities. Recently, Palomar *et al.* [107] used the COSMO-RS methodology to achieve deeper

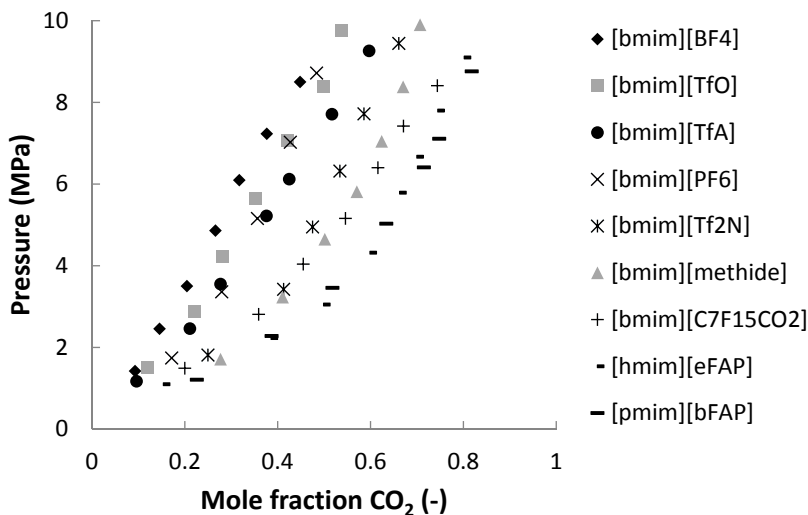


Figure 2.9: Effect of anion fluorination on CO₂ solubility. CO₂ solubility increases as the number of fluor groups increases in the anion. Data at 333 K taken from Refs [97, 102].

insight into the dissolution behavior of CO₂ in ionic liquids. To this end, a wide number of ILs liquids were screened and the Henry's constants of CO₂ were successfully related to the excess enthalpy of dissolution of CO₂ in ILs. This indicated that higher solubilities are associated with a higher exothermicity of the mixture. Further, the intermolecular interactions (electrostatic, hydrogen bonding, and van der Waals) between the species in the fluid phase were computed. The contribution of each of these interactions to the solubility of CO₂ in ILs was determined and the results indicate that the attractive van der Waals forces dominate the behavior of CO₂ dissolution in ILs. The electrostatic interactions had a secondary contribution to the excess enthalpy of dissolution, whereas the contribution of hydrogen bonds were found insignificant [107]. On the basis of this finding, Palomar *et al.* [107] carried out a guided COSMO-RS screening to find ILs, which have increased van der Waals interactions with the CO₂. The screening resulted

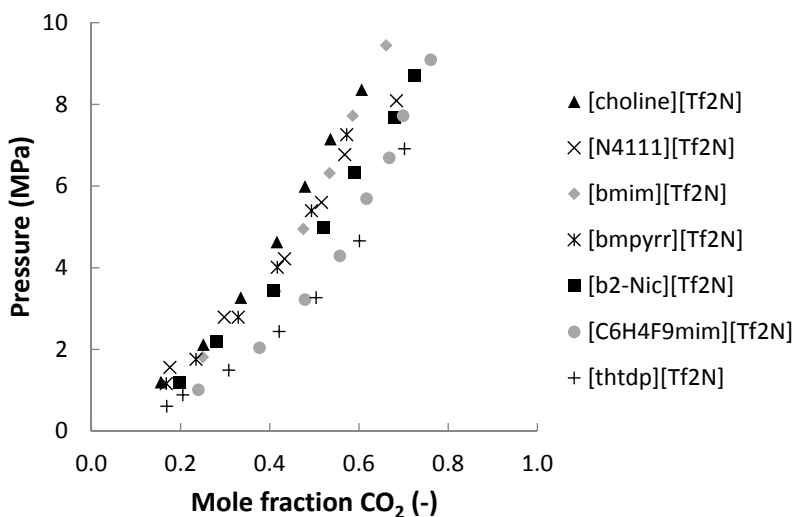


Figure 2.10: Effect of cation on CO₂ solubility. The cation seems to have a minor influence on the solubility of CO₂. Data at 333 K taken from Refs [97, 102, 108, 109].

in new potential ILs with highly brominated anions (e.g. [emim][PBr₆]) with high CO₂ solubilities.

It is widely accepted that the anion dominates the dissolution of CO₂, although the cation is believed to play a secondary role. The small effect of the cation on the CO₂ solubility is clearly shown in Figure 2.10. Cholinium, ammonium, imidazolium, pyridinium, pyrrolidinium and phosphonium cations were paired with the [Tf₂N] anion. Nevertheless, fluorination of the cation (e.g. [C₆H₄F₉mim]) can significantly improve the solubility, although to a lesser extent than anion-fluorination [111]. Moreover, using long alkyl chains on the phosphonium cation [P66614] can also improve the solubility. Generally, the CO₂ solubility increases slightly by increasing the alkyl chain length as shown in Figure 2.11. All the ionic liquids were paired with a common bis(trifluoromethylsulfonyl)amide [Tf₂N] anion, while the alkyl chain length on the imidazolium cation was varied. Clearly, as the alkyl

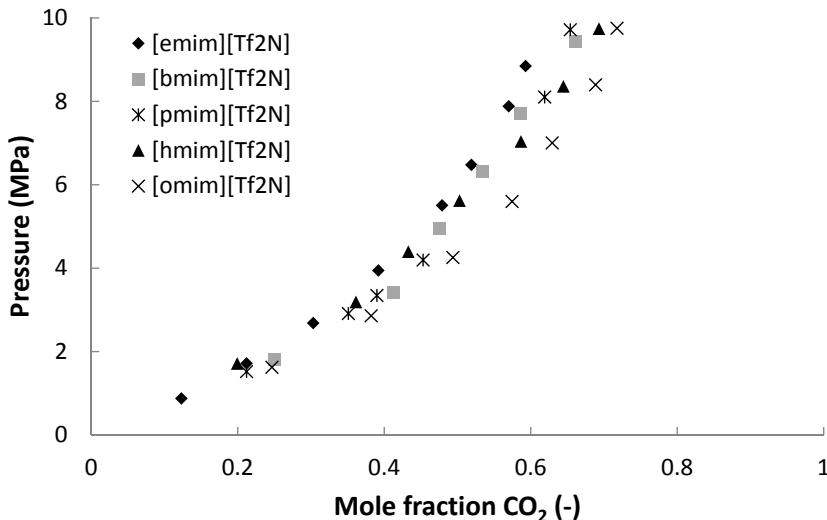


Figure 2.11: Effect of alkyl chain length on CO₂ solubility. CO₂ solubility increases as the alkyl chain length becomes longer. Data at 333 K taken from Refs [94, 97, 110].

chain becomes longer the solubility increases in the following order: [omim] > [hmim] > [pmim] > [bmim] > [emim]. These trends have also been predicted using the COSMO approach [104, 105, 107, 112]. It is known that the hydrogen attached to the C₂ position (C₂-H) on the imidazolium ring is acidic (i.e. it has a relatively large positive charge). Therefore, additional CO₂ may be dissolved at this C₂ site via hydrogen bonds. The effect of this acidic site has been investigated by means of molecular simulations and experiments [97, 99]. Molecular simulation shows that replacing the proton in the C₂ position with a methyl group (C₂-methyl) slightly decreases the CO₂ solubility [99]. Experiments support this finding, as the Henry's constant at 298 K for CO₂ in [bmim][PF₆] and [bmmim][PF₆] are 53.4 bar and 61.8 bar, indicating a lower solubility in the methyl-substituted [bmmim] IL [99].

Although molecular simulations have been used extensively to study the

solvation behavior of CO₂ in ILs, computed solubility isotherms of CO₂ in ILs have been reported scarcely due to the increased computational effort [7, 18, 113, 114]. For choosing an optimal IL for CO₂ capture from flue-gases, from a tremendous amount (around 10¹⁸) of possible ILs, fast screening methods like COSMO are beneficial. However, several other methods using surface tension or viscosity as an input have been reported in the literature to predict gas solubilities in ILs [115, 115–117]. A review of the different approaches that have been used to model the phase behavior of IL-gas systems is provided by Vega *et al.* [118]. Camper *et al.* [117, 119–123] demonstrated that regular solution theory (RST) is also able to predict solubility trends of various gases in ILs at low pressures. This is an interesting finding, since RST without taking into account the intermolecular interactions between the gas and the anion was used for describing solubility trends. Indeed, this contradicts the conventional wisdom that CO₂ solubility is dominated by CO₂-anion interactions. In RST, Equation (2.1), the activity coefficient of a solute, γ_1 , is related to its liquid molar volume, V_1 , and the difference in solubility parameters δ_1 and δ_2 of solute and solvent, respectively.

$$RT \ln \gamma_1 = V_1 \Phi_2^2 [\delta_1 - \delta_2]^2 \quad (2.1)$$

Shi and Maginn [124] showed that when the RST parameters are known one can calculate the complete solubility isotherm for a gas. However, until recently the solubility parameter of ILs, δ_2 , was unknown and was adjusted to fit experimental isotherms [113]. Recently, enthalpies of vaporization for many ILs were determined experimentally allowing to calculate directly the solubility parameter by $\delta_2 = (\Delta_{\text{vap}} U_2 / V_2)$. Using experimentally obtained solubility parameters, RST was found to significantly underpredict the solubility of CO₂ in [hmim][Tf₂N]. The poor performance of the RST when using actual, instead of correlated, solubility parameters to describe CO₂ solubility is not surprising. As shown in Figure 2.12, CO₂ solutions in ILs at low pressure show negative deviations from ideality as represented by Raoult's law:

$$y_1 P = x_1 P_1^{\text{sat}} \quad (2.2)$$

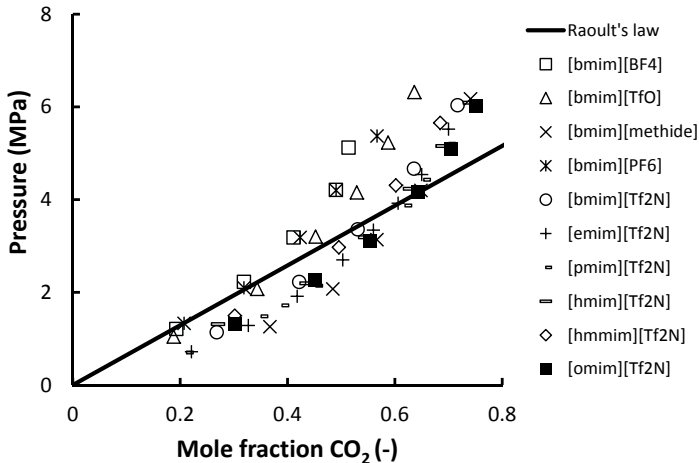


Figure 2.12: Comparison of the behavior of CO₂-ILs systems with Raoult's law predictions. Typically, CO₂-ILs systems show negative deviations to the ideality as represented by Raoult's law. Data at 298 K taken from Refs [94, 97].

where P is the pressure, P_1^{sat} the vapor pressure of CO₂, x_1 the mole fraction of CO₂ in the liquid phase and y_1 the mole fraction of CO₂ in the gas phase, which is equal to 1 assuming nonvolatility of ILs. As a consequence, the activity coefficient of CO₂ in ILs is lower than 1, while RST can only describe solutions with positive deviations from ideality. The performance of RST to predict solubilities should further be tested in the future using experimentally solubility parameters.

So far, CO₂ solubilities on mole fraction basis were considered. Recently, Carvalho and Coutinho [125] claimed that physical CO₂ absorption in ILs is dominated by entropic effects, hence CO₂ solubilities when plotted as molality (e.g mole/kg) versus pressure are solvent independent and fall on a common universal curve. Subsequently, they developed a universal correlation for the solubility of CO₂ in nonvolatile solvents with a validity for pressures up to 5 MPa, molalities up to 3 mole/kg and temperatures

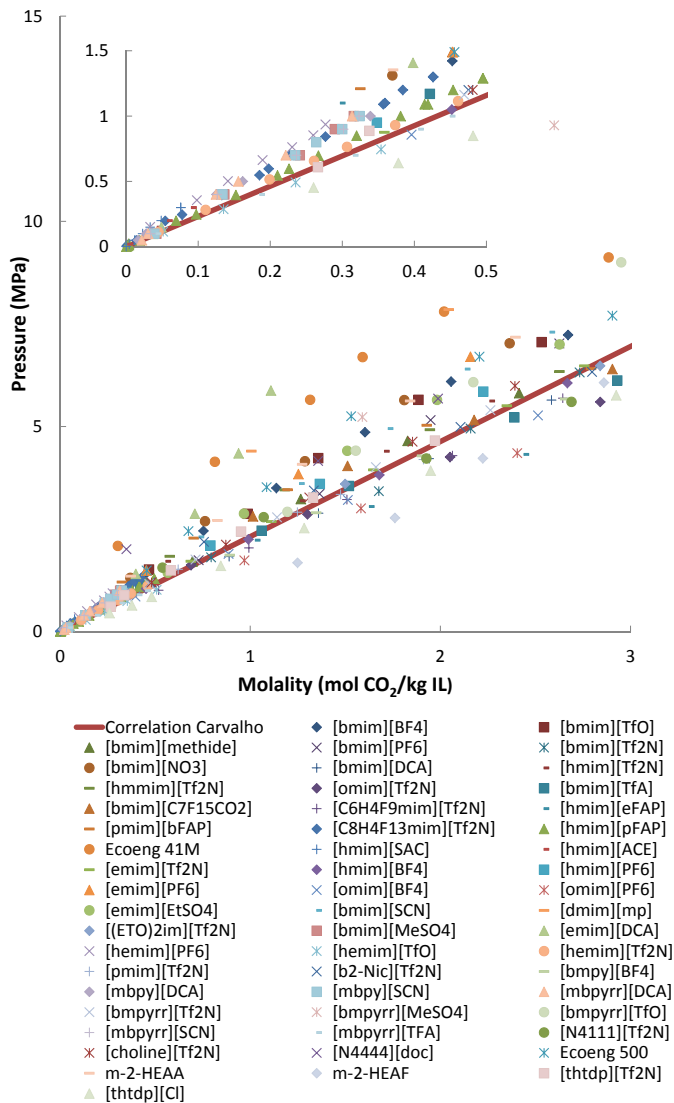


Figure 2.13: Solubility of carbon dioxide expressed as molality in different ionic liquids. Data show that many ILs do not fall on the universal curve proposed by Carvalho and Coutinho [125]. Data at 333 K taken from Refs [89, 93, 97, 102, 103, 108–110, 126–136].

ranging from room temperature to 363 K. This universal correlation is given by the following equation, where p is the pressure in MPa, m_i^0 the molality in mole/kg and T the temperature in Kelvin:

$$p = m_i^0 e^{6.8591 - \frac{2004.3}{T}} \quad (2.3)$$

Unfortunately, many ILs that do not obey the trend were excluded in the analysis [66, 125]. The validity of the model, Equation (2.3), proposed by Carvalho and Coutinho is explored by plotting a large number of ILs in the pressure-molality diagram shown in Figure 2.13. Indeed, the differences in CO₂ solubilities among many of the ILs are minimized. However, there are many ILs that significantly deviate from the curve proposed by Carvalho and Coutinho [66, 125]. In the case of acetates (m-2-HEAA) and formates (m-2HEAF) the solubility is dominated by the formation of electron donor-acceptor (EDA) complexes and do not follow the universal curve, which was also noted by Carvalho and Coutinho. Furthermore, ILs with the following anions, regardless of the cation, also do not obey the curve: [SO₄], [SCN], [mp], [doc] and [NO₃]. Even the simple IL [bmim][BF₄] and many of the [PF₆], [DCA] and [TfO] ILs do not follow the trend. It is likely that the model suggested by Carvalho and Coutinho [125] is a severe oversimplification. Nevertheless, these authors correctly noticed that there is a strong influence of the IL molecular weight on the CO₂ solubility as can be seen in Figure 2.13. In the following, we will show that the CO₂ solubility increases with increasing IL molecular weight, but first we consider the CO₂ solubility as given in molarity (mol/m³). The solubility data of CO₂, which are the same as in Figure 2.13, but now expressed in molarity is shown in Figure 2.14. We can see in Figure 2.14 that a pressure-molarity plot for many ILs yield nearly straight lines up to ~60 bar. The slope of these lines gives a first-order approximation of the (molarity based) Henry constants. This Henry constants are plotted against the molecular weight of the IL in Figure 2.15. Clearly, the Henry constant (CO₂ solubility) show a decreasing (increasing) trend with an increasing IL molecular weight. The Henry constants of CO₂ in the imidazolium-based ILs when plotted against the IL molecular weight seems to fall on a common curve, while this is apparently

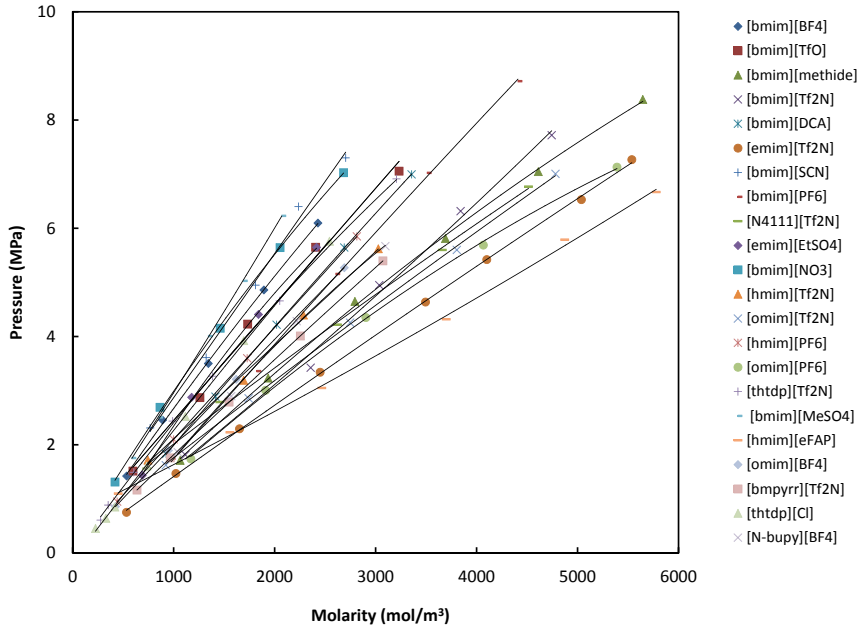


Figure 2.14: Solubility of carbon dioxide expressed as molarity ($\text{mol CO}_2/\text{m}^3$ solvent) in different ionic liquids. Solubility data at 333 K as used in Figure 2.13. Density data at 333 K taken from Refs [137–146].

different for phosphonium-based ILs. However, considering the free-space mechanism it would be more interesting to analyze the CO₂ solubility with respect to the IL molar volume or IL free volume. In Figure 2.16 the Henry constants are plotted as a function of the molar volume of the IL. The trend is similar as for molecular weight effects, i.e., the Henry constant (CO₂ solubility) shows a decreasing (increasing) trend with an increasing IL molar volume. The free volumes of the ILs listed in the legend of Figure 2.14 have been estimated by:

$$V_f = V_m - 1.3V_{\text{vdW}} \quad (2.4)$$

where V_f is the free volume of the IL, V_m the IL molar volume and V_{vdW} the

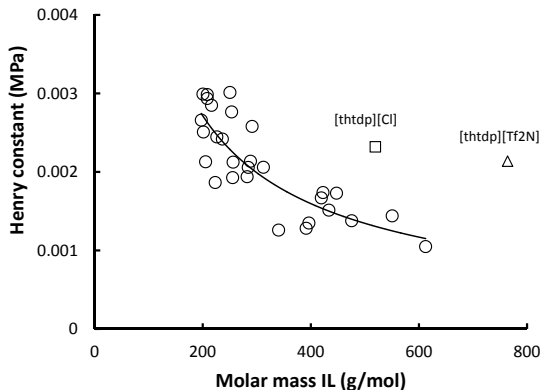


Figure 2.15: Henry constants (molarity based) at 333 K plotted as a function of the molecular weight of the IL show that the Henry constant (CO₂ solubility) is decreasing (increasing) with an increasing molecular weight. Imidazolium-based ILs (circles), phosphonium-based ILs (square and triangle) and the lines are fit through the imidazolium-based data to guide the eye.

van der Waals molar volume. Zhao *et al.* [147] provide a correlation based on Bondi principles [148] to estimate V_{vdW} ($\text{\AA}^3/\text{molecule}$) rapidly with very good accuracy using only atomic and bond contributions:

$$V_{\text{vdW}} = \sum AAC - 5.92N_{\text{B}} - 14.7R_{\text{A}} - 3.8N_{\text{NR}} \quad (2.5)$$

where AAC is the atomic contribution of all atoms V_{vdW} (as given by Bondi [148]), N_{B} is the number of total bonds, R_{A} is the number of aromatic rings and N_{NR} is the number of nonaromatic rings. Zhao *et al.* [147] used Equation (2.5) to calculate V_{vdW} of 677 organic compounds and compared their values with the values computed using the TSAR program (Oxford Molecular) having a regression coefficient value of 0.992 and a standard error of 8.6 $\text{\AA}^3/\text{molecule}$. Using Equation (2.4) and Equation (2.5) we have estimated the free volume of all ILs listed in the legend of Figure 2.14. Subsequently, we have correlated the Henry constants (molarity based) with the free volume of the IL as shown in Figure 2.17. Again, the Henry constant (CO₂ solubility) shows a decreasing (increasing) trend with an increasing

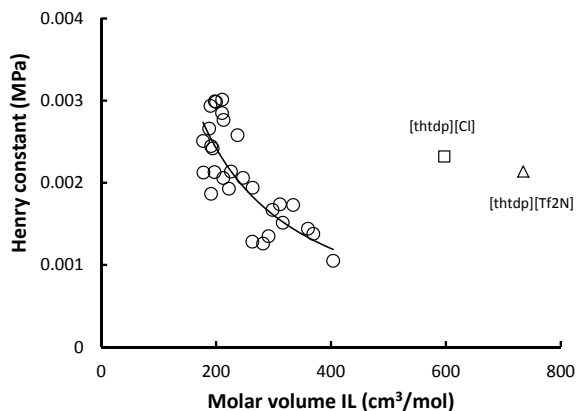


Figure 2.16: Henry constants (molarity based) at 333 K plotted as a function of the molar volume of the IL show that the Henry constant (CO₂ solubility) is decreasing (increasing) with an increasing molar volume. Imidazolium-based ILs (circles), phosphonium-based ILs (square and triangle) and the lines are fit through the imidazolium-based data to guide the eye.

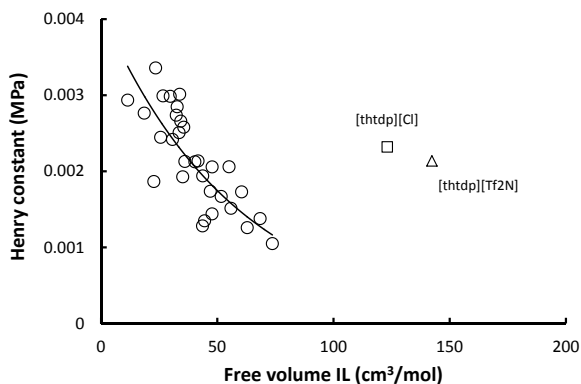


Figure 2.17: Henry constants (molarity based) at 333 K plotted as a function of the free volume of the IL show that the Henry constant (CO₂ solubility) is decreasing (increasing) with an increasing free volume. Imidazolium-based ILs (circles), phosphonium-based ILs (square and triangle) and the lines are fit through the imidazolium-based data to guide the eye.

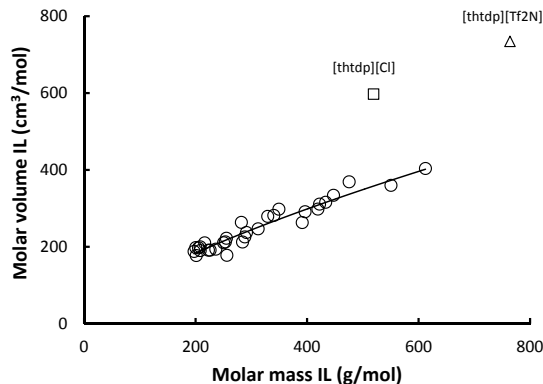


Figure 2.18: Molecular weight plotted as a function of the IL molar volume at 333 K show that the molar volume almost linearly increases with increasing IL molecular weight. Imidazolium-based ILs (circles), phosphonium-based ILs (square and triangle) and the lines are fit through the imidazolium-based data to guide the eye.

IL free volume. We note that in the calculation of the free volume based on Equation (2.5), the imidazolium and the pyridine rings have been considered as aromatic, while the pyrrolidine ring has been taken as nonaromatic. Furthermore, the molar volume of ILs seems to be correlated with their molecular weight, see Figure 2.18. The molar volume increases with an increasing IL molecular weight, although the trends seems to be different for imidazolium and phosphonium-based ILs.

Recently, Shannon *et al.* [149] also showed that CO₂ solubility and selectivity in ILs are governed by the free volume of the IL. These authors used the COSMOtherm program to calculate the free volume of 165 existing and theoretical imidazolium-based ILs. Subsequently, they showed that the volume-normalized solubility of CO₂ is proportional to the free volume to the power -0.5, while the solubility of CH₄ and N₂ exhibited a linear dependence on the IL free volume.

In summary, CO₂ solubility increases with increasing IL molecular weight, molar volume and free volume. All these results support the claim by Carvalho and Coutinho [125] that CO₂ solubility in ILs is dominated by

entropic effects rather than solute-solvent interactions as claimed by many authors. It is clear that the solubility trends as a function of molality or molarity will be different than the trends established on mole fraction basis at the beginning of this chapter. The only trend that seems to survive (see Figure 2.14) is that the CO₂ solubility in fluor-containing ILs is higher than in nonfluorinated ILs. This suggests that in addition to the dominating free-space mechanism also solute-solvent interactions are important. The most important message here is that CO₂ solubility should not be evaluated on mole fraction basis due to the strong molecular weight (molar volume) effect. In fact, from an application point of view it is more interesting to analyze the solubility per volume solvent (molarity) or on a molality basis [17].

CO₂ Selectivity

In practice, separation processes involve mixtures of two or more components that have to be purified or separated, hence solubility data only is not enough to judge the separation performance of a solvent, but also selectivity is essential. Although dozens of CO₂ solubility data are available in the literature, selectivity data of CO₂ in ionic liquids are scarcely reported. Nevertheless, for CO₂ capture from flue-gas and natural gas the following selectivities are mainly relevant: CO₂/N₂, CO₂/H₂ and CO₂/CH₄. Flue-gas or natural gas can contain a large number of impurities and selectivities like CO₂/H₂S, CO₂/SO_x, H₂S/CH₄ and CO₂/CO might also become important. Anderson *et al.* [150] measured the solubility of various gases in the IL [hmpy][Tf₂N], see Figure 2.19. The solubility of the gases in [hmpy][Tf₂N] at 298 K decreases by the following order: SO₂ > CO₂ > C₂H₄ > C₂H₆ > CH₄ > O₂ > N₂. Similar gas solubility trends (i.e. CO₂ > C₂H₄ > C₂H₆ > CH₄ > O₂) were observed in the ILs [hmim][Tf₂N], [bmim][PF₆] and [bmim][Tf₂N] [42, 98, 150]. In general, N₂ and O₂ solubilities are much lower compared to CO₂ leading to a high CO₂/N₂ or CO₂/O₂ selectivity. The hydrocarbons show moderate solubilities, thereby reducing the CO₂/hydrocarbon selectivity. SO₂ is by far the most soluble component in [hmpy][Tf₂N], suggesting that it could compete with CO₂ in an absorption

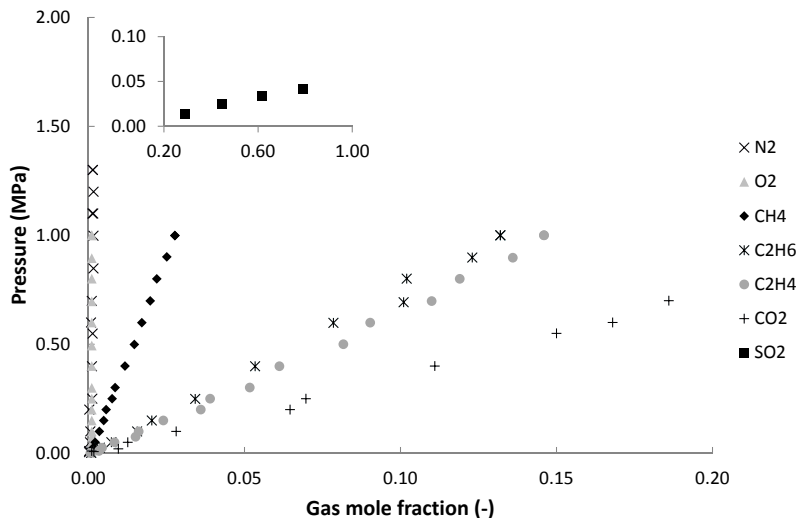


Figure 2.19: Solubility of gases in the ionic liquid [hmpy][Tf₂N]. Solubility of the gases show the following trend: N₂ < O₂ < CH₄ < C₂H₆ < C₂H₄ < CO₂ < SO₂. The inset shows the solubility behavior of SO₂ in [hmpy][Tf₂N] (axis the same as in the main figure). Data at 298 K taken from Refs [150, 151].

process. As usual, the solubility of CO₂, C₂H₄, and C₂H₆ decreases as the temperature increases, however the solubilities of CH₄ and O₂ were nearly temperature independent. Kumelan *et al.* [152] also observed the temperature independence of O₂ solubilities in [bmim][PF₆].

Recently, Carvalho and Coutinho [153] measured CH₄ solubilities in imidazolium, phosphonium and ammonium ILs. They also noticed that an increase in temperature had a small or even negligible impact on CH₄ solubility. The peculiarities of CH₄ + IL systems do not end here, Carvalho and Coutinho also observed a crossover in the $P - x$ diagram above which the temperature dependency is reversed such that the CH₄ solubility increases with increasing temperature. Furthermore, the solubility of CH₄ was shown to relate to the polarity of the IL and CO₂/CH₄ or H₂S/CH₄ selectivities

were correlated using the Kamlet-Taft β parameter. The Kamlet-Taft parameters, α the hydrogen bond donor, β the hydrogen bond acceptor and π the polarizability properties, are measures for the overall solvent polarity. The selectivities of sour gases/CH₄ were shown to increase with the β parameter, hence it could be used as a basis for designing ILs which maximize sour gases/CH₄ selectivities.

Hydrogen and carbon monoxide (CO) solubility was measured, respectively in [hmim][Tf₂N] and [bmim][PF₆] by Kumelan *et al.* [154, 155]. Solubility of both gases in the ILs was remarkably low compared to CO₂, which is indicative for high CO₂/H₂ and CO₂/CO selectivities in the corresponding ILs. The solubility of H₂ in [hmim][Tf₂N] and [bmpy][Tf₂N] was shown to increase with temperature [108]. This is in contrast with CO₂ + IL systems where the solubility decreases with temperature. CO solubility in [bmim][PF₆] was not influenced upon increasing the temperature, while the CO solubility increased in [bmim][CH₃SO₄] with increasing temperature [156]. Jacquemin *et al.* [157, 158] measured low pressure solubilities of several gases in [bmim][BF₄] and [bmim][PF₆]. The solubility of CO₂ was the highest in both ILs, whereas the solubility of H₂ was the lowest. In addition, the hydrogen solubility was shown to increase with temperature at lower temperatures, but it started to decrease with increasing temperatures at higher temperatures. The solubility of the gases in [bmim][BF₄] and [bmim][PF₆] increases in the order: H₂ < CO < N₂ < O₂ < Ar < CH₄ < C₂H₆ < CO₂. The effect of the cation on the solubility of hydrogen was investigated by Jacquemin *et al.* [159]. The [bmim], [emim] and [N4111] cation was paired with the [Tf₂N] anion and the subsequent solubility results show that the cation had a small effect on the H₂ solubility, although the solubility was higher in the ammonium [N4111] IL. For all the three systems, the hydrogen solubility decreased with temperature, this is opposite to what was found for [bmim][PF₆], [hmim][Tf₂N] and [bmpy][Tf₂N] systems. Shiflett and Yokozeki [160] showed that much higher CO₂/H₂ selectivities (about 30-300) could be obtained with [bmim][PF₆] compared to novel polymeric membranes which had selectivities ranging from 10 to 30 under typical operating conditions. The same authors developed an equation of state (EOS) for the CO₂/H₂S/[bmim][PF₆] and CO₂/H₂S/[bmim][MeSO₄]

systems [161, 162]. Subsequently they showed that competition between the two solutes exists, leading to a low (about 3.2 to 4) CO₂/H₂S selectivity in the [bmim][PF₆] system. For the [bmim][MeSO₄] system the selectivity was dependent on the CO₂/H₂S feed ratios, for large and intermediate feed ratios the selectivity was 10 to 13 [162]. In particular, solubilities of diatomic gases (e.g. H₂, O₂, CO, N₂) measured in the same IL but by different authors show large discrepancies [42, 152, 155, 157, 158, 163]. For example, the Henry constant for O₂ in [bmim][PF₆] at 283 K was reported by Anthony *et al.* [42] to be 650 ± 425 MPa, while Kumelan *et al.* [152] reported a value of 51.5 ± 0.6 MPa at 283 K. Nevertheless, the solubility trends of several gases observed in ILs are more or less similar. Simple gases often interact weakly with the IL ions, hence the polarizability of the gases is reflected in the solubility behavior, leading to the series H₂ < CO < N₂ < O₂ < Ar < CH₄ < C₂H₆ < CO₂. Molecules that possess an electric quadrupole moment (e.g. CO₂ and C₂H₄) show higher solubilities [164]. Accordingly, polar gases like SO₂, H₂S and water vapor show very high solubilities.

Applying regular solution theory, Camper *et al.* [117, 119–123] showed that the physical solubility of gases in ILs was well correlated with the liquid molar volume of the IL and that ideal selectivities for CO₂/N₂ and CO₂/CH₄ should increase as the molar volume of the IL decrease. Finotello *et al.* [123] measured CO₂, N₂ and CH₄ solubilities in pure [bmim][BF₄] and [bmim][Tf₂N] and in mixtures of these ILs. They showed that CO₂/N₂ and CO₂/CH₄ ideal selectivity in [bmim][BF₄] could be enhanced by adding 5 mole % [bmim][Tf₂N], which is consistent with RST as this IL mixture represented the lowest liquid molar volume. Bara *et al.* [165] measured the solubility and ideal selectivities of the gas pairs CO₂/N₂ and CO₂/CH₄ in imidazolium-based ILs functionalized with oligo(ethylene glycol). They showed that the CO₂ solubility in these oligo(ethylene glycol) functionalized ILs were similar to their corresponding alkyl analogues, but N₂ and CH₄ solubilities were lower corresponding to a higher ideal selectivity for the two gas pairs. Similar results were reported by Carlisle *et al.* [166] for nitrile-functionalized ILs. The nitrile-functionalized ILs exhibited lower CO₂, N₂ and CH₄ solubilities, but showed improved CO₂/N₂ and CO₂/CH₄ selectivi-

ties compared to alkyl-substituted analogues. Mahurin *et al.* [167] measured CO₂/N₂ ideal selectivities in imidazolium, pyridinium and pyrrolidinium ILs functionalized with a benzyl group. Improved CO₂/N₂ ideal selectivities, ranging from 22 to 33, were reported for these benzyl-functionalized ILs. It should be stressed here that mainly ideal selectivities (i.e. the ratio of pure gas solubilities) are reported in the literature. Unfortunately, real or actual selectivities in mixtures of gases can not always be determined from pure gas solubilities with the assumption of ideal mixing. In general, measuring mixed-gas solubilities is significantly more difficult, therefore almost no mixture data can be found in the literature [113]. One of the first mixed gas solubilities was reported by Hert *et al.* [168]. In this study, the authors reported an enhancement of the sparingly soluble gases O₂ and CH₄ in the IL [hmim][Tf₂N] in the presence of CO₂. However, using molecular simulations Shi and Maginn [124] showed that there is no or very little enhancement of O₂ solubility in the presence of CO₂. Revised experiments on CO₂/O₂ support this finding, hence CO₂/O₂ selectivities can be expected to have near-ideal selectivities [113]. The literature on mixed gas solubilities has mostly focused on the gas pairs CO₂/H₂S, CO₂/SO₂ and CO₂/H₂. The CO₂/H₂S and CO₂/SO₂ selectivities are extremely important in desulfurization processes and the natural gas sweetening process as natural gas can contain large amounts of sulfur compounds. CO₂/H₂S solubilities in ILs were investigated by Shiflett *et al.* [161, 162] in the ILs [bmim][MeSO₄] and [bmim][PF₆], while Jalili *et al.* measured CO₂/H₂S solubilities in [omim][Tf₂N]. CO₂/H₂S (gas phase) selectivity in [bmim][MeSO₄] and [bmim][PF₆] is somewhat dependent on the CO₂/H₂S feed ratio, but at 298.15 K it was ~10 and 1-4, respectively. Jalili *et al.* [135] reported a (gas phase) selectivity of ~3 at 303.15 K in the [omim][Tf₂N] IL. Yokozeki and Shiflett [169, 170] investigated experimentally the CO₂/SO₂ (gas phase) selectivity in the ILs [hmim][Tf₂N] and [bmim][MeSO₄], while Shi and Maginn [124] used molecular simulation for the CO₂/SO₂/[hmim][Tf₂N] system. The CO₂/SO₂ (gas phase) selectivity in the ILs [hmim][Tf₂N] and [bmim][SO₄] was highly dependent on the gas feed ratio and IL addition, but for a CO₂/SO₂ ratio of 9/1 the selectivity was ~30 and 226-348, respectively. We note that H₂S and SO₂ are much more soluble than CO₂ and

the selectivities reported here are gas phase selectivities (i.e. a high H₂S or SO₂ solubility in the liquid phase result in a high gas phase CO₂/sulfuric gas selectivity.) Beside CO₂/H₂S, also CO₂/CH₄ selectivities are important in the natural gas sweetening process, however, no data could be found for real CO₂/CH₄ selectivities. Nevertheless, the natural gas process operates at high pressures and ideal selectivity should not be expected for CO₂/CH₄ separation. As previously noted, in the pre-combustion process the relevant separation/selectivity is CO₂/H₂. Mixed gas solubility of CO₂/H₂ mixtures has been investigated by Yokozeki and Shiflett [160], Kumelan *et al.* [171] and Shi *et al.* [172]. Yokozeki and Shiflett reported a CO₂/H₂ selectivity of 30-300 in the IL [bmim][PF₆], but the selectivity was shown to decrease with increasing temperature. Kumelan *et al.* investigated a mixture of CO₂/H₂/[hmim][Tf₂N] and found that CO₂ act as a cosolvent for hydrogen, thereby enhancing the solubility of the sparsely soluble hydrogen gas. Shi *et al.* found a CO₂/H₂ selectivity of ~30 in the IL [hmim][Tf₂N] at 313 K, but this number decreased to about 3 at 573 K. The CO₂ solubility decreases with increasing temperature, while this is the opposite for hydrogen resulting in a lower CO₂/H₂ selectivity at higher temperatures. The most relevant separation in the post-combustion process is the CO₂/N₂ separation, hence CO₂/N₂ selectivities are important in this process. Kim *et al.* [173] measured the mixed gas solubility of CO₂/N₂ mixtures in the IL [hmim][Tf₂N]. Their results show that negligible amounts of N₂ were absorbed in the IL suggesting a high and ideal selectivity for this gas pair.

In summary, the most important separation in the post-combustion process is CO₂/N₂. Ideal CO₂/N₂ selectivity in ILs is expected to be high and close to real selectivity, since N₂ solubility in ILs is not influenced by the presence of the CO₂. In the pre-combustion process, assuming that the CO₂ is captured after the WGS reaction, the relevant separation is CO₂/H₂. Although ideal CO₂/H₂ selectivity in ILs are relatively high, real selectivity is expected to be lower than ideal selectivity especially at higher temperatures, since H₂ solubility in ILs shows a increasing trend with increasing temperature while this is the opposite for CO₂. In the natural gas sweetening process many impurities can be present, but the relevant separations considered here are CO₂/CH₄ and CO₂/H₂S. Ideal selectivity

of CO₂/CH₄ in ILs is comparable to that in conventional physical solvents, however real CO₂/CH₄ selectivity in ILs is also expected to be lower than the ideal selectivity, since CH₄ solubility in many ILs also increases for increasing temperature while this is the opposite for CO₂. Ideal selectivity should not be expected for the gas pair CO₂/H₂S, since CO₂ solubility is significantly inhibited by the presence of H₂S. In fact, H₂S is much more soluble in ILs and both gases will compete in an absorption column. It is possible to remove both gases simultaneously, but this is not necessarily an advantage as an additional step may be required for separating CO₂ from H₂S.

Viscosity of Ionic Liquids

The shear viscosity, η , of an IL is one of the key material properties in process design, because high viscosities often form barriers for many applications and may lead to mass transfer limitations in chemical reactions [164]. Many ILs form highly viscous gel-like materials. Nevertheless, the tunability property of ILs can be invoked to design ILs with a broad range of viscosities. Figure 2.20 shows a plot of the shear viscosity η versus $1/T$ of some commonly used ILs. Simple liquids obey Arrhenius law, according to which the η versus $1/T$ plot yields a straight line. However, the data given in Figure 2.20 significantly deviates from Arrhenius law and are usually described by the Vogel-Fulcher-Tammann (VFT) equation:

$$\eta = A \cdot \exp(B/(T - T_0)) \quad (2.6)$$

where A , B and T_0 are specific adjustable parameters [164]. Also the pressure dependence of the viscosity of ILs shows notable differences from the typical behavior of molecular solvents [174, 175]. It can readily be seen in Figure 2.20 that the IL viscosities are much higher than for conventional solvents like water, alcohols or acetonitrile. Therefore designing ILs with low viscosities by manipulating the nature of cations and anions has been the objective of many researchers. An analysis of the effect of the cation on the viscosity is given in Figure 2.21. In this figure the viscosity of imidazolium, pyridinium, pyrrolidinium, phosphonium and ammonium ILs

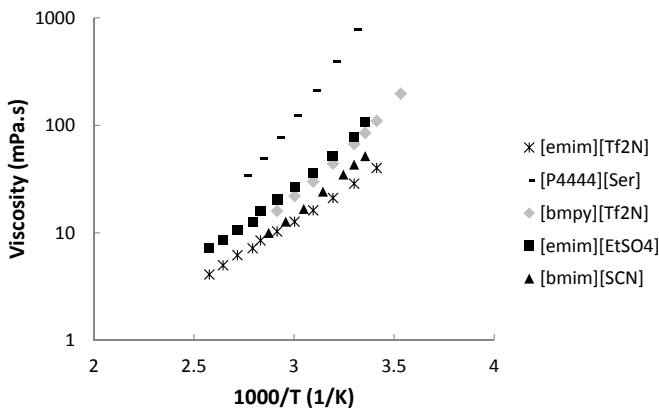


Figure 2.20: Temperature dependence of the viscosity. The data significantly deviates from Arrhenius law and is usually described by the Vogel-Fulcher-Tammann [138, 139, 176, 177].

with a common [Tf₂N] anion at 298 K is given. The viscosity increases with the cation series: imidazolium [hmim] < pyridinium [hmpy] < pyrrolidinium [hmpyrr] < phosphonium [P2228] < ammonium [N2228]. It should be mentioned here that physical properties of ILs like density and viscosity are influenced by the amount of water and other impurities present in the IL [139]. To make a fair comparison in this section only viscosity data of dried ILs (i.e. water content lower than 1000 ppm) are considered. The effect of the anion on the viscosity at 303 K for ILs with a common [bmim] cation is given in Figure 2.22. The viscosity increases with the anion order: [DCA] < [Tf₂N] < [SCN] < [TfA] < [TfO] < [BF₄] < [BETI] < [NO₃] < [MeSO₄] < [PF₆] < [Ac]. The dicyanamide anion [DCA] possess the lowest viscosity for the [bmim] cation. The relatively high viscosity of [bmim][PF₆] is remarkable, since fluorinated ILs (e.g. [Tf₂N], [TfO] and [BF₄]) generally show lower viscosities. The effect of the alkyl-chain length for several ILs is given in Figure 2.23. The viscosity increases almost linearly with alkyl-chain length for all ILs. Gardas and Coutinho [186, 187] developed a group contribution method to estimate thermophysical and transport properties

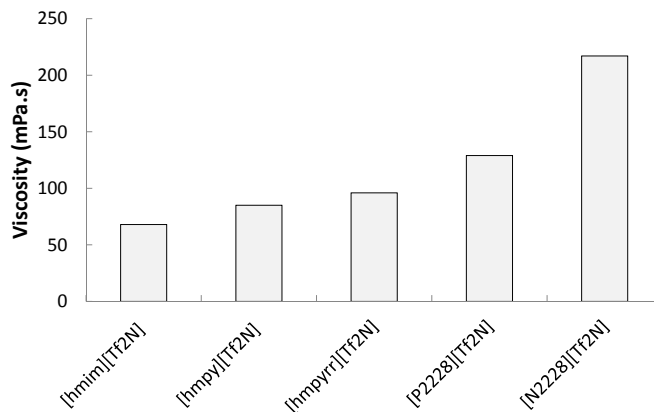


Figure 2.21: Effect of cation on viscosity for a common [Tf₂N] anion. Viscosity shows the following trend: [imidazolium] < [pyridinium] < [pyrrolidinium] < [phosponium] < [ammonium]. Data at 298 K taken from Refs [177–179].

(i.e. viscosity, electrical conductivity, thermal conductivity, refractive index, isobaric expansivity and isothermal compressibility) of ILs. The group contribution approach estimated the viscosity of 29 ILs with a mean percent deviation of 7.7% and a maximum deviation of 28%. Molecular simulations have also been used for studying the dynamics of ILs. Recently, Maginn [113] gave an excellent state-of-the-art review on the dynamics of ILs and in general about molecular simulations of ILs. Although simulations generally capture the slow dynamics of IL systems the simulations in the past were performed on too short timescales to calculate reliable viscosities [113, 188]. In chemical reactions, viscosity plays an important role, since in diffusion-controlled reactions the rate constant should be inversely proportional to the viscosity of the solvent [164]. For this reason, many reactions are slower in ILs than in conventional solvents due to the high viscosity of ILs. The self-diffusion coefficients (D) of cations and anions at 298 K are of the order $D = 10^{-11} - 10^{-10} \text{ m}^2/\text{s}$, compared to $D = 10^{-10} - 10^{-9} \text{ m}^2/\text{s}$ for simple molecular liquids [113, 164]. The self-diffusion of a spherical particle with a radius r is often related to the viscosity, η , through the Stokes-Einstein

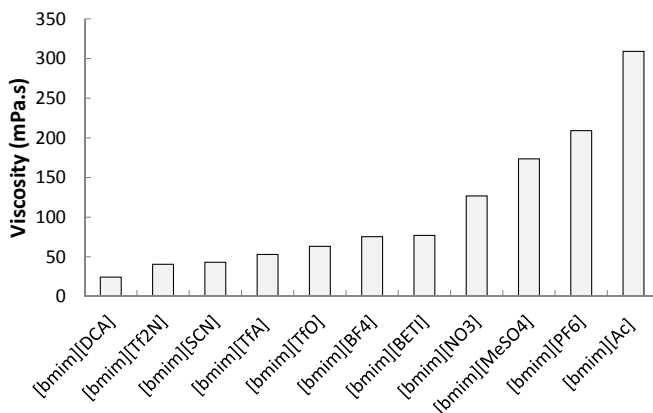


Figure 2.22: Effect of anion on viscosity for a common [bmim] cation. Data at 303 K taken from Refs [138–140, 143, 177, 180–182].

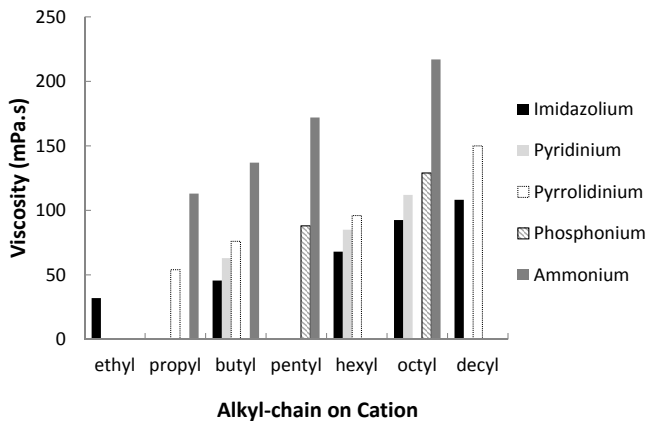


Figure 2.23: Effect of alkyl-chain length on viscosity for different ionic liquids with a common Tf₂N anion. Viscosity increases with increasing alkyl chain length for all IL classes. Data at 298 K taken from Refs [177–179, 183–185].

relation, where k_B is the Boltzman constant:

$$D = \frac{k_B T}{6\pi\eta r} \quad (2.7)$$

The relation of CO₂ diffusivity normalized with temperature and solvent viscosity is shown in Figure 2.24. The figure contains data of several imidazolium, ammonium, phosphonium and pyridinium ILs as well as alcoholic and hydrocarbonous solvents. Despite the complex structure of ILs the CO₂ diffusivity dependency on solvent viscosity appears to be universal, with self-diffusivities proportional to solvents viscosity to the power -0.43. Similarly, Moganty and Baltus [183] found a power of -0.45 by taking fewer data points of ILs into account. It is surprising to note that a power of around -0.45 was found for CO₂ diffusion in organic solvents and dilute liquids [189–191]. The data for diffusion of gases in ILs reported so far indicate a fractional Stokes-Einstein behavior having the form given by:

$$D \propto (T/\eta)^m \quad (2.8)$$

The exponent m in Equation (2.8) is generally lower than 1 ($m < 1$) and has been determined for imidazolium, ammonium and phosphonium ILs. Morgan *et al.* [182] used a Lag-Time technique to measure gas diffusivities in imidazolium based ILs. They found $m = 0.6$ for imidazolium ILs. Furthermore, they provided a correlation based on IL viscosity and solute molar volume for the diffusivity of gases in imidazolium ILs. However, Hou and Baltus [193] used a different correlation for CO₂ diffusivity in imidazolium ILs taking IL viscosity, molar mass, density and temperature into account. Diffusion of gases in phosphonium ILs was investigated by Ferguson and Scovazzo [194]. They found that the diffusivity was inversely related to the phosphonium IL viscosity with a power of 0.35 ($m = 0.35$). The diffusivity of gases in phosphonium ILs was correlated with the solvent viscosity, solvent and solute molar volumes. Diffusivities of gases in ammonium ILs were measured by Condemarin and Scovazzo [195] and they found a viscosity dependence with a power of 0.5 ($m = 0.5$). In this study the authors correlated the diffusion of gases in ammonium ILs with IL viscosity, molar

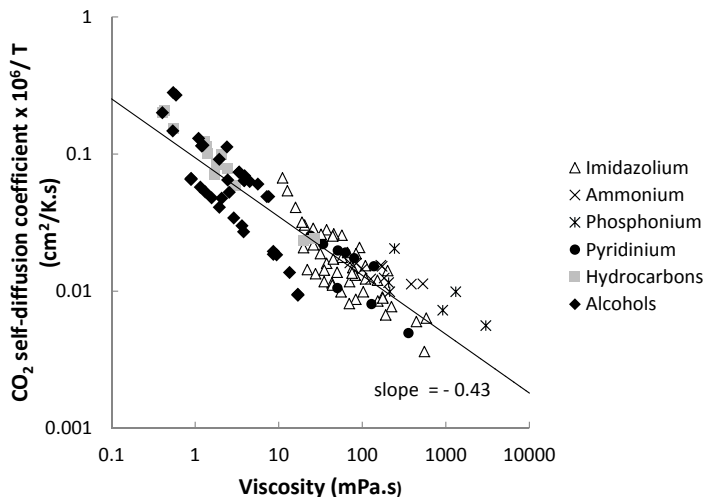


Figure 2.24: Viscosity/diffusivity relationship for ionic liquids and conventional solvents. Self-diffusivities of CO₂ in different solvents appears to be proportional to solvents viscosity to the power -0.43. Ionic liquids data taken from Refs [182, 183, 192–195]. Data of alcohols and hydrocarbonous solvents taken from Refs [189, 191, 196–198].

volume of solvent and solute. Clearly, the power dependency of diffusivity is different for different classes of ionic liquids. The diffusivity of gases in ILs are less dependent on the viscosity ($0.3 < m < 0.7$) than predicted by Stokes-Einstein equation ($m = 1$). This is probably not very surprising, since the Stokes-Einstein equation generally represents the case where a large solute molecule is diffusing in a solvent of relatively small molecules [182]. Nevertheless, the self-diffusion coefficients of CO₂ at room temperature in all the ILs are $\sim 1 \times 10^{-10}$ m²/s, which is an order of magnitude lower than for conventional solvents. Molecular simulations have also been used to calculate diffusivities, however the simulation runs in many of these computational studies in the past were too short (i.e. ps scale) to calculate reasonably transport properties [113, 164, 188, 199]. More recent studies

with much longer simulation times (i.e. several to hundreds of ns) have overcome this problem and reliable transport properties could be calculated [113, 188, 200].

Volatility of Ionic Liquids

The discussion here will be limited to aprotic ionic liquids, since protic ILs contain an acidic proton on the cation, which can be abstracted by the basic anion. This acid-base reaction leads to the formation of neutral molecular species that can readily evaporate, hence protic ILs are volatile by their nature [201]. Since its origins ionic liquids were considered substances with zero vapor pressure, but this general belief changed abruptly after the publication by Earle *et al.* [202] In this study the authors showed that several commonly used aprotic ionic liquids, pure and mixed, could be distilled at 300 °C and high vacuum without significant decomposition. For example the IL [hmim][Tf₂N] could be distilled at 170 °C and 0.07 mbar. Since the breakthrough publication by Earle *et al.* several studies have been reported concerning the nature of the vapor phase, vapor pressure (P^{sat}), enthalpy of vaporization ($\Delta_{\text{vap}}H$), boiling point (P_b) and boiling temperature (T_b) of ILs. Review on these topics are provided by Ludwig and Kragl [203] and Esperanca *et al.* [201] Both reviews address the difficulty in experimentally determining the liquid-vapor equilibrium (VLE) properties (e.g. $\Delta_{\text{vap}}H$, P^{sat}) for ILs. This is mainly due to the competition between evaporation and decomposition mechanisms at sufficiently high temperatures complicating the experimental interpretation. A detailed study on the nature of the vapor phase and enthalpy of vaporization was first given by Armstrong *et al.* [204] The ionic liquid was evaporated under ultra-high vacuum and the vapor phase was analyzed by line of sight mass spectroscopy (LOSMS). The vapor phase was shown to consist of neutral ion pairs, where the enthalpy of vaporization was primarily dependent on the Coulombic interactions between the gas-phase and the liquid-phase ion pair [204]. Similar results on the nature of the vapor phase were found by Leal *et al.* [205] using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) at reduced-pressure distillation conditions. The FTICR-MS results indicated

that at low pressures and at temperatures above 474 K the vapor phase consist of neutral ion pairs, without free ions, and larger clusters. By contrast, the vapor phase of protic ILs was shown to consist of isolated neutral molecules, supporting the proton transfer mechanism. Much recently, Rai and Maginn [206] investigated the nature of the vapor phase by means of molecular simulations. Their simulation results support the experimental finding that the vapor phase predominantly consist of isolated ion pairs. However, the molecular simulations also indicate that a substantial fraction of the ions is present in larger aggregates, and this fraction increases as the temperature and pressure increases. The enthalpy of vaporization, $\Delta_{\text{vap}}H$, has been measured by several techniques: the Knudsen method, surface tension, microcalorimetry, temperature-programmed-desorption, transpiration and Molecular Dynamics (MD) simulation [201, 207]. Unfortunately, the different techniques do not yield uniform enthalpies of vaporizations for a given IL, for example the measured values of $\Delta_{\text{vap}}H$ for [omim][Tf₂N] range from 150 to 192 kJ/mol [203]. Nonetheless, reliable $\Delta_{\text{vap}}H$ values range from 120 to 200 kJ/mol rather than the very high values up to 300 kJ/mol reported by Rebelo *et al.* [208] Recently, Fumino *et al.* [209] used Far-Infrared measurements to measure the enthalpy of vaporization of several imidazolium ILs. The values reported were in the range of 128-165 kJ/mol. Deyko *et al.* [210] used LOSMS for the measurement of twelve ILs and provided a simple theory for estimating the enthalpy of vaporization as a sum of a Coulombic contribution and two van der Waals contributions resulting from the anion and the cation. Verevkin [211] developed a simple group contribution approach to accurately estimate the enthalpy of vaporization of several imidazolium and pyrrolidinium based ILs. Furthermore, the experimental data compiled by Esperanca *et al.* [201] indicate that Trouton's rule ($\Delta_{\text{vap}}H_{T_b}/T_b = \text{constant}$) is not obeyed by [C_nmim][Tf₂N] IL family. The $\Delta_{\text{vap}}H_{T_b}$ values showed an increasing and decreasing trend with maximum at $n = 4$. This is opposite to what is found by molecular simulation for [C_nmim][BF₄] series where it was shown that $\Delta_{\text{vap}}H_{T_b}$ decreases with increasing chain length showing a Trouton-like correlation with a Trouton's constant of approximately 65 kJ/mol [206]. The vapor pressure of ILs in the homologues series of [C_nmim][Tf₂N] was measured

by Zaitsau *et al.* using a Knudsen effusion method [212]. They obtained vapor pressures between 10^{-1} and 10^{-3} Pa for temperatures ranging from 450 to 550 K. Recently, Rocha *et al.* [213] presented high-accuracy vapor pressure data of nine imidazolium based ILs. These authors provided for the first time a quantitative evidence for the structural percolation phenomenon in ILs and its relation with the thermodynamic properties of ILs. Furthermore, the high-accuracy vapor pressure data of all the ILs at 450 K were ~ 0.02 Pa. Since these pressures are so low and even lower at standard experimental conditions, it is not very surprising that it took some time to notice the volatility of ionic liquids. However, the proven (negligible) volatility of ionic liquids will not damage the reputation, which is largely built on their nonvolatility property, as green solvents [214].

2.3.2 Functionalized Ionic Liquids

Large scale application of physical ILs for CO₂ capture from flue-gas is mainly hindered by the low CO₂ absorption capacity at post-combustion conditions. The partial pressure of CO₂ at post-combustion conditions (see Table 2.1) is rather low, hence CO₂ solubility is lower than 5 mol-% even for the best physical ILs. To overcome this problem researchers appealed to the amine chemistry by arguing that including an amine moiety to conventional ILs (amine-functionalized ILs) could greatly improve CO₂ absorption capacity. The progress in this branch of research is reported in this section.

Cation Functionalization

The concept of ionic liquid functionalization or task-specific ionic liquid (TSIL) was first introduced by Bates *et al.* [215, 216]. In this study the authors functionalized the imidazolium cation with a primary amine moiety. This new TSIL was shown to react in a 2:1 stoichiometry with CO₂ according to Figure 2.25. We note that this stoichiometry is similar to the theoretical maximum molar uptake of CO₂ by conventional amines under the carbamate formation scheme.

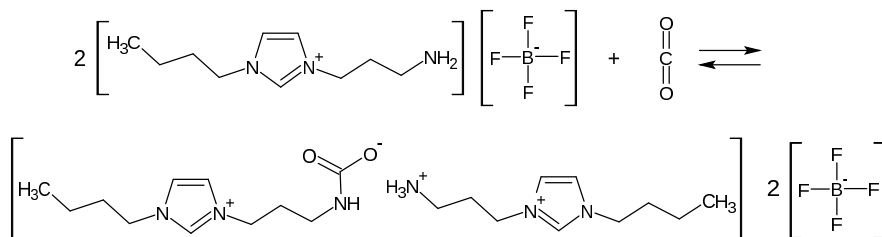


Figure 2.25: Reaction between cation functionalized ionic liquid and CO₂. The IL react in a 2:1 stoichiometry with CO₂ forming a carbamate salt [215].

Evidence for carbamate formation as proposed in Figure 2.25 was given by FT-IR and NMR spectra analysis of the CO₂ treated and CO₂ untreated ionic liquids. Furthermore, the authors reported that the reaction was reversible and the CO₂ could be released upon heating (80-100 °C) for several hours under vacuum. Although the authors observed a relatively high viscosity of the synthesized ionic liquid, they did not notice the dramatic viscosity increase after reacting the CO₂ with the TSIL. Galán Sánchez *et al.* [128, 217] further verified this concept by functionalizing the [bmim] cation by a primary and tertiary amine. These functionalized cations were paired with [BF₄] and [DCA] anions. The CO₂ solubility in the physical non-functionalized ILs, [bmim][BF₄] and [bmim][DCA], does not vary significantly. Functionalization of the [bmim] cation with an amino group [Ambim] improved the CO₂ absorption, relative to the non-functionalized counterparts, by a factor 13 and 4, respectively for [Ambim][BF₄] and [Ambim][DCA] at 0.1 MPa and 303 K. Clearly, the CO₂ solubility can be enhanced by including amine groups in the cation and by choosing a proper anion. Furthermore, the isotherms of CO₂-functionalized ILs show a trend which is typical for chemical absorption. At low pressures the solubility increases sharply, while a steady increase in solubility is observed at higher pressures due to contribution of the physical mechanism. Although a similar trend was observed for the tertiary-amine-functionalized

IL [3Amim][BF₄]-CO₂ system the solubility was significantly lower compared to the primary-amine-functionalized ILs. This is likely due to the lower reactivity of tertiary amines towards CO₂ [34]. The ILs did not show reduced absorption capacity after regenerating it at 353 K in vacuum. However, the viscosity problem after reaction with CO₂ was again noted. To overcome the viscosity problem of the amine-functionalized ILs to some extent, Camper *et al.* [218] proposed the use of (nonfunctionalized) RTIL-amine solutions. They showed that a RTIL solution containing 50 mol % MEA is capable of rapidly and reversibly capture CO₂ approaching a stoichiometry of 1 mol of CO₂ per 2 moles of MEA. Since the viscosity of the used IL was much lower than the amine-functionalized IL by Bates *et al.*, the absorption rate in the IL-MEA solution was much faster. Nevertheless, the lowest viscosity of an IL measured up to now is ~ 20 mPa.s, which is still much higher than for aqueous MEA solutions (e.g. the viscosity of 30 wt% MEA solution at 25 °C is 2.2 mPa.s).

To help understanding the high viscosities in neat cation-amine-functionalized IL Yu *et al.* [219] used molecular simulations. They found that amino addition does not significantly affect the organization of the anions around the imidazolium ring, instead the anions strongly organize around the -NH₂ forming strong hydrogen bonds. The calculated ionic self-diffusion coefficients of the functionalized ILs were roughly 2 orders of magnitude lower than of the nonfunctionalized counterparts, consistent with the observed high viscosities in the experiments. A mechanistic explanation for the dramatic viscosity increase upon reaction of CO₂ with the amine-functionalized ionic liquid was given by Gutowski and Maginn [220] using molecular simulations. They performed a detailed hydrogen bond analysis and found evidence for the formation of strong, dense hydrogen-bonded networks, primarily between the zwitterion and dication species formed during the reaction.

Anion Functionalization

It is obvious that CO₂ uptake by ILs with amine-functionalized cations is much greater (at pre-combustion conditions) than by physical absorption. However, the 1:2 reaction stoichiometry for cation-functionalized ILs is atom inefficient and the question remains whether a more favorable stoichiometry can be achieved. To answer this question Gurkan *et al.* [221] used *ab initio* calculations to investigate the relationship between the position of amine functional group and the reaction stoichiometry. They showed that tethering the amine to the cation favored the formation of the carbamate leading to 1:2 stoichiometry, while tethering the amine to the anion favored 1:1 reaction stoichiometry. Accordingly, they synthesized two amino acid-based ILs, trihexyl(tetradecyl)phosphonium proline [P66614][Pro] and trihexyl(tetradecyl)phosphonium methionate [P66614][Met], which were experimentally shown to react with CO₂ in a 1:1 stoichiometry. Figure 2.26 shows clearly a CO₂ uptake greater than one mole CO₂ per two mole IL which approaches the 1:1 stoichiometry. The isotherms can be subdivided in two distinct parts: a sharp increase at low pressures due to chemical absorption and a marginal increase in capacity at higher pressures which is typical for physical absorption. Nonetheless, it was shown that the vast majority of the uptake was due to chemical absorption. Furthermore, the 1:1 stoichiometry was confirmed by FTIR spectroscopy [221]. Inherent to these amine-functionalized ILs is the increase in the enthalpy of reaction and the increase in the viscosity. The enthalpy of reaction of CO₂ with [P66614][Pro] and [P66614][Met] was measured at 25 °C with calorimetry to be -80 kJ/mol and -64 kJ/mol, respectively. These values are intermediate compared to physical absorption (-10 to -20 kJ/mol) and chemical absorption with conventional amines (-85 to -100 kJ/mol). Of course the increased reaction enthalpy will bring extra expenses in the regeneration step. Similar to the case of cation-functionalized ILs, the viscosity increases further upon reaction with CO₂. The occurrence of the latter phenomena was recently demonstrated for amino-acid based ionic liquids [222]. In this study the trihexyl(tetradecyl)phosphonium [P66614] cation was paired with several deprotonated amino acid anions, like glycinate, isoleucinate, etc.

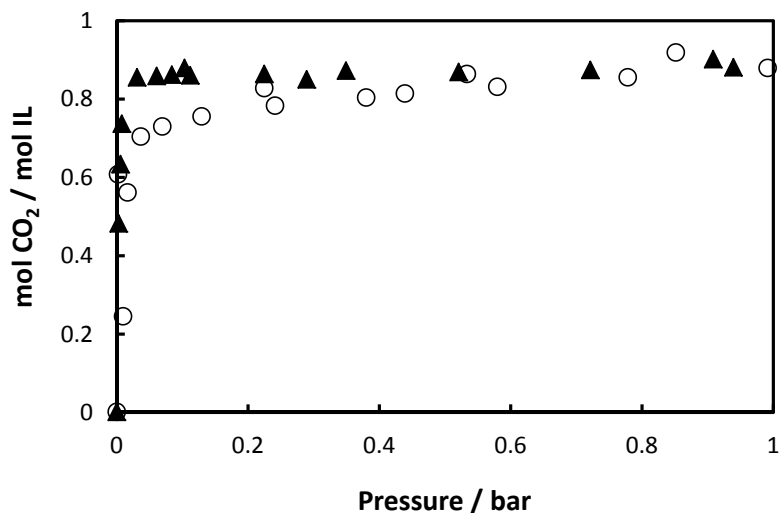


Figure 2.26: Experimental CO₂ absorption isotherm by anion-functionalized ILs [P66614][Pro] (triangles) and [P66614][Met] (circles) at 22 °C [221]. Note that the reaction stoichiometry of these ILs with CO₂ approaches 1:1, which is better than the 2:1 stoichiometry for conventional amines and CO₂.

The viscosity of the isoleucinate IL was shown to increase 240-fold, relative to the neat IL. Such high viscosities will preclude the application of these viscous, gel like, ionic liquids in an industrial absorber-stripper configuration. The energy requirement for pumping the viscous IL will increase, but also the absorption kinetics will deteriorate as diffusion might be slow in these viscous ILs. The slow diffusion will cause mass transfer limitations, requiring more (equivalent) trays in a typical absorption column, thereby increasing the capital cost.

Carboxylate functionalized anions, such as acetate, also deserve special attention. Chinn *et al.* [223] investigated the [bmim][acetate] IL diluted in a 14 wt% water solution and showed that CO₂ absorption in this IL exhibit an absorption behavior, which is typical for a chemical complexation process. The volumetric absorption capacity of this acetate-based

IL ($\sim 25 \text{ m}^3/\text{m}^3$) is intermediate between amines ($\sim 65 \text{ m}^3/\text{m}^3$ for 30 wt% aqueous MEA solution) and physical ILs ($\sim 3 \text{ m}^3/\text{m}^3$). The enthalpy of reaction of CO₂ in the acetate IL is -40 kJ/mol, which is also intermediate compared to MEA (-85 kJ/mol) and physical ILs (-15 kJ/mol). Therefore, the regeneration step requires a much lower energy input than the MEA process. Chinn *et al.* [223] put forward a mechanism where the acetate group interacts with the water and the CO₂ is captured as a bicarbonate group. The CO₂+ [bmim][acetate] system has also been studied experimentally by Maginn *et al.* [224], but they offered a different mechanism involving a proton extraction by the acetate anion from the C₂-position of the imidazolium ring leading to acetic acid in the process. In a next step, the CO₂ reacts with the carbene to form a bicarbonate. Shiflett *et al.* [225] performed a detailed experimental study on the CO₂+ [bmim][acetate] system in presence or absence of water. These authors used spectroscopic analyses to show that the acetic acid formation mechanism put forward by Maginn *et al.* is not very likely. However, the authors did smell some acetic acid during the experiments, which suggests that at least a limited amount of acetic acid is produced. They classified the phase behavior of CO₂+ [bmim][acetate] system as an extremely rare case with strong intermolecular interactions and complex formation. An economic evaluation of the process using [bmim][acetate] for CO₂ capture carried out by Shiflett *et al.* [226] showed that the IL-process could reduce the energy losses by 16% compared to a the MEA process. Furthermore, they estimated a 11% lower investment for the IL-process and 12% reduction in equipment footprint relative to the MEA process. Shiflett and Yokozeki [227] investigated CO₂ solubility in the ILs [emim][acetate], [emim][trifluoroacetate] and mixtures of both ILs. The [emim][acetate] IL absorbed the CO₂ chemically, while the [emim][trifluoroacetate] IL showed physical absorption behavior. The mixture of both ILs showed a combination of a physical and a chemical absorption behavior. Carvalho *et al.* [228] studied the specific interactions of CO₂ with imidazolium-based [bmim] ILs containing the [acetate] and [trifluoroacetate] anion. Their experimental data showed that CO₂ solubility in [bmim][acetate] unlike in [bmim][trifluoroacetate] is spontaneous due to the differences in enthalpies of solvation. Furthermore, these

authors used ab initio calculations and high resolution spectroscopy to provide evidence for an acid/base type of solvation mechanism in the acetate IL. Recently, Gurau *et al.* [229] demonstrated the chemisorption of CO₂ in 1,3-dialkylimidazolium acetate ILs using NMR spectroscopy and X-ray diffraction analysis. These authors explored the reactivity of CO₂ with [emim][acetate] by bubbling CO₂ through the acetate IL at atmospheric and ambient temperature conditions. Using NMR spectroscopy after 24 h bubbling, the formation of 1-ethyl-3-methylimidazolium-2-carboxylate was observed. In addition, X-ray diffraction analysis of single crystals clearly showed that imidazolium carboxylate and acetic acid are formed in the absence of water. Water was shown to inhibit the interaction of acetate with the proton at the C₂ position of the imidazolium ring, thereby inhibiting the CO₂ reaction. Almost simultaneously, Besnard *et al.* [230] also studied the [bmim][acetate]+CO₂ system using Raman, infrared spectroscopy, DFT calculations and NMR spectroscopy. They also showed that CO₂ reacts with [bmim][acetate] to form an imidazolium carboxylate and acetic acid originating from the deprotonation of the C₂ of the imidazolium ring.

Much recently, Gurkan *et al.* [231] used a computational approach to design a new class of ILs, namely aprotic heterocyclic anions (AHAs). The authors computed the structure and energetics of pyrrolide, an AHA, and CO₂ reaction product using molecular electronic structure calculations at the G3 level. The pyrrolide was computed to directly combine with CO₂ to form a carbamate product with a computed enthalpy of reaction of -109 kJ/mol. Subsequently, they showed that the reaction enthalpy could be tuned depending on the position of substitution on the pyrrolide ring. Further, MD simulations were used to probe the viscosity of the pyrrolide-based IL with CO₂. For this purpose 2-cyanopyrrolide anions (AHA) were paired with tetrabutylphosphonium [tbp] cations. The MD simulations suggest that the viscosity will not suffer the large viscosity increase upon reaction with CO₂. This result stands in stark contrast with previously reported results for amine-functionalized TSILs where the viscosity increases dramatically upon complexation with CO₂. In addition, experiments with trihexyl(tetradecyl)phosphonium 2-cyanopyrrolide [thtdp][2-CNpyr] confirmed the findings of the simulations. The [thtdp][2-CNpyr] IL was shown to react

in a 1:1 stoichiometry with CO₂ forming carbamate, which was identified using in situ infrared spectrometry. The viscosity was also measured and indeed the viscosity of the reacted and unreacted IL remained nearly the same. Differential calorimetry was used to measure the enthalpy of reaction with a value of -53 kJ/mol, which was in good agreement with the G3-computed value of -49 kJ/mol. Furthermore, these authors state that the approach is not limited to pyrrolides only but imidazolides and pyrazolides may also show similar chemistry. For proving this they synthesized a 3-(trifluoromethyl)pyrazolide [3-CF₃pyra] IL containing the [thtdp] cation. Indeed, CO₂ uptake of this IL was similar to the [2-CNpyr]-IL showing a stoichiometry close to 1:1. Again the viscosity increase was not significant, while the calorimetrically measured enthalpy of reaction for [3-CF₃pyra] was -46 kJ/mol. Hence, AHA-ILs provide a platform with the possibility to tune the reaction enthalpy, to enhance reaction stoichiometry relative to conventional amines and to circumvent the viscosity increase when reacting with CO₂. Unfortunately the viscosity problem remains also for AHA-ILs, since the neat or CO₂ reacted AHA-ILs given by Gurkan *et al.* [231] had viscosities at room temperature higher than 100 cP. Such a high viscosity may be still a barrier for using AHAs in industrial CO₂ capture processes. Nonetheless, there is still some room to improve the viscosity and enthalpy of reaction of AHAs by including proper functional groups.

Wang *et al.* [232–235] also reported equimolar CO₂ absorption in IL-superbase mixtures. Superbases are neutral organic bases, which possess very high proton affinities enabling their protonated conjugate acids to withstand deprotonation by the hydroxide ion [233]. Hence, superbases play an important role as proton acceptors, thereby providing the opportunity to capture CO₂. Wang *et al.* [233] investigated the CO₂ absorption performance of the IL-superbase system containing two ILs 1-(2-hydroxyethyl)-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide [Im21OH][Tf₂N] and 2-hydroxyethyl(dimethyl)-isopropylammonium bis-(trifluoromethylsulfonyl)imide [Nip,211OH][Tf₂N] and four superbases 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), 1,3,4,6,7,8-hexahydro-1-methyl-2H-pyrimido[1,2-a]pyrimidine (MTBD), 2-tert-butylamino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) and 1-ethyl-2,2,4,4,4-pentakis(di-methylamino)-

2λ⁵,4λ⁵-catenadi(phosphazene) (EtP2(dma)). The performance of the [Im21OH][Tf₂N]-DBU system was the best achieving a molar ratio of CO₂ to DBU slightly more than one, indicating a combination of physical and chemical absorption. NMR results showed that CO₂ reacted with DBU forming an amidinium alkylcarbonate salt. Furthermore, the absorbed CO₂ could be released easily by heating and minor loss of activity was observed during several absorption-desorption cycles. The authors reported similar results using imidazolium-based ILs containing different type of anions and the bases DBU, MTBD, EtP2 and tetramethyl guanidine (TMG). Recently, Wang *et al.* [232] synthesized superbase-derived protic ionic liquids (PILs) for CO₂ capture. They combined the superbases MTBD or P2Et with six weak proton donors (i.e. partially fluorinated alcohols (TFE, TFPA, HFPD), imidazole, pyrrolidone and phenol) to obtain the superbase-derived PILs. These superbase-derived PILs showed excellent CO₂ capture properties, for example the [MTBDH⁺][TFE⁻] PIL absorbed 1.13 mol of CO₂ per mol of PIL. Since the viscosity of [MTBDH⁺][TFE⁻] was relatively low (8.63 cP at 23 °C), the absorption of CO₂ in [MTBDH⁺][TFE⁻] was very fast. Furthermore, the CO₂ could be released completely by bubbling nitrogen at 80°C and the PILs showed only a slight capacity loss after several absorption-desorption cycles. The same group reported equimolar CO₂ capture by tuning the basicity of ILs. These basic ILs were synthesized by deprotonating several weak proton donors (i.e. trizole, tetrazole, imidazole, pyrazole, oxazolidinone, phenol, indole and benzotriazole) with trihexyltetradecylphosphonium hydroxide [thtdp][OH]. ILs containing the [thtdp] cation and the [pyrazole], [imidazole], [indole] [trizole] or [oxazolidinone] anion showed an absorption capacity close to 1 mol CO₂ per mol of basic IL. Moreover, the absorption capacity and the enthalpy of reaction was shown to increase with an increasing p*K*_a value of the ILs. Although the CO₂ could be released easily, the viscosity of the basic ILs after reacting with CO₂ was very high (> 550 cP), which will cause serious problems in a typical absorption-desorption process.

2.3.3 Reversible Ionic Liquids

The relatively new approach to capture CO₂ with reversible ionic liquids (RILs) was introduced by Jessop *et al.* [236, 237]. Jessop *et al.* showed that RILs could be formed from a non-ionic liquid (an alcohol and an amine base) by exposing it to CO₂ forming a salt (ionic liquid), which can revert back to its non-ionic initial state by exposing it to nitrogen or other inert gas [236]. These kind of solvents are also referred to as switchable solvents, since the polarity of the solvent can be tuned upon reaction with CO₂ [238]. Heldebrant *et al.* [237] investigated the reaction of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with carbon dioxide in the absence and presence of water. Their spectroscopic data showed that an IL [DBUH⁺][HCO₃⁻] is formed when DBU (amidine) is exposed to CO₂ in the presence of water, while there is no reaction in the absence of water. Phan *et al.* [239] showed that a guanidine/alcohol mixture also exhibit a similar chemistry as an amidine/water or amidine/alcohol mixture when exposing it to CO₂, thereby forming a carbonate salt. The solution could be reversed to its non-ionic state by bubbling nitrogen or mild heating. Heldebrant *et al.* [240] performed a detailed study on organic liquid CO₂ capture using DBU, TMG, Barton's base and Hunig's base mixed with water or an alcohol. These authors showed that CO₂ reversibly and chemically bind in a mixture of alcohols and amidine/guanidine bases to form a liquid alkylcarbonate. The CO₂ capacity of these RILs was up to 19% by weight, which is comparable to that of MEA. CO₂ was shown to absorb selectively in the presence of N₂ and the RILs did not show any loss of activity or selectivity after five cycles. The enthalpy of reaction of CO₂ in the Barton's base is comparable with MEA, while it was significantly higher for the TMG/alcohol and DBU/alcohol mixtures. However, the authors estimated that 50% less energy would be required in the regeneration step for the RILs compared to the MEA process, since the anticipated specific heat of RILs is three times lower than water. Unfortunately, in the presence of water undesired bicarbonates were formed, which will cause problems when considering that fluegas can contain substantial amounts of water. Blasucci *et al.* [241] developed an one-component RIL derived from siloxylated amines, which formed a carbamate

salt upon reaction with CO₂. Blasucci *et al.* [242] investigated four silylated amines and their corresponding RILs in combination with CO₂ absorption. They showed that the silyl amines were stable also in presence of water, while the siloxylated amines were susceptible to degradation. Furthermore, they showed these RILs obeyed both physical and chemical absorption mechanism to have a absorption capacity of 13-20 mole CO₂/kg amine at 35 °C and 62.5 bar. For more information on this topic, the reader is referred to the reviews by Blasucci [241], Jessop [243] and Shannon [244].

2.3.4 CO₂ Capture Performance: ILs vs. Commercial Solvents

The application potential of ILs for CO₂ capture depends on their performance with respect to already commercialized solvents. The measures that can be used to gauge a solvents' performance are for example: absorption capacity, gas selectivity, viscosity, stability, solvents' cost and most importantly the overall process cost. Table 2.2 provides an overview of the performance of ILs for CO₂ capture with respect to six commercially applied solvents. The Selexol, Fluor Solvent, Purisol and Rectisol processes utilize a physical solvent, while the Sulfinol process uses a mixed solvent, either DIPA or MDEA with Sulfolane. The standard Econamine process of Fluor uses 30 wt% MEA, which runs on a chemical reaction [245]. However, Fluor has recently improved the Econamine process allowing a higher MEA concentration [245]. All these physical or chemical solvents are applied industrially in the natural gas sweetening process. Tennyson and Schaaf [10] provide useful guidelines for solvent selection depending on acid gas conditions (e.g. partial pressure of acid gas, impurities and product specification). Ionic liquids exhibiting only physical absorption have been considered in Table 2.2. Upon comparison of the data presented in Table 2.2 it becomes clear that ILs are much more expensive than conventional solvents. Current (lab-scale) prices of ILs are ~1000 \$/kg, but economy of scale should apply and according to BASF the price for a large scale process will drop to <40 \$/kg. The cost of ILs, even at this price level, would still be a factor of 10 to 20 higher than conventional solvents.

Table 2.2: Comparison of the properties^a of commercially used solvents and ionic liquids for CO₂ capture. Many other commercial solvents exist, only the ones commonly used are listed.*

Process name	Selexol	Fluor	Solvent	Purisol	Rectisol	Sulfolin	Econamine	FG	Ionic liquids
chemical	DMPEG	PC	NMP	MeOH	DIPA+Sulfolane	MEA ^j	Salts		
licensor	UOP	Fluor	Lurgi	Linde+Lurgi	Shell	Fluor	n/a		
type absorption	physical	physical	physical	physical	chem. ^e /phys. ^f	chemical	physical		
solvent cost (\$/kg) ^b	2.5	1.5-2	4	0.7	2.5/4	1.5-2	<40 ^m		
viscosity (mPa.s)	5.8	3	1.65	0.6	186 ^g /10	18.98 ^k	20-1000		
density (kg/m ³)	1030	1195	1027	785	1004/1261	1017	800-1500		
molar mass (g/mol)	280	102	99	32	133.19/120.17	61.09	200-750		
vapor pressure (mmHg)	0.00073	0.085	0.4	1.25	0.035/0.02	0.36	0.000001		
freezing point (°C)	-28	-48	-24	-92	44/26	10.5	-140 to 180		
boiling point (°C)	275	240	202	65	249/285	171	> 250		
max. operating Temp. (°C)	175	65	202	65	150	150	> 200		
operating pressure	high	high	high	high	low	low	high		
$\Delta_{abs}H$ (kJ/mol CO ₂)	-14.3	-15.9	-16.4	-13	-73.7 ^h	-85	-10 to -20		
CO ₂ solubility (m ³ /m ³)	3.63	3.4	3.57	14.4 ^d	30-40 ⁱ	50-85 ^l	> 2.51		
CO ₂ /CH ₄ selectivity ^c	15	26	14	20 ^d	n/a	n/a	8-35		
H ₂ S/CO ₂ selectivity ^c	8.8	3.3	10.2	7 ^d	1-2 ^t	1-2 ^t	2-10		
CO ₂ /H ₂ selectivity ^c	77	126	178	185 ^d	n/a	n/a	50-150		
CO ₂ /N ₂ selectivity ^c	50	117	50	83 ^d	n/a	n/a	30-100		
$\Delta_{vap}H$ (kJ/mol)	76.16 ⁿ	60.2	54.5 ^o	35.27	57.4/66.8	49.8	>120		
H ₂ O miscibility	yes	partial	yes	yes	yes	yes	variable ^p		

^a Properties at 25 °C and 1 bar, unless otherwise stated. ^b Indicative prices (\$/2007) taken from www.iclis.com or from supplier info.

^c Ideal selectivity, real H₂S/CO₂ selectivity will differ significantly from ideal selectivity. ^d Solubility, selectivity data at -25 °C.

^e Pure compound property of DIPA / ^f pure compound property of Sulfolane. ^g Property at 45.5 °C taken from Henni *et al.* [246].

^h Enthalpy of reaction of CO₂ in diisopropanolamine. ⁱ Property in a mixture of 40 wt% DIPA + 40 wt% Sulfolane + 20 wt% water.

^j Properties of pure MEA is reported, unless otherwise stated. ^k Viscosity of 30 wt% aqueous MEA solution is 2.2 mPa.s at 25 °C.

^l Solubility, selectivity in a solution of 30 wt% MEA. ^m Estimation of BASF (30 euro/kg) for ton scale production of ionic liquids.

ⁿ Property of tetra-ethylene glycol dimethyl ether. ^o Property at 20 °C. ^p Ranging from completely miscible to immiscible.

* Majority of the data taken from Refs [11, 247-250]. Other data taken from Refs [108, 122, 123, 160-162, 171, 251-263].

This means that a successful application of ILs would rely on other properties of ILs. This property is certainly not the viscosity, since the viscosity of ILs is also significantly higher than of conventional solvents. We note that the viscosity of pure DIPA and MEA are also very high, but these solvents are always used in diluted form with viscosities not much higher than that of water. A property, which is inherently related to and in favor of ILs is the vapor pressure. Indeed, the vapor pressure of ILs is much lower than of the currently used solvents. However, the Selexol process also uses a solvent with a very low vapor pressure, but with a much lower viscosity compared to ILs. The volatility of a number of amines, including MEA, has been reported by Nguyen *et al.* [264, 265]. However, volatility is not the only cause for the solvent losses in a CO₂ capture process, but also losses due to thermal and chemical degradation should be considered. Rochelle *et al.* [266, 267] estimated the total MEA loss at stripper conditions to be 80-540 g/ton CO₂ captured, where the lower and upper limit correspond to a stripper operating temperature of ~ 110 °C and ~ 130 °C, respectively. In terms of process cost, this loss would result in a solvent replacement cost of \$0.19-\$1.31/ton CO₂ removed assuming a price of \$1.10/lb of MEA. Reddy *et al.* [268] estimated the solvent replacement cost of Fluor's Econamine FG PlusSM process to be \$2.30/ton CO₂ removed. A property not considered in Table 2.2 is the corrosivity and degradation sensitivity of the solvents. Although MEA is known to be corrosive and sensitive to chemical degradation, these properties have been scarcely investigated and reported for ILs. However, some of the commonly used ILs are also known to be corrosive especially at higher temperatures and for copper alloys, but carbon steel show very low corrosion rates [269–277]. Surprising to note is that some ILs have been considered as anti-corrosion agents [278, 279]. Nonetheless, a systematic analysis of the corrosion and degradation behavior of ILs is still lacking, but these issues should be considered in future research. Considering the price/performance ratio of ILs and conventional solvents for CO₂ capture it seems that we will not gain much utilizing physical ILs. We could take advantage of the tunability property of ILs, which can be used to design ILs with an improved selectivity of a gas pair over conventional solvents. Furthermore, ILs can

be designed to operate in a range where conventional (physical) solvents can not be applied. For example, at post-combustion conditions where the CO₂ partial pressure is very low, none of the physical solvents including ILs can be applied. Nevertheless, in this case an amine functionalized IL with a better energy efficiency and reaction stoichiometry than the Sulfinol or MEA process could be used. In this regard, it is very promising and challenging to design ILs with a lower enthalpy of reaction than conventional amines. At pre-combustion and natural gas sweetening conditions where the CO₂ partial pressure can be quite high (see Table 2.1), one can optionally choose for a physical IL solvent. However, the price/performance ratio of existing ILs is still insufficient to compete with existing commercial solvents (e.g. Selexol).

In the following we will discuss an another approach for gas separation, namely supported ionic liquid membranes (SILMs), which is a promising alternative for low pressure applications.

2.4 Supported Ionic Liquid Membranes (SILMs)

A relatively new research field is the application of ILs as a solvent in supported liquid membranes (SLMs) technology. Usually, SLMs consist of two phases, a supporting porous (or nonporous) membrane and a liquid solvent phase, which resides in the pores (or are being held between two non porous membrane sheets). Solute molecules diffuse/dissolve into the membrane facilitating a reaction or separation in the liquid phase and finally desorb at the opposite side of the membrane [280]. One of the disadvantages of conventional SLMs is the loss of solvent due to evaporation of the stabilized liquid phase [281–283]. This problem can be circumvented by using ILs as the liquid phase and taking advantage of their unique properties such as, relatively low volatility, high chemical and thermal stability [284]. The potential of supported ionic liquid membranes (SILMs) for gas separation has been studied by several researchers [281, 285–290]. Reviews of SILMs for gas separation are given by Bara *et al.* [291] and by Noble and Gin [284]. The performance of SILMs is generally evaluated through a 'Robeson plot'

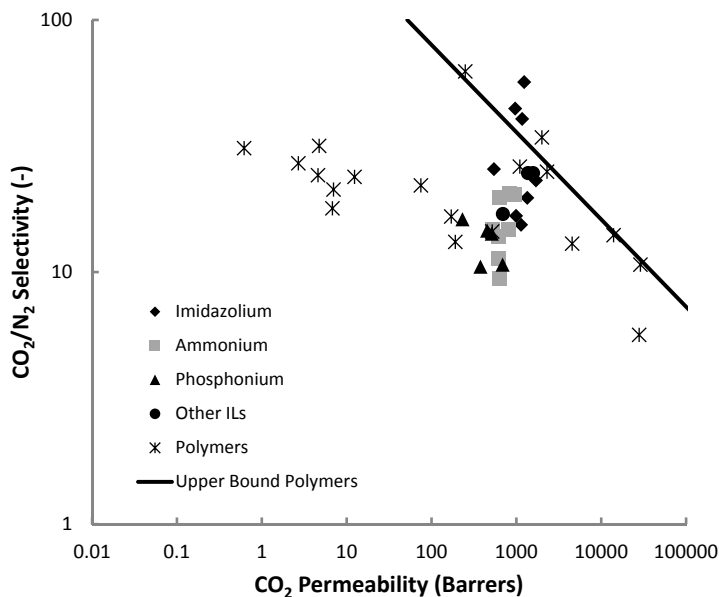


Figure 2.27: Robeson plot showing the performance of polymeric membranes and supported IL membranes (SILMs) for CO₂/N₂ separation. Some of the SILMs cross the 'upper bound' [292] limit of polymeric membranes. SILMs data at 303 K taken from Scovazzo [293] and data of polymers taken from Robeson [292] and Stern [294].

together with polymeric membranes data. An example of a Robeson plot, which shows a tradeoff between permeability and selectivity for CO₂/N₂ separation by polymers, is given in Figure 2.27. Interesting to see in Figure 2.27 is that some SILMs crosses the upper bound limit set for polymeric membranes. This means that SILMs can be designed with a permeability and selectivity superior to traditional polymeric membranes.

The transport mechanism of gases through membranes is extremely important and for SILM it is assumed that a solution-diffusion mechanism governs this transport [293]. Therefore, the ideal permeability (P_i) of a gas through a SILM can be expressed as a product of the solubility coefficient

(in moles per volume per partial pressure) and the diffusion coefficient:

$$P_i = S_i \cdot D_i \quad (2.9)$$

The ideal selectivity (α_{ij}) is then calculated by taking the ratio of the ideal gas permeabilities for a given gas pair:

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \cdot \frac{D_i}{D_j} \quad (2.10)$$

Several correlations for predicting gas solubilities [115, 121, 295] and diffusivities [182, 194, 195] in ILs have been proposed. Recently, Scovazzo [293] reviewed the progress in the SILM field and presented upper limits and benchmarks for guiding future research. Scovazzo provide a correlation, depending only on the molar volume of the IL, for the selectivity of the gas pairs CO₂/N₂ and CO₂/CH₄. A correlation, only depending on the IL viscosity, for CO₂ permeability through SILMs is also provided by Scovazzo. The (ideal) selectivity correlation by Camper [120] and the universal correlation by Scovazzo [293] both predict an increasing selectivity with decreasing IL molar volume for the gas pairs CO₂/N₂ and CO₂/CH₄. Ideal CO₂/N₂ selectivity in SILMs has been reported by Scovazzo *et al.* [280], Bara *et al.* [296], Neves *et al.* [289] and Cserjesi *et al.* [297]. Scovazzo investigated SILMs based on [emim][Tf₂N], [emim][CF₃SO₃], [emim][dca] and [thtdp][Cl] reporting CO₂ permeabilities in the range of 350-1000 barrers (1 barrer = 10⁻¹⁰ cm³ (STP) cm/cm² s cmHg) and ideal CO₂/N₂ selectivities of 15-61. Bara *et al.* measured the solubility of CO₂, N₂, O₂ and CH₄ in fluoroalkyl-functionalized imidazolium-based SILMs. They reported CO₂ permeabilities of 210-320, while the ideal selectivity of CO₂/N₂ and CO₂/CH₄ was 16-27 and 13-19, respectively. Neves *et al.* studied the ideal and mixed gas solubility of several gases in imidazolium-based ILs using two membrane supports with different hydrophobicity. They reported mixed-gas CO₂/N₂ and CO₂/CH₄ selectivities, which was not much different than the ideal selectivities, ranging from 20-32 and 98-200, respectively. Furthermore, they showed that the hydrophobic supports were more stable than the hydrophilic ones. Cserjesi *et al.* investigated the solubility of several

gases in SILMs using different type of ILs. Ideal selectivities of the gas pairs CO₂/N₂, CO₂/H₂ and CO₂/CH₄ ranged from 10-52, 5-13 and 5-23, respectively. Mixed gas solubilities of the gas pairs CO₂/N₂ and CO₂/CH₄ in several SILMs were reported by Scovazzo *et al.* [281]. The highest mixed-gas selectivity for CO₂/N₂ and CO₂/CH₄ was 21.2 and 27 for [emim][Tf₂N] and [emim][BF₄] based SILMs, respectively. Furthermore, the mixed-gas selectivities were approximately equal to the ideal selectivities for the corresponding gas pairs. Mixed gas solubility of the gas pair CO₂/H₂ was measured by Myers *et al.* [287] using an amine-functionalized IL in a cross-linked Nylon 66 support. They reported selectivities greater than 15 and CO₂ permeabilities ranging from 100-1000 barrers. Ideal CO₂/CH₄ selectivity has also been studied by Iarikov *et al.* [290] and Yoo *et al.* [288], while Hanioka *et al.* [286] measured mixed-gas solubilities. Iarikov *et al.* studied SILMs based on ammonium, imidazolium, pyridinium and pyrrolidinium an phosphonium ILs obtaining a ideal selectivity of 5-30. Yoo *et al.* obtained an ideal CO₂/CH₄ selectivity of 26 using imidazolium-based ILs in a Nafion membrane. Hanioka *et al.* used an amine-functionalized IL membrane obtaining high CO₂/CH₄ selectivity and a high membrane stability. On the basis of limited amount of data, Scovazzo [293] concluded that solubility selectivity dominate the selectivity in SILMs, whereas diffusion determines the selectivity in polymers. Since, diffusion selectivity plays a minor role, mixed gas solubilities in SILMs are expected to be approximately equal to ideal selectivities [281]. For more information on SILMs, the reader is referred to the excellent reviews by Scovazzo [293] and Lazano[298].

2.5 Biodegradability and Toxicity of Ionic Liquids

Ionic liquids are often referred to as 'green' and environment benign. This classification was initially justified on the ground of their low vapor pressure, nonflammability and reusability. However, important issues within the context of green chemistry [299, 300] (e.g. biodegradability and toxicity) were initially neglected [301]. The importance of biodegradability and toxicity should not be underestimated, since these parameters are relevant

in the authorization process of any substance [302]. Persistent and toxic ionic liquids, due to their potential hazard to environment and humans, may fail the authorization process or their use will be restricted to only a few applications [303]. Anticipating on the large scale application of ionic liquids, disposal of exhausted non-biodegradable ionic liquids may also become an issue [304]. Therefore, a thoroughly assessment of the potential risks of ILs is essential before commercializing IL processes. Since recently much more attention has been paid to these issues, as a result the IL literature for biodegradability and toxicity has grown considerably. Here, we analyze data from existing literature and aim to provide rules of thumbs or generalizations, which might be relevant for designing inherently safer ionic liquids.

In the next section we will discuss the biodegradability and toxicity of ILs. As the research field is expanding and IL processes are close to reaching the market, it is important to analyze the environmental fate of IL. An IL may come in contact with several streams, in which they might be soluble (for example water) thereby having a chance to end in the environment via the effluent streams of a process. Environmental issues of ILs have been characterized as a major barrier to commercialize IL processes, therefore these topics will be discussed next [305].

2.5.1 Biodegradability of Ionic Liquids

It is well known that biodegradability is affected not only by a compounds structure, but also by the environmental conditions. However, safe design of a product should start at the earliest phase in the long process of commercializing a new chemical. The earliest phase in product/process design is often the design of the molecule itself, hence the principles of safe design should preferentially be applied at molecular level [306]. The emphasis, here, is the effect of molecular structure (i.e. anion, cation, functional groups) on the biodegradability of ionic liquids. Before starting with the analysis of the reported data, it is informative to mention the rules of thumbs given by Boethling *et al.* [306] for the biodegradability of small molecules.

Rules of Thumb

These rules of thumb are not specifically for ionic liquids, but originate from decades of research mainly in the detergent and pesticide industry. However, initial research suggest that designing ILs according to some of these rules of thumbs may also improve the biodegradability of ionic liquids [304, 307]. According to Boethling *et al.* the following molecular features generally result in poor biodegradation and should be avoided when possible: halogens (e.g. chlorine and fluorine), extensive chain branching (e.g. quaternary C), tertiary amine, nitro, nitroso, azo, arylamino groups, polycyclic residues (e.g. polycyclic aromatic hydrocarbons), heterocyclic residues (e.g. imidazole) and aliphatic ether bonds.

The following molecular features generally improve biodegradation: esters, amides, hydroxyl, aldehyde, carboxylic acid groups, probably ketone, unsubstituted linear alkyl chains (≥ 4 carbons) and phenyl rings. The rules of thumb given here should not be used as universal generalizations, since exceptions exist for these rules of thumb [306]. Nevertheless, it can serve as a good starting point in the design of biodegradable ILs.

Biodegradation Studies of Ionic Liquids

Biodegradability of substances are generally assessed according to the guidelines laid down by the Organization for Economic Co-operation and Development (OECD) [308]. Several standard methods compliant with the OECD guidelines exist: Die-Away test (OECD 301 A), Modified Sturm test (OECD 301 B), Closed Bottle test (OECD 301 D), CO₂ Headspace test (ISO 14593), OECD 309 and ASTM D 5988 test. Each method employs a different principle, whereby depending on the chosen method one of the following is monitored as a measure for biodegradability: the dissolved organic carbon (DOC), CO₂ production and O₂ uptake. However, care should be taken in the selection, since the suitability of each method for assessing biodegradation depends on several physical properties of the compound in question (i.e. water solubility, volatility and the tendency to adsorb on solid phases). Detailed information on the measuring principle

of each method, a selection criterion and a review on the biodegradation of ILs is given by Coleman and Gathergood [308]. The group of Scammells [304, 307, 309] was the first to report the poor biodegradability of commonly used imidazolium ILs. Garcia *et al.* [309] used the Closed Bottle test to evaluate the biodegradability of [bmim][X] ILs, where X = Br, BF₄, PF₆, TF₂N, DCA and octylsulphate. All the ILs, except for the octylsulphate IL, underwent a biodegradation less than 5 % while the octylsulphate IL had a modest biodegradability of 25 %. Clearly, these ILs cannot be classified as "readily biodegradable", which is an arbitrary classification for substances that undergo more than 60 % biodegradation within a specified test period (normally 28 days) [309]. In a subsequent study, Gathergood *et al.* [304] applied some of the rules of thumbs given by Boethling *et al.* [306] to improve biodegradation of the above mentioned ILs. Accordingly, they incorporated an ester or an amide group in the alkyl side chain of the imidazolium cation. The ester-functionalized ILs were shown to significantly improve biodegradation, while the effect of the amide-functionalization was negligible. Furthermore, biodegradability was shown to increase with alkyl-chain length of the ester-functionalized cation. Introduction of a methyl group at the C₂-position of the imidazolium ring was shown to have negligible effect on biodegradability compared to the C₂-unsubstituted ILs. Although biodegradability of the ester-functionalized ILs was higher than of the nonfunctionalized ILs, only a combination of [mim-ester] cation and [octylsulphate] anion resulted in biodegradabilities higher than 60 %. These ester-functionalized imidazolium cations with the [octylsulphate] anion formed the first readily biodegradable ILs [310]. Morrissey *et al.* [311] measured the biodegradability of a large number of imidazolium-based ILs containing an ester and/or ether group in the alkyl side chain, using the "CO₂ Headspace" test. Ester-functionalized ILs were shown to have a higher degree of degradation, while including ether groups into the side chain did not have a detrimental effect on the biodegradation of the ILs. Morrissey *et al.* paired the ester/ether-functionalized cations with several commonly used anions (i.e. Br, BF₄, PF₆, Tf₂N, DCA and octylsulphate), however, only ILs containing the [octylsulphate] anion passed the readily biodegradable test. Clearly, the [octylsulphate] anion has a impor-

tant role in determining the high biodegradation of ILs [311, 312]. Moreover, the data reported by Morrissey *et al.* [311] and Docherty *et al.* [313] show close agreement with Boethling's rules of thumb where biodegradability increases as the alkyl chain length (≥ 4 carbons) increases.

Biodegradability of pyridinium-based ILs has been measured by several authors [313–317]. Docherty *et al.* [313] used the "Die-Away" test to investigate the biodegradability of six imidazolium and pyridinium ILs ([bmim], [hmim], [omim], [bmpy], [hmpy] and [ompy]), all containing the [bromide] anion as the counter ion. None of the imidazolium ILs could be classified readily biodegradable, while the pyridinium IL with the longest alkyl chain [ompy] passed the test. The data showed further that the pyridinium ILs had higher biodegradabilities than the imidazolium analogues and that the biodegradability improved with increasing alkyl length. Harjani *et al.* [315] evaluated the biodegradability of several (ester-functionalized) pyridinium ILs using the "CO₂ Headspace" test. The (ester-functionalized) pyridinium cations were paired with a range of anions (i.e. Br, PF₆, octylsulphate, bis(trifluoromethylsulfonyl)imide and iodide). Pyridinium ILs bearing an ester side chain moiety was shown to have high levels of biodegradation and could be classified as 'readily biodegradable'. In contrast, pyridinium ILs with alkyl side chains without an ester functionality did not pass the biodegradability test. In this case, the biodegradability did also not improve as the alkyl chain length was increased, contradicting Boethling's rules of thumb. Further, the effect of the anion on the biodegradability was shown to be insignificant [314, 315]. Ford *et al.* [316] studied the biodegradability (CO₂ Headspace test) of pyridinium and thiazolium ILs containing one of the following functionalities: hydroxyethyl side chain, methyl or ethyl ether side chain, acetal and carbamate. Pyridinium ILs, regardless of the anion, containing the hydroxyethyl functionality showed higher levels of biodegradation and passed the readily biodegradable test. In contrast, thiazolium ILs containing the hydroxyethyl functionality showed surprisingly low biodegradation. Pyridinium ILs bearing an ether, acetal or carbamate functionality showed significantly lower biodegradation. Biodegradation studies of ammonium and phosphonium ILs are relatively scarce so far. Yu *et al.* [318] and Pavlovica *et al.* [319] reported that cholinium (i.e.

2-hydroxyethylammonium) ILs containing naphthenic acid or lactate anion were highly biodegradable. Atefi *et al.* [320] used the 'CO₂ Headspace' test to evaluate biodegradation of phosphonium-based ILs. The phosphonium cation was functionalized with an ester, ether, alcohol or alkane moiety and paired with halide, triflimide or octylsulphate anions. As expected, ILs containing the octylsulphate anion showed an increased biodegradation, but in all cases the biodegradability was lower than 30 %. It is surprising to note that ester-functionalization of phosphonium, in contrast to imidazolium and pyridinium, ILs failed to promote biodegradation.

In summary, pyridinium and cholinium ILs are more biodegradable than imidazolium and phosphonium ILs. Biodegradation can be improved by including ester-functionalities in the imidazolium and pyridinium cations, while the phosphonium cation is an exception to this rule of thumb. A longer alkyl chain seems to promote biodegradation in many cases, however exceptions exist also for this rule of thumb. The anion seems to play a minor role in biodegradation, although the octylsulphate anion generally yields higher biodegradation. Overall, the rules of thumbs given by Boethling *et al.* [306] should not be used as universal generalizations, but can serve as guidelines for designing biodegradable ILs.

2.5.2 Toxicity of Ionic Liquids

Toxicological studies are essential in determining the impact of ILs on the environment and humans. Generally, toxicity of ILs is evaluated according to standard methods (i.e. OECD, ISO or ASTM), where a test model (e.g. microorganisms) is exposed to the IL and the response of it is a measure of toxicity, often expressed as a LC₅₀, EC₅₀ or IC₅₀ value. Many studies appeared in the last few years addressing the toxic nature of some commonly used ILs. Compilation of raw data on the toxicity of ILs can be found in several recent reviews and the references cited therein [321–325]. However, the emphasis here is to show toxicity trends with respect to anions, cations and functional groups of ILs.

The cation is believed to play a key role in determining the toxicity of an IL, while the anion has a minor influence [303, 326]. Wells and Coombe [317]

studied the ecotoxicity of quaternary-ammonium, imidazolium, quaternary-phosphonium and pyridinium ILs towards two aquatic test models. All the investigated ILs were shown to have EC₅₀ based toxicities much greater ($\sim 10^4$ - 10^6 for the worse cases) than conventional solvents like methanol and acetonitrile. Further, toxicity was shown to increase as the alkyl chain length on the imidazolium cation was increased for an IL containing the [chloride] anion [317, 327]. This trend has consistently been reported for ammonium [328], morpholinium [328], phosphonium [317], pyridinium [329, 330] and pyrrolidinium [330] ILs. Stolte *et al.* [331] studied the aquatic toxicity of a large number of ILs with a different head group. These authors found a correlation between the lipophilicity of ILs and (eco)toxicity, where the toxicity increases as the lipophilicity (i.e. hydrophobicity) becomes higher [332]. This may explain the increased toxicity of ILs containing a large alkyl chain (i.e. increased lipophilicity). Furthermore, the toxicity not only increases with an increasing alkyl chain length also the number of alkyl chains on the cation increases the toxicity [324]. The latter explains the higher toxicity of quaternary-ammonium and quaternary-phosphonium ILs compared to imidazolium and pyridinium analogues. Couling *et al.* [326] developed a quantitative structure-property relationship (QSPR) for assessing and predicting the toxicity of a range of ILs. The QSPR-model predicted the following toxicity trend with cation: ammonium < pyridinium < imidazolium < triazolium < tetrazolium. Unfortunately, this trend is not universal since many ammonium and pyridinium ILs are shown to be more toxic than imidazolium ones [328, 331, 333].

Although the anion is believed to play a secondary role in the toxicity of ILs, it can significantly increase or reduce toxicities. Toxicity data for aquatic organisms compiled by Frade *et al.* [324] show the following anion trend: [Br] < [DCA] < [Cl] < [BF₄] < [PF₆] < [Tf₂N]. Especially the fluorinated anions (e.g. BF₄ and Tf₂N) are highly toxic and forms a serious risk for the environment [303, 332, 334].

In summary, the toxicity data reported in the literature should be treated with some caution. Different test models have been used in the separate studies to evaluate toxicity, which complicate data interpretation since different test models can respond differently to the same IL. This is also the

reason why data extrapolation from one test model to another should be avoided [325]. So far, the only consistently reported trend is that toxicity increases with alkyl chain length and with the number of alkyl chains on the cation. Further, the [morpholinium] cation and the [DCA] anion seems to be good candidates for reducing toxic effects [324, 333]. In the future more unified and systematic approaches should be used to evaluate toxicity of ILs.

2.6 Conclusions and Future Directions

Efficient removal of the greenhouse gas carbon dioxide (CO_2) from fluegas turns out to be extremely challenging from an economic and technical point of view. The energy penalty, hence also the cost, for CO_2 removal from fluegas/natural gas is extremely high, thus, unattractive for large scale applications. Many new processes/materials, in particular ionic liquids (ILs) due to their unique properties, have been proposed to overcome this problem. In this review we have analyzed the literature data of the last decade on CO_2 capture with ILs and aimed to present trends regarding: CO_2 solubilities and selectivities in different ILs, effect of anions, cations and functional groups on physical properties, volatility, biodegradability and toxicity of ionic liquids. In addition, recent developments on functionalized ILs and supported IL membranes have also been addressed. Among the many solubility trends reported here, the main finding is that the CO_2 solubility in conventional ILs based on a physical mechanism is still too low at post-combustion capture conditions to compete with the amine process. Furthermore, the Henry constant (CO_2 solubility) tends to decrease (increase) with an increasing IL molecular weight, molar volume and free volume. Therefore, the CO_2 solubility in ILs should be compared on molality (mol/kg) or molarity (mol/m³) basis, instead of mole fraction basis. CO_2 absorption capacity have successfully been improved by functionalizing conventional ILs with an amine moiety, thereby allowing the CO_2 to react chemically with the amine. In this way even a better (1:1) reaction stoichiometry, compared to conventional CO_2 -amine chemistry, could be

achieved when the amine was functionalized to the anion of the IL. Not only solubility, but also selectivity is of great importance in industrial separation processes. Selectivity analysis show that CO₂ is generally much more soluble than other simple gases (e.g. H₂, N₂, O₂), however SO₂ and H₂S are by far the most soluble gases in ILs. This means that the selectivity will be high for CO₂/simple-gas systems, while the selectivity will likely drop for CO₂/sour-gas systems. Regular solution theory predict that CO₂/N₂ and CO₂/CH₄ selectivity can be improved by using ILs with a low molar volume. A common problem to all functionalized or nonfunctionalized ILs is their high viscosity, which forms a great barrier for industrial application. Trends are shown in this review, which can be used to design low viscosity ILs. Biodegradability and toxicity data analysis show that many commonly used ILs are nonbiodegradable and highly toxic. Rules of thumbs from the detergent industry have been used to improve biodegradation, however only some of the rules of thumbs applies also to ILs. Within the limited amount of toxicity data some trends are apparent, which could be used to design inherently safer ILs. As a final note, we want to address the following issues [305], which should be resolved in the future to commercialize IL processes: (1) Lack of physicochemical and thermodynamic data. Although some physical properties of ILs have been reported recently, there is need for more data on density, viscosity, surface tension, diffusion coefficients, specific heat, chemical/thermal stability, heat of fusion, water solubility, corrosivity, etc. These properties of ILs have scarcely been reported in the literature and accurate property predicting tools are still lacking. (2) Lack of lifetime and recyclability studies. Analysis of long term chemical and thermal stability of ILs is required under severe conditions to prevent degradation during absorption/desorption cycles. (3) Lack of scale-up studies. Lab-scale processes need to be scaled up to a pilot plant scale to assess the feasibility of ILs on industrial scale. Industry almost always demand demonstration on pilot scale before commercialization. (4) Lack of engineering studies. Manufacturing and process cost of ILs can only be reduced/optimized by systematic process engineering studies. These studies are lacking, mostly due to the absence of physicochemical properties of ionic liquids. (5) Lack of safety, health and environmental studies. Biodegradability and toxicity

of candidate ILs should be assessed thoroughly to prevent environmental pollution. (6) High price of ILs. The current lab-scale price of ILs is extremely high (~ 1000 \$/kg), which is 100-1000 times more expensive than conventional solvents. The price will drop for a large scale production of ILs, but a price level typical for conventional solvents should not be expected since ILs are complex molecules, requiring advanced synthesis and purification steps. To conclude, a lot of research is going on to improve CO₂ absorption capacities by taking advantage of the tunability property of ILs. Nevertheless, many barriers need to be overcome before ILs can be applied at a commercial scale.

Chapter 3

CO₂/CH₄ Solubility in Ionic Liquids: Ideal Selectivity

This chapter is based on the paper: M. Ramdin, A. Amplianitis, S. Bazhenov, A. Volkov, V. Volkov, T. J. H. Vlught and T. W. de Loos. Solubility of CO₂ and CH₄ in Ionic Liquids: Ideal CO₂/CH₄ Selectivity. Ind. Eng. Chem. Res., 53 (2014) 15427-15435.

3.1 Introduction

Natural gas contains a variety of impurities including the sour gases carbon dioxide (CO₂) and hydrogen sulfide (H₂S) [10, 11]. These sour gases have to be removed in order to meet customer specifications and to avoid technical problems during gas transportation. CO₂ should be eliminated, because of its low caloric value and due to the risk of dry ice formation during the liquefaction of natural gas. H₂S concentrations should be reduced drastically to avoid pipeline corrosion [17]. The sweetening of the natural gas is typically performed in an absorber-stripper configuration using either a physical solvent, a chemical solvent or a mixture of both depending on the type and concentration of the impurities [10]. Despite

the inherent high pressure of the sweetening process, which is favorable for physical absorption purposes, the majority of the units in the field utilizes chemical solvents (*e.g.*, monoethanolamine (MEA)) [9]. The use of physical solvents (*e.g.*, Purisol, Rectisol, Selexol etc.) is not uncommon in the natural gas industry and is in fact preferred over chemical solvents at high acid gas partial pressures [10]. The selection of the proper solvent for natural gas sweetening is not trivial, since it depends on many factors (*e.g.*, composition, temperature and partial pressures of the acid gases, and product specifications). For guidelines the reader is referred to the work of Tennyson and Schaaf [10] and Kohl and Nielsen [11]. Although the aqueous amine process is effective at removing acid gas components from natural gas for a wide range of conditions, it suffers a number of serious drawbacks. These include the high energy requirement for solvent regeneration, the low CO₂/H₂S selectivity, the corrosivity, and the volatility of the used amines [15]. Therefore, many researchers have posed alternatives to overcome some of the problems associated with the amine process. In the last few years, ionic liquids (ILs), which are salts with melting points lower than 100 °C and characterized by very low vapor pressures, have emerged as a promising solvent for acid gas removal [16, 17]. In the past decade, a large number of studies reported the solubility of CO₂ and to a lesser extent of other acid gas components in many different kinds of ionic liquids [9, 335]. In practice, however, not the solubility, but the selectivity of one component towards the another is more important for judging the separation performance of an absorption process [9]. This implies that a potential IL for natural gas sweetening should not only have a high individual CO₂ and H₂S solubility, but at the same time also a low CH₄ solubility. In other words, the IL should have a high CO₂/CH₄ and CO₂/H₂S selectivity. Lei *et al.* [335] provide an excellent review of the solubility of different gases in ILs, whereas Karadas *et al.* [17], Ramdin *et al.* [9] and Kumar *et al.* [16] review the application potential of ILs for natural gas sweetening. Recently, Mortazavi-Manesh *et al.* [336] used the COSMO-RS model to screen more than 400 ILs for the separation of acid gases. Unfortunately, the amount of experimental data on CO₂/CH₄ and CO₂/H₂S selectivities in ILs are extremely scarce, which is mainly due to the high toxicity of H₂S for the latter system, but this

reason is less obvious for the CO₂/CH₄ system.

This motivated us to study CO₂ and CH₄ solubilities and CO₂/CH₄ (ideal) selectivities in a total of 10 ILs composed of 8 different classes of cations and 4 different types of anions. A synthetic method has been used to measure the bubble-point pressures of CO₂ and CH₄, for a temperature range of 303.15 - 363.15 K and for pressures up to 14 MPa, in the ionic liquids: 1-ethyl-3-methylimidazolium diethylphosphate [emim][dep], trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate [thtdp][phos], trihexyltetradecylphosphonium dicyanamide [thtdp][dca], 1-allyl-3-methylimidazolium dicyanamide [amim][dca], 1-butyl-1-methylpyrrolidinium dicyanamide [bmpyr][dca], 1,2,3-tris(diethylamino)cyclopropenylum dicyanamide [cprop][dca], 1,2,3-tris(diethylamino)cyclopropenylum bis(trifluoromethylsulfonyl)imide [cprop][Tf₂N], 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide [bmpip][Tf₂N], triethylsulfonium bis(trifluoromethylsulfonyl)imide [tes][Tf₂N] and methyl-trioctylammonium bis(trifluoromethylsulfonyl)imide [toa][Tf₂N]. The experimental data has been reduced by calculating the Henry constants from which the ideal CO₂/CH₄ selectivities are obtained. The ideal CO₂/CH₄ selectivities of the investigated ILs are compared with those of conventional solvents used in the natural gas industry. Furthermore, the experimental data has been modeled with the Peng-Robinson equation of state in combination with van der Waals mixing-rules.

3.2 Experiments

The gases CO₂ and CH₄ used in the experiments had a purity of 99.995 mole % and were purchased from the Linde Group. The ILs, purchased from Sigma-Aldrich, were always dried in vacuo at a temperature of 80 °C for several days before usage. The molecular structures of the investigated ILs are shown in Figure 3.1. The water content of the ILs after drying was determined by Karl Fischer titration and the results together with other properties are shown in Table 3.1. Note that the purity of the ILs reported in Table 3.1 is prior to drying, while the water content is only measured

Table 3.1: Properties of the used ILs. The water content was measured with Karl Fischer titration, whereas the purities were reported by the supplier (Sigma-Aldrich) [339].

Name IL (Abbreviation)	Molecular weight (g/mol)	Purity ^a (mole %)	Water content ^b (ppm)
[emim][dep]	264.26	≥ 98.0	< 250
[thtdp][phos]	773.27	≥ 95.0	< 350
[thtdp][dca]	549.90	≥ 95.0	< 350
[amim][dca]	189.22	≥ 98.5	< 200
[bmpyrr][dca]	208.30	≥ 97.0	< 200
[cprop][dca]	318.46	≥ 96.5	< 200
[cprop][Tf ₂ N]	532.56	≥ 96.5	< 150
[bmpip][Tf ₂ N]	436.43	≥ 96.5	< 150
[tes][Tf ₂ N]	399.39	≥ 99.0	< 150
[toa][Tf ₂ N]	648.85	≥ 99.0	< 150
[bmim][Tf ₂ N]	419.36	≥ 98.0	< 150

^a Purity of ILs before drying

^b Water content of ILs after drying

and reported after the drying step. The ILs contained typically 1-2% water, therefore the actual purity of the ILs will always be higher than the reported values. The VLE experiments start with filling a Pyrex glass-tube with a known amount of IL. This tube is then connected to a gas-dosing system, which is used to degas the IL and to dose a known amount of gas into the tube using mercury as a displacement fluid. The exact amount of gas is calculated through the virial equation of state truncated after the second term [337]. Subsequently, the tube with a known composition is disconnected from the gas-dosing system and placed in the Cailletet apparatus. Here only a brief description of the Cailletet apparatus will be presented, since a detailed explanation of the experimental procedure can be found elsewhere [338]. The Cailletet apparatus allows phase equilibria measurements in a temperature and pressure range of 255-470 K and 0.1-15 MPa, respectively. For a binary system at bubble point conditions, the Gibbs phase-rule unequivocally requires two independent variables to be fixed. Therefore, the composition and the temperature were fixed in the experiments, while the

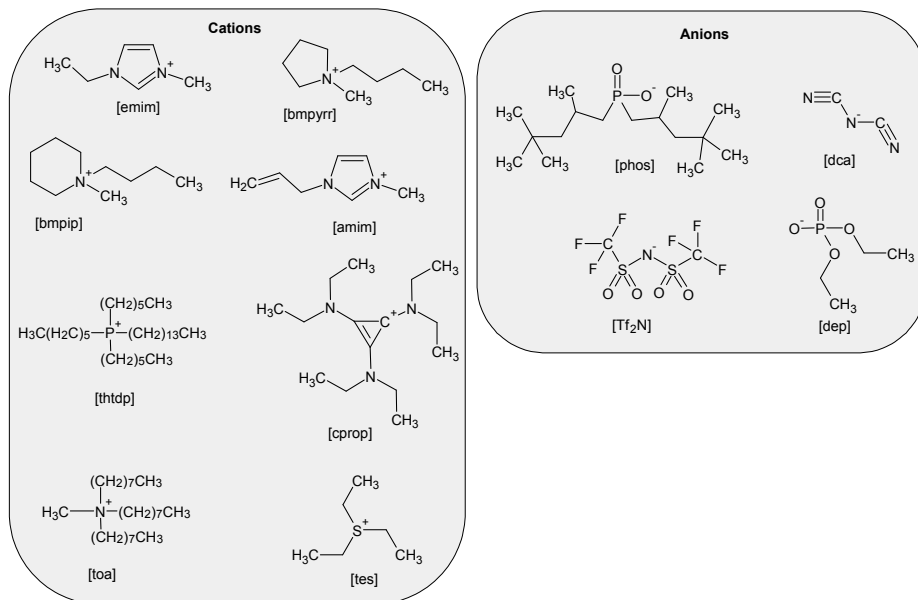


Figure 3.1: Cations and anions of the investigated ILs. Abbreviation cations: 1-allyl-3-methylimidazolium [amim], 1-ethyl-3-methylimidazolium [emim], 1,2,3-tris(diethylamino)cyclopropenylium [cprop], 1-butyl-1-methylpiperidinium [bmpip], 1-butyl-1-methylpyrrolidinium [bmpyrr], methyl-trioctylammonium [toa], trihexyltetradecylphosphonium [thtdp] and triethylsulfonium [tes]. Abbreviation anions: bis(trifluoromethylsulfonyl)imide [Tf₂N], dicyanamide [dca], bis(2,4,4-trimethylpentyl)phosphinate [phos] and diethylphosphate [dep].

pressure was gradually increased until the disappearance of the last bubble in the liquid (*i.e.*, the bubble-point pressure). The VLE measurements then involve the determination of bubble-point pressures at different, but fixed compositions and temperatures. The pressure is obtained by a dead weight gauge, while the temperature is controlled by a thermostatic bath equipped with a Pt-100 (ASL F250) thermometer. The standard uncertainty in the experimental pressure, temperature and composition is ± 0.005 MPa, ± 0.01 K (*i.e.*, the fluctuations in temperature were within the accuracy of

the thermometer) and ± 0.003 in the mole fraction, respectively.

3.3 Thermodynamic Modeling

The Peng-Robinson (PR) equation of state [340] (EoS) has been applied to model the experimental data,

$$P = \frac{RT}{v - b_m} - \frac{a_m}{v(v + b_m) + b_m(v - b_m)} \quad (3.1)$$

where v is the molar volume, a_m and b_m are constants for the mixture accounting for the molecular interaction and covolume, respectively. The PR EoS is used in combination with the quadratic van der Waals (vdW) mixing rules [337]:

$$a_m = \sum_i \sum_j x_i x_j a_{ij}, \quad a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}), \quad k_{ii} = k_{jj} = 0 \quad (3.2)$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = \frac{1}{2}(b_i + b_j)(1 - l_{ij}), \quad l_{ii} = l_{jj} = 0 \quad (3.3)$$

where k_{ij} and l_{ij} represent the binary interaction parameters, a_i and b_i the pure component parameters accounting for molecular interaction and covolume, respectively. Calculation of the pure component parameters requires the critical properties and acentric factors of all the components participating in the mixture. These properties are not known (*i.e.*, not experimentally available) for ILs, since many ILs start to decompose before reaching the critical point. Therefore, one has to rely on group-contribution methods [341], molecular simulations [206, 342] or suitable correlations [208]. Here, the modified Lydersen-Joback-Reid group-contribution method proposed by Valderrama *et al.* [341] is used to obtain the critical properties of all the investigated ILs. The critical parameters and acentric factors of all the ILs are listed in Table 3.2. Once these properties have been obtained, the PR EoS can readily be applied to calculate the bubble point of the gas-IL

Table 3.2: Critical temperature (T_c), pressure (P_c) and acentric factor (ω) of the components used in the modeling.

Component	T_c / K	P_c / MPa	ω
[emim][dep] ^a	877.2	2.147	0.722
[thtdp][phos] ^a	1878.8	0.551	-0.139
[thtdp][dca] ^a	1525.5	0.765	0.582
[amim][dca] ^a	1019.2	2.799	0.788
[bmpyrr][dca] ^a	887.2	2.061	0.855
[cprop][dca] ^a	1073.7	1.615	1.073
[cprop][Tf ₂ N] ^a	1255.7	1.803	0.588
[bmpip][Tf ₂ N] ^a	1108.0	2.264	0.392
[tes][Tf ₂ N] ^a	1189.9	2.190	0.160
[toa][Tf ₂ N] ^a	1376.1	1.064	0.996
[bmim][Tf ₂ N] ^a	1269.9	2.765	0.3004
CH ₄ ^b	190.6	4.599	0.012
CO ₂ ^b	304.12	7.374	0.225

^a Calculated using the method of Valderrama *et al.* [341].

^b Taken from Poling *et al.* [344].

systems. The binary interaction parameters k_{ij} and l_{ij} are simultaneously optimized using a simplex algorithm in MATLAB [343] minimizing the objective function:

$$\text{OF} = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_i^{\text{exp}} - P_i^{\text{pred}}}{P_i^{\text{exp}}} \right| \quad (3.4)$$

where N is the number of experimental points, P_i^{exp} and P_i^{pred} the experimental and predicted bubble-point pressure, respectively.

3.4 Results and Discussion

Due to space constraints, only a selection of the data will be presented here. The raw experimental data, extensive $p - T$ and $p - x$ diagrams of all the

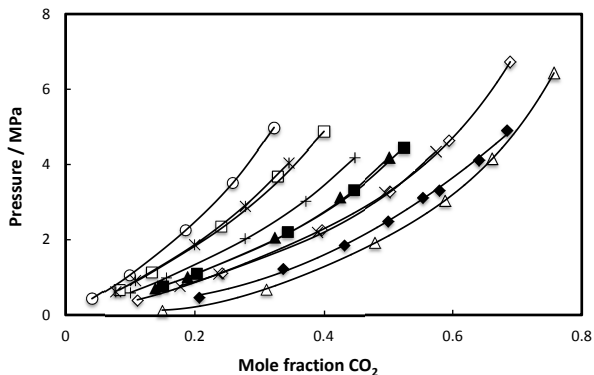


Figure 3.2: Comparison of CO₂ solubility at 313.15 K in the investigated ILs: [emim][dep] (open squares), [thtdp][phos] (open triangles) [346], [thtdp][dca] (open diamonds) [346], [amim][dca] (open circles), [bmpyrr][dca] (stars), [cprop][dca] (plusses), [cprop][Tf₂N] (crosses), [bmpip][Tf₂N] (closed squares), [tes][Tf₂N] (closed triangles) and [toa][Tf₂N] (closed diamonds) [347]. The lines are PR EoS modeling results using the parameters of Table 3.2.

systems can be found in the Supporting Information of Ref. [345]. A comparison of the CO₂ solubility in the investigated ILs is shown in Figure 3.2. The CO₂ + IL systems show a typical behavior: the solubility increases with increasing pressure and decreases with increasing temperature. The solubility trend, on mole fraction basis, observed for CO₂ obeys the following order: [thtdp][phos] > [toa][Tf₂N] > [thtdp][dca] > [cprop][Tf₂N] > [bmpip][Tf₂N] > [tes][Tf₂N] > [cprop][dca] > [emim][dep] > [bmpyrr][dca] > [amim][dca]. However, this trend completely vanishes if the solubility is compared on molality basis indicating a strong molecular weight effect. The data more or less collapse on the universal solubility curve proposed by Carvalho and Coutinho [125] as can be seen in Figure 3.3. The behavior of CH₄ is similar to that of CO₂, but the solubility of CH₄ is an order of magnitude lower compared to CO₂ at similar conditions, see Figure 3.4. It is surprising to see that the data for CH₄ do not collapse on an universal absorption curve as in the case of CO₂, see Figure 3.5. The CH₄ solubility is higher in ILs containing large nonpolar alkyl-chains, which obviously inter-

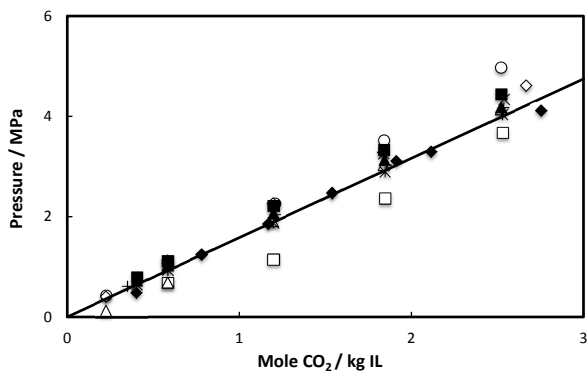


Figure 3.3: Comparison of CO_2 solubility on molality scale at 313.15 K in the investigated ILs: [emim][dep] (open squares), [thtdp][phos] (open triangles) [346], [thtdp][dca] (open diamonds) [346], [amim][dca] (open circles), [bmpyrr][dca] (stars), [cprop][dca] (pluses), [cprop][Tf_2N] (crosses), [bmpip][Tf_2N] (closed squares), [tes][Tf_2N] (closed triangles) and [toa][Tf_2N] (closed diamonds) [347]. The line is correlation by Carvalho and Coutinho [125].

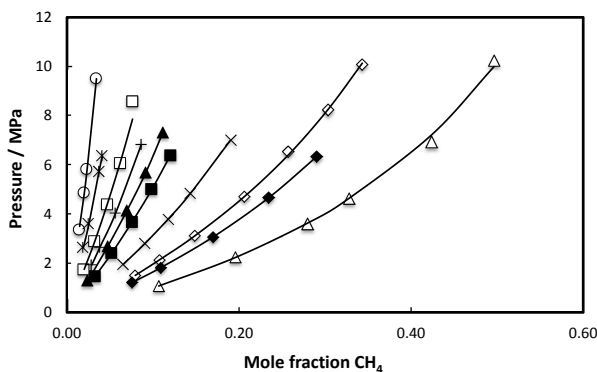


Figure 3.4: Comparison of CH_4 solubility at 313.15 K in the investigated ILs: [emim][dep] (open squares), [thtdp][phos] (open triangles) [346], [thtdp][dca] (open diamonds) [346], [amim][dca] (open circles), [bmpyrr][dca] (stars), [cprop][dca] (pluses), [cprop][Tf_2N] (crosses), [bmpip][Tf_2N] (closed squares), [tes][Tf_2N] (closed triangles) and [toa][Tf_2N] (closed diamonds) [347]. The lines are PR EoS modeling results using the parameters of Table 3.2.

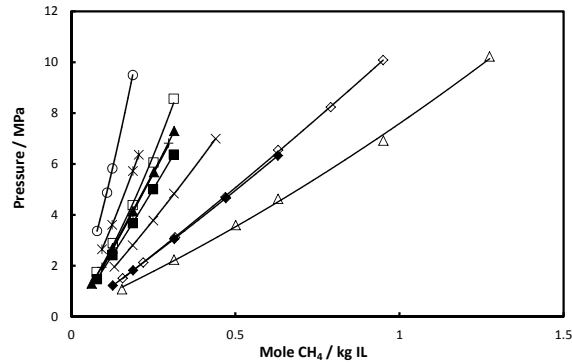


Figure 3.5: Comparison of CH₄ solubility on molality scale at 313.15 K in the investigated ILs: [emim][dep] (open squares), [thtdp][phos] (open triangles) [346], [thtdp][dca] (open diamonds) [346], [amim][dca] (open circles), [bmpyrr][dca] (stars), [cprop][dca] (plusses), [cprop][Tf₂N] (crosses), [bmpip][Tf₂N] (closed squares), [tes][Tf₂N] (closed triangles) and [toa][Tf₂N] (closed diamonds) [347]. The lines are polynomial fits to guide the eye.

acts with the nonpolar CH₄ molecule (*i.e.*, 'like dissolve like' principle). As explained earlier, in practice not the solubility, but the selectivity is the key parameter for judging the separation performance. There are several ways to obtain the ideal selectivity, ($S_{i/j}^I$), from VLE data. The first approach to calculate the selectivity is to use the liquid-phase mole fractions of the individual gases at a constant temperature and pressure:

$$S_{\text{CO}_2/\text{CH}_4}^I = \left(\frac{x_{\text{CO}_2}}{x_{\text{CH}_4}} \right)_{p,T} \quad (3.5)$$

The second approach is to use the the ratio of the bubble-point pressures at a constant temperature and composition:

$$S_{\text{CO}_2/\text{CH}_4}^I = \left(\frac{p_{\text{CH}_4}}{p_{\text{CO}_2}} \right)_{T,x} \quad (3.6)$$

The third approach is to use the ratio of the Henry constants of CH₄ over that of CO₂:

$$S_{\text{CO}_2/\text{CH}_4}^{\text{I}} = \left(\frac{H_{\text{CH}_4}}{H_{\text{CO}_2}} \right) \quad (3.7)$$

In principle, the ideal selectivity will be different depending on which of the above equations are used for the calculations. For convenience, we will use Equation (3.7) for all the ideal selectivity calculations, since Equation (3.5) and Equation (3.6) will require interpolations or extrapolations, because the data of CO₂ and CH₄ are generally not measured at the same mole fraction or pressure. The Henry constants, H_{12} , are calculated as [337]:

$$H_{12} = \lim_{x_1 \rightarrow 0} \frac{f_1^L}{x_1} \quad (3.8)$$

The fugacity of the solute '1', either CO₂ or CH₄, in the solvent '2', f_1^L , is calculated using a suitable equation of state for CO₂ [348] and CH₄ [349] assuming pure CO₂ or CH₄ in the gas phase and applying the equilibrium condition $f_1^L = f_1^V$. The calculated Henry constants for CO₂ and CH₄ in all the ILs are listed in Table 3.3 and Table 3.4, respectively. The Henry constants (solubility) increases (decreases) with increasing temperature for both, CO₂ and CH₄, systems. Henry constants for the systems CO₂-[emim][dep] and CO₂-[tes][Tf₂N] have been reported by Palgunadi *et al.* [350] and Nonthanasin *et al.* [351], respectively. The values for Henry constants reported in Table 3.3 agree within 10% of the literature data (*e.g.*, the Henry constant of CO₂ in [tes][Tf₂N] reported by Nonthanasin *et al.* is 4.5 MPa at 313 K, which is slightly lower than the 5.0 MPa reported here). The deviation in the Henry constants is likely due to errors using Equation (3.8) as the extrapolation $x_1 \rightarrow 0$ is performed. Information on the dissolution behavior at the molecular level can be obtained by calculating the enthalpy and entropy of absorption of the solute in the solvent. These properties are closely related to the strength of the interaction between the solute and the solvent and the degree of ordering of the solvent molecules around a solute molecule, respectively.

Table 3.3: Henry constants (H_{12} /MPa) of CO₂ (1) in the investigated ILs (2) obtained by plotting the fugacity versus the mole fraction and taking the limit of $x_1 \rightarrow 0$.

ILs Abbreviation	Temperature / K						
	303.15	313.15	323.15	333.15	343.15	353.15	363.15
[emim][dep]	6.53	7.91	9.38	10.95	12.60	14.35	16.19
[thtdp][phos] ^a		0.71	0.86	1.08	1.37	1.73	2.16
[thtdp][dca] ^a	3.00	3.58	4.14	4.67	5.18	5.68	6.15
[amim][dca]	8.19	10.04	11.99	14.02	16.16	18.39	20.71
[bmpyrr][dca]	6.62	7.96	9.44	11.07	12.84	14.77	16.85
[cprop][dca]	4.98	5.88	6.82	7.82	8.88	9.99	11.15
[cprop][Tf ₂ N]	3.61	4.26	4.94	5.65	6.40	7.19	8.01
[bmpip][Tf ₂ N]	4.19	5.01	5.88	6.81	7.79	8.83	9.92
[tes][Tf ₂ N]	4.20	5.03	5.93	6.89	7.93	9.02	10.19
[toa][Tf ₂ N] ^b	1.67	2.28	2.89	3.49	4.05		

^a Data taken from Ramdin *et al.* [346].^b Calculated from Nam and Lee. [347].Table 3.4: Henry constants (H_{12} /MPa) of CH₄ (1) in the investigated ILs (2) obtained by plotting the fugacity versus the mole fraction and taking the limit of $x_1 \rightarrow 0$.

ILs Abbreviation	Temperature / K						
	303.15	313.15	323.15	333.15	343.15	353.15	363.15
[emim][dep]	82.02	85.79	89.26	92.42	95.26	97.77	99.96
[thtdp][phos]	9.38	9.92	10.42	10.89	11.32	11.72	12.09
[thtdp][dca]	18.02	18.95	19.83	20.66	21.42	22.12	22.76
[amim][dca]	216.3	218.94	220.97	222.4	223.23	223.46	223.1
[bmpyrr][dca]	128.36	133.25	137.65	141.55	144.95	147.82	150.18
[cprop][dca]	63.56	65.35	66.92	68.27	69.40	70.30	70.97
[cprop][Tf ₂ N]	27.87	29.03	30.12	31.13	32.07	32.94	33.73
[bmpip][Tf ₂ N]	41.77	43.93	45.94	47.80	49.50	51.04	52.42
[tes][Tf ₂ N]	50.22	52.34	54.33	56.20	57.94	59.55	61.03
[toa][Tf ₂ N]	15.06	15.84	16.60	17.32	18.01	18.66	19.28

The calculation of the Gibbs energy, the enthalpy and entropy of absorption requires an appropriate correlation of the Henry constants as a function of temperature. Therefore, the temperature dependency of the Henry constant was fitted to the Benson-Krause (BK) equation [352]:

$$\ln[H_{12}/\text{MPa}] = \sum_{i=0}^m a_i (T/\text{K})^{-i} \quad (3.9)$$

Using the BK equation, the Gibbs energy, the enthalpy and entropy of absorption of the solute in the IL can be calculated using the thermodynamic relations [157]:

$$\Delta_{\text{abs}}G^\infty = RT[\ln(H_{12})] \quad (3.10)$$

$$\Delta_{\text{abs}}H^\infty = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{\Delta_{\text{abs}}G^\infty}{T} \right) \right] = -RT^2 \left[\frac{\partial \ln(H_{12})}{\partial T} \right] \quad (3.11)$$

$$\Delta_{\text{abs}}S^\infty = \frac{(\Delta_{\text{abs}}H^\infty - \Delta_{\text{abs}}G^\infty)}{T} = -RT \left[\frac{\partial \ln(H_{12})}{\partial T} \right] - R \ln(H_{12}) \quad (3.12)$$

The calculated properties of CO₂ and CH₄ are listed in Table 3.5 and Table 3.6, respectively. The negative value of the enthalpy of absorption of CO₂ and CH₄ indicates that the dissolution process is exothermic and the higher values of CO₂ compared to CH₄ is consistent with the higher solubilities of CO₂. However, the solubility trend of CO₂ observed in the ILs can not solely be explained by solute-solvent interactions. For example, the enthalpy of absorption of CO₂ in [amim][dca] is higher (*i.e.*, stronger interaction) than in [thtdp][phos], while the solubility of CO₂ is much lower in the former IL. The solubility trend can be explained by the entropic effects, which dominate the dissolution behavior of CO₂ in the ILs. This is completely opposite for CH₄, as can be seen in Table 3.6.

Table 3.5: The Gibbs energy ($\Delta_{\text{abs}}G$), the enthalpy ($\Delta_{\text{abs}}H$) and entropy of absorption ($\Delta_{\text{abs}}S$) of CO₂ in the ILs. The values of $\Delta_{\text{abs}}G$, $\Delta_{\text{abs}}H$ and $\Delta_{\text{abs}}S$ are consistent with a reference state of 0.1 MPa and 313.15 K.

CO ₂ + IL	$\Delta_{\text{abs}}G/\text{kJ mol}^{-1}$	$\Delta_{\text{abs}}H/\text{kJ mol}^{-1}$	$\Delta_{\text{abs}}S/\text{J mol}^{-1} \text{K}^{-1}$
[emim][dep]	11.4	-14.7	-83.2
[thtdp][phos] ^a	5.1	-12.5	-56.1
[thtdp][dca] ^a	9.3	-13.1	-71.5
[amim][dca]	12.0	-15.4	-87.4
[bmpyrr][dca]	11.4	-14.4	-82.4
[cprop][dca]	10.6	-12.7	-74.5
[cpop][Tf ₂ N]	9.8	-12.7	-71.7
[bmpip][Tf ₂ N]	10.2	-13.7	-76.3
[tes][Tf ₂ N]	10.2	-14.0	-77.2
[toa][Tf ₂ N] ^b	8.1	-22.3	-97.1

^a Calculated from Ramdin *et al.* [346].

^b Calculated from Nam and Lee. [347].

Table 3.6: The Gibbs energy ($\Delta_{\text{abs}}G$), the enthalpy ($\Delta_{\text{abs}}H$) and entropy of absorption ($\Delta_{\text{abs}}S$) of CH₄ in the ILs. The values of $\Delta_{\text{abs}}G$, $\Delta_{\text{abs}}H$ and $\Delta_{\text{abs}}S$ are consistent with a reference state of 0.1 MPa and 313.15 K.

CH ₄ + IL	$\Delta_{\text{abs}}G/\text{kJ mol}^{-1}$	$\Delta_{\text{abs}}H/\text{kJ mol}^{-1}$	$\Delta_{\text{abs}}S/\text{J mol}^{-1} \text{K}^{-1}$
[emim][dep]	17.6	-3.5	-67.2
[thtdp][phos]	12.0	-4.3	-51.9
[thtdp][dca]	13.7	-3.9	-56.1
[amim][dca]	20.0	-0.9	-66.8
[bmpyrr][dca]	18.7	-2.9	-69.0
[cprop][dca]	16.9	-2.1	-60.7
[cpop][Tf ₂ N]	14.8	-3.2	-57.3
[bmpip][Tf ₂ N]	15.8	-3.9	-63.0
[tes][Tf ₂ N]	16.3	-3.2	-62.3
[toa][Tf ₂ N]	13.2	-4.0	-54.8

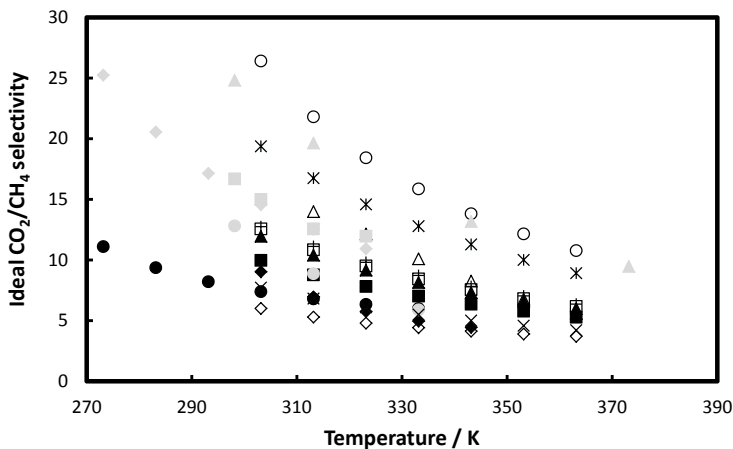


Figure 3.6: Comparison of the ideal CO₂/CH₄ selectivity in the investigated ILs and in conventional solvents at 313.15 K: [emim][dep] (open squares), [thtdp][phos] (open triangles), [thtdp][dca] (open diamonds), [amim][dca] (open circles), [bmpyrr][dca] (stars), [cprop][dca] (plusses), [cprop][Tf₂N] (crosses), [bmpip][Tf₂N] (black squares), [tes][Tf₂N] (black triangles), [toa][Tf₂N] (black diamonds), Rectisol (black circles), Fluor solvent (gray squares), Sulfolane (gray triangles), Purisol (gray diamonds) and Selexol (gray circles). Data of conventional solvents taken from Refs [260, 263, 353–362].

The CH₄ solubility trend observed in the ILs is consistent with the enthalpy of absorption values reported in Table 3.6. The enthalpy of absorption of CH₄ is higher for ILs containing long nonpolar alkyl-chains, which is due to nonpolar-nonpolar interactions. This suggests that the solute-solvent interactions dominate the dissolution of CH₄, while entropic effects are much more important for CO₂. Subsequently, the ideal CO₂/CH₄ selectivities are calculated using Equation (3.7) and the results are presented in Table 3.7. Interestingly, the ideal selectivity decreases rapidly with increasing temperature for all the investigated systems. However, Figure 3.6 shows that this trend is not unique for IL-systems, but also holds for conventional solvents like Selexol, Purisol, Rectisol, Fluor solvent and Sulfolane. The reason for this dramatic reduction of selectivity at higher temperatures

Table 3.7: Ideal CO₂/CH₄ selectivity obtained by calculating the ratio of the Henry constants of CH₄ over CO₂.

ILs Abbreviation	Temperature / K						
	303.15	313.15	323.15	333.15	343.15	353.15	363.15
[emim][dep]	12.6	10.8	9.5	8.4	7.6	6.8	6.2
[thtdp][phos]		14.0	12.1	10.1	8.3	6.8	5.6
[thtdp][dca]	6.0	5.3	4.8	4.4	4.1	3.9	3.7
[amim][dca]	26.4	21.8	18.4	15.9	13.8	12.2	10.8
[bmpyrr][dca]	19.4	16.7	14.6	12.8	11.3	10.0	8.9
[cprop][dca]	12.8	11.1	9.8	8.7	7.8	7.0	6.4
[cprop][Tf ₂ N]	7.7	6.8	6.1	5.5	5.0	4.6	4.2
[bmpip][Tf ₂ N]	10.0	8.8	7.8	7.0	6.4	5.8	5.3
[tes][Tf ₂ N]	12.0	10.4	9.2	8.2	7.3	6.6	6.0
[toa][Tf ₂ N]	9.0	7.0	5.8	5.0	4.4		

is that the methane solubility is only slightly influenced by the temperature, while the effect for CO₂ is much larger. The consequence of this is that the Henry constant of CH₄ is nearly independent of temperature, while the Henry constant of CO₂ increases rapidly with temperature. Nevertheless, some of the ILs (*e.g.*, [amim][dca] and [bmpyrr][dca]) perform better in terms of ideal selectivities than most of the conventional solvents. Moreover, the ideal selectivity decreases, with some exceptions, with increasing IL molecular weight, see Table 3.8 and Figure 3.7. This suggests that a low molecular weight IL should be used if a high selectivity is desired, which is consistent with the finding of Camper *et al.* [120] and Scovazzo [293], since molar volumes of ILs generally increases with increasing IL molecular weight [9]. Unfortunately, the CO₂ solubility on mole fraction basis is not very high for low molecular weight ILs. In conclusion, there is a trade-off between solubility, which increases with IL molecular weight, and selectivity, which decreases with increasing IL molecular weight. However, the poor CO₂/CH₄ selectivity for higher molecular weight ILs is not a surprise, since the molecular weight of the ILs is mainly increased by adding alkyl-groups. The obvious consequence of this is that the CH₄ solubility increases as the number or length of the nonpolar alkyl-chains increases.

Table 3.8: Effect of IL molecular weight on the ideal CO₂/CH₄ selectivity at 313.15 K.

Name IL (Abbreviation)	Molecular weight (g/mol)	Selectivity (CO ₂ /CH ₄)	Reference
[emim][dep]	264.26	10.8	this work
[thtdp][phos]	773.27	14.0	this work
[thtdp][dca]	549.90	5.3	this work
[amim][dca]	189.22	21.8	this work
[bmpyrr][dca]	208.30	16.7	this work
[cprop][dca]	318.46	11.1	this work
[cprop][Tf ₂ N]	532.56	6.8	this work
[bmpip][Tf ₂ N]	436.43	8.8	this work
[tes][Tf ₂ N]	399.39	10.4	this work
[toa][Tf ₂ N]	648.85	7.0	this work
[hmpy][Tf ₂ N]	458.43	10.8	[150]
[thtdp][Tf ₂ N]	764.00	6.2	[153]
[bmim][Tf ₂ N]	419.36	18.5	[153]
[hmim][Tf ₂ N]	447.42	8.1	[122, 123, 153]
[emim][dca]	177.21	21.0	[122, 123]
[emim][CF ₃ SO ₃]	260.23	17.3	[122, 123]
[emim][Tf ₂ N]	391.31	11.2	[122, 123]
[mmim][MeSO ₄]	208.24	17.6	[122, 123]
[emim][BF ₄]	197.97	20.0	[122, 123]
[bmim][BF ₄]	226.02	14.9	[157]
[bmim][PF ₆]	284.18	12.2	[157]
[bmim][MeSO ₄]	250.32	14.1	[363]
[emim][FAP]	556.17	9.7	[364]

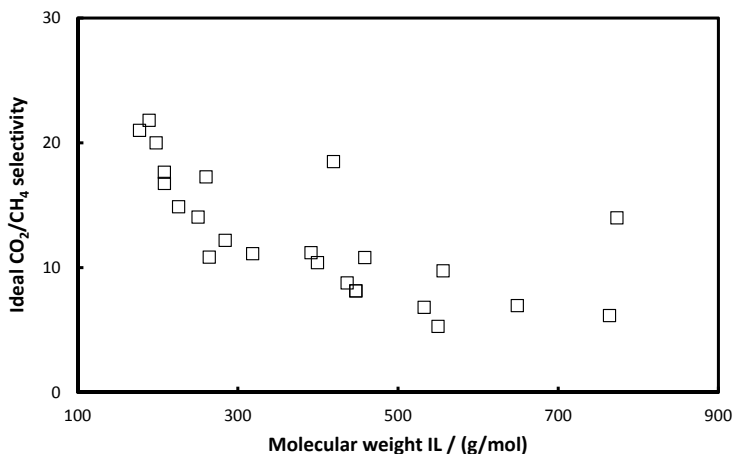


Figure 3.7: Effect of IL molecular weight on the ideal CO₂/CH₄ selectivity at 313.15 K

So far we have considered the ideal CO₂/CH₄ selectivities, but in the real natural gas sweetening process, which operates at high pressures, nonidealities are likely to occur. Consequently, the real selectivities will probably differ from the ideal selectivities. Since measurements of mixed-gas solubilities are more difficult, almost no CO₂-CH₄-IL mixture data can be found in the literature. Hert *et al.* [168] reported the solubility of the binary gas mixture CO₂-CH₄ in the IL [hmim][Tf₂N] and concluded that the solubility of the sparingly soluble CH₄ is enhanced in the presence of CO₂. This indicates that in a real process, which typically contains many gaseous components in the feed, interaction and competition between different solutes may influence the dissolution process. In the following chapter, we will provide solubility data and a thorough discussion of CO₂-CH₄ mixtures in several ILs. We will also show that the data reported by Hert *et al.* is most likely wrong, which accentuates the difficulty of measuring mixed-gas solubilities.

3.5 Conclusions

The solubility of CO_2 and CH_4 has been measured in the following ionic liquids: [emim][dep], [thtdp][phos], [thtdp][dca], [amim][dca], [bmpyrr][dca], [cprop][dca], [cprop][Tf₂N], [bmpip][Tf₂N], [tes][Tf₂N] and [toa][Tf₂N]. The solubility data has been reduced by calculating the Henry constants of CO_2 and CH_4 in all the ILs, from which the ideal CO_2/CH_4 selectivities are obtained. The ideal CO_2/CH_4 selectivities of the investigated ILs are in the range of the conventional solvents like Selexol, Purisol, Rectisol, Fluor solvent, and Sulfolane. The ideal CO_2/CH_4 selectivity decreases with increasing temperature and increasing IL molecular weight. Therefore, a low molecular weight IL should be used if a high selectivity is desired. Furthermore, the experimental data has been modeled accurately with the Peng-Robinson equation of state in combination with van der Waals mixing-rules.

Chapter 4

CO₂/CH₄ Solubility in Ionic Liquids: Real Selectivity

This chapter is based on the paper: M. Ramdin, A. Amphianitis, T. W. de Loos and T. J. H. Vlugt. Solubility of CO₂/CH₄ gas mixtures in ionic liquids. Fluid Phase Equilib., 375 (2014) 134-142.

4.1 Introduction

As explained in Chapter 3, natural gas is usually contaminated with several impurities like the acid gases carbon dioxide (CO₂) and hydrogen sulfide (H₂S), which should be removed at the well to avoid technological problems during transportation and liquefaction of the gas [11]. In Chapter 3, we focused on the application potential of ionic liquids for CO₂ removal from natural gas [345]. Ideal CO₂/CH₄ selectivities, defined as the ratio of the Henry constant of CH₄ over that of CO₂, were calculated for 10 different ILs using pure component solubility data. In practice, the real CO₂/CH₄ selectivity (i.e., the selectivity of CO₂ in the presence of CH₄ in the ternary mixture CO₂-CH₄-IL) may differ from the ideal selectivity due to solute-solute interactions as both gases are simultaneously being dissolved in the IL.

The evaluation of real selectivities requires mixed-gas solubility data, which are extremely scarce in the literature [345]. Hert *et al.* [168] investigated the ternary system CO₂+CH₄+ [hmim][Tf₂N] and they reported a substantial enhancement of CH₄ solubility in the presence of CO₂ compared to the binary system at the same conditions. In this case, it is obvious that the ideal CO₂/CH₄ selectivity will differ from the real selectivity. Petermann *et al.* [365] studied the system CO₂-CH₄-[emim][EtSO₄] and their experimental data show a slight enhancement (deterioration) of the CH₄ (CO₂) solubility relative to the pure component solubilities. These two studies are to the best of our knowledge the only literature dealing with the ternary CO₂-CH₄-IL system.

The aim of the present study is to investigate the effect of the presence of one gas (CO₂) on the other (CH₄) as both are simultaneously being dissolved in a single IL. More specifically, the solubility of gas-mixtures containing carbon dioxide (CO₂) and methane (CH₄) has been measured in the following ILs: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf₂N], 1-ethyl-3-methylimidazolium diethylphosphate [emim][dep], trihexyltetradecylphosphonium dicyanamide [thtdp][dca], and trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate [thtdp][phos]. The ILs were selected based either on their relatively low price ([emim][dep]), good CO₂ solubility ([thtdp][dca] and [thtdp][phos]) or as a reference ([bmim][Tf₂N]). The experiments involve bubble-point measurements in the temperature range 303.15 - 363.15 K and at pressures up to 14 MPa using a visual synthetic method. The effect of gas composition on the bubble-point pressure has been studied systematically by using three different gas-mixtures with a composition of 25 mole % CO₂ - 75 mole % CH₄, 50 mole % CO₂ - 50 mole % CH₄ and 75 mole % CO₂ - 25 mole % CH₄. Real CO₂/CH₄ selectivities (i.e., the selectivity of CO₂ in the presence of CH₄) were calculated using the Peng-Robinson equation of state in combination with van der Waals mixing rules. A comparison between ideal and real CO₂/CH₄ selectivities in the investigated ILs are presented. The results show that the real selectivity does not differ significantly from the ideal selectivity (i.e., the ratio of the pure gas Henry constants) regardless of the gas phase composition.

4.2 Experiments

Three different gas cylinders containing CO₂-CH₄ mixtures with a fixed composition (in mole % CO₂-mole % CH₄) of 25.1 ± 0.5-74.9 ± 0.5, 50.2 ± 1.0-49.8 ± 1.0 and 74.7 ± 0.5-25.3 ± 0.5, henceforth referred as 25-75, 50-50 and 75-25 mixtures, were purchased from the Linde Group. The ILs 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium diethylphosphate, trihexyltetradecylphosphonium dicyanamide, and trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)-phosphinate were purchased from Sigma-Aldrich. The gas-mixtures were used as received, while the ILs were dried for several days in vacuo at 80 °C. After drying, the water content of the ILs was measured using a Karl-Fischer titrator and the results are provided in Table 3.1. The same experimental procedure, as outlined in Chapter 3, was used to measure bubble-point pressures of CO₂-CH₄ mixtures in ILs. A detailed explanation of the Cailletet method can be found elsewhere [338]. The exact amount of gas used in the experiments was calculated through the virial equation of state, where the second virial cross-coefficients required for the CO₂-CH₄ mixtures were obtained by the Tsonopoulos method [366]. The binary interaction parameter, k_{ij} , was obtained by fitting the calculated virial cross-coefficients to the experimental data of Mallu *et al.* [367]. It is important to note that the Cailletet apparatus operates according to the visual synthetic method and that sampling of the phases is not possible.

We recall that the aim of the present work is to investigate the effect of the presence of one gas (e.g., CO₂) on the solubility of the other gas (e.g., CH₄) when both are simultaneously being dissolved in a single IL. In other words, the objective is to obtain real CO₂/CH₄ selectivities from the VLE data. This is a very challenging task without sampling the composition of the phases, since a synthetic method was used. Therefore, the VLE experiments have to be designed systematically and the adopted approach is illustrated in Figure 4.1. The ternary diagram is only shown for the CO₂-CH₄-[thtdp][dca] system, but similar diagrams can be constructed for the other three systems. Note that the diagram is drawn for bubble-point conditions, hence the liquid-phase composition of all the components is known.

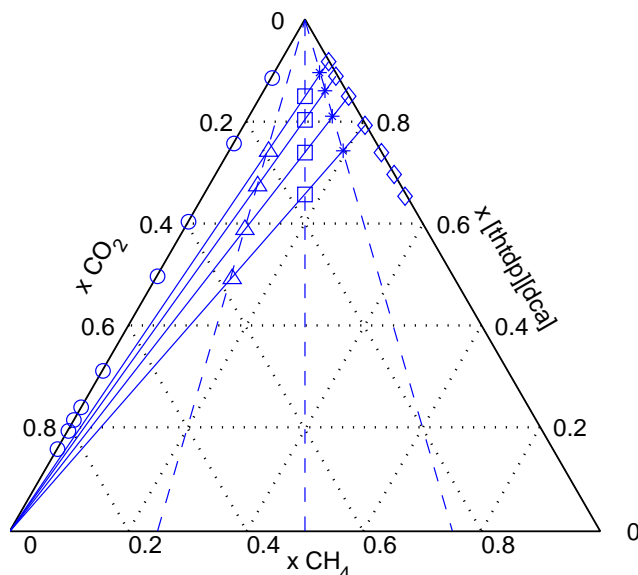


Figure 4.1: Experimental design of the ternary system CO₂ + CH₄ + [thtdp][dca]. Binary data are located on the edges of the triangle: CO₂ + [thtdp][dca] (circles) and CH₄ + [thtdp][dca] (diamonds). Ternary mixture prepared with (CO₂-CH₄) gas mixture: 25-75 (triangles), 50-50 (squares) and 75-25 (stars). Solid lines are lines of constant CH₄/IL ratio and dashed lines are lines of constant CO₂/CH₄ ratio.

The points on the edges of the triangular diagram correspond to the data of the binary systems CO₂+IL (circles) and CH₄+IL (diamonds). The ternary mixtures containing CO₂, CH₄ and IL were prepared using three different (i.e., 25-75, 50-50 and 75-25) gas mixtures. Consequently, the prepared mixtures will always lie on a line of constant CO₂/CH₄ ratio (dashed lines). Furthermore, the molar ratio of CH₄/IL in the ternary mixtures are kept the same as the molar CH₄/IL ratio in the corresponding binary mixtures (solid lines). This implies that the ternary mixture in fact resemble a pseudo-binary system. So, all the prepared ternary mixtures (triangles, squares and stars) will coincide with the point of intersection of two lines, one of constant CH₄/IL ratio and the other of constant CO₂/CH₄ ratio.

The importance of this approach will become apparent while elucidating the results.

4.3 Thermodynamic Modeling

The experimental data has been modeled using the Peng-Robinson (PR) equation of state (EoS) [340]. The details of the PR EoS have been outlined in the previous chapter. As mentioned before, the critical parameters of ILs are not experimentally available, because most of the ILs start to decompose before attaining the critical point. Therefore, group-contribution methods [341], molecular simulations [206, 342] or suitable correlations [208] have been devised to overcome this problem. The absence of measurable critical properties of ILs makes the application of PR EoS for IL systems vulnerable, but it has successfully been applied by many authors using estimated properties [118, 368]. In this work, the modified Lydersen-Joback-Reid group-contribution method developed by Valderrama *et al.* [341] is applied to obtain the critical properties of the ILs. The critical parameters and acentric factors used in the modeling are listed in Table 3.2. Subsequently, the PR EoS is applied to predict bubble-point pressures of the binary gas mixture in the ternary system using temperature dependent binary interaction parameters listed in Table 4.1. The binary interaction parameters of the gas-IL systems have been fitted to binary VLE data from our previous work [345]. Thus for each gas-IL (CO₂-IL and CH₄-IL) system two binary interaction parameters ($k_{ij}=k_{ji}$ and $l_{ij}=l_{ji}$) were fitted to binary VLE (CO₂-IL and CH₄-IL) data. A total of five (two for each gas-IL pair and one for the CO₂-CH₄ system) binary interaction parameters were used to predict the bubble-point pressure of the ternary system. The binary interaction parameter (k_{ij}) for the CO₂/CH₄ system is according to Kordas *et al.* [369] temperature independent for the studied temperature range. Note that the l_{ij} parameter for the CO₂/CH₄ interaction was set to zero. The ternary CO₂-CH₄-[thtdp][phos] system is not modeled, because the Valderrama-method yields an unrealistic (i.e., negative) value for the acentric factor of [thtdp][phos]. Recently, Valderrama *et al.* [372] have extended

Table 4.1: Binary interaction parameters used in the PR EoS modeling.

Pair	Interaction parameter
CO ₂ -CH ₄ ^a	$k_{ij} = 0.1$
CO ₂ -[bmim][Tf ₂ N] ^b	$k_{ij} = -5.0833 \times 10^{-6}(T/K)^2 + 2.9980 \times 10^{-3}(T/K) - 0.4967$ $l_{ij} = 1.3297 \times 10^{-5}(T/K)^2 - 9.5584 \times 10^{-3}(T/K) + 2.0321$
CO ₂ -[emim][dep] ^c	$k_{ij} = -1.9642 \times 10^{-6}(T/K)^2 + 1.9598 \times 10^{-3}(T/K) - 0.3809$ $l_{ij} = 2.6595 \times 10^{-5}(T/K)^2 - 1.9986 \times 10^{-2}(T/K) + 3.9723$
CO ₂ -[thtdp][dca] ^c	$k_{ij} = -1.9404 \times 10^{-6}(T/K)^2 + 6.8258 \times 10^{-4}(T/K) - 0.0597$ $l_{ij} = -1.9357 \times 10^{-5}(T/K)^2 + 1.1749 \times 10^{-2}(T/K) - 1.0569$
CH ₄ -[bmim][Tf ₂ N] ^b	$k_{ij} = -2.8452 \times 10^{-6}(T/K)^2 + 1.3568 \times 10^{-3}(T/K) - 0.0704$ $l_{ij} = 1.5404 \times 10^{-5}(T/K)^2 - 9.1784 \times 10^{-3}(T/K) + 1.2921$
CH ₄ -[emim][dep] ^c	$k_{ij} = 3.2619 \times 10^{-6}(T/K)^2 - 1.4419 \times 10^{-3}(T/K) + 0.3826$ $l_{ij} = -9.5619 \times 10^{-5}(T/K)^2 + 6.4610 \times 10^{-2}(T/K) - 10.9227$
CH ₄ -[thtdp][dca] ^c	$k_{ij} = -6.4524 \times 10^{-6}(T/K)^2 + 3.7542 \times 10^{-3}(T/K) - 0.4708$ $l_{ij} = 2.3035 \times 10^{-5}(T/K)^2 - 1.5637 \times 10^{-2}(T/K) + 2.9260$

^a From Kordas *et al.* [369]. ^b Fitted to VLE data Raeissi *et al.* [370, 371].

^c Fitted to VLE data Ramdin *et al.* [345, 346].

their group contribution method to correctly predict the critical properties of ILs with a high molecular weight.

4.4 Results and Discussion

The experimental data of the systems CO₂ + CH₄ + [bmim][Tf₂N], CO₂ + CH₄ + [emim][dep], CO₂ + CH₄ + [thtdp][dca] and CO₂ + CH₄ + [thtdp][phos] are listed in Tables 4.2 to 4.5, respectively. The bubble-point isopleths of the ternary systems are shown in Figures 4.2 to 4.13. Note that for every gas mixture (i.e., 25-75, or 50-50 or 75-25) at least three ternary mixtures with a constant CH₄/IL ratio have been investigated. The solubility behavior of the binary gas mixture in the ILs is not much different from the behavior of the single gas solubilities. For a fixed composition, the

Table 4.2: Bubble point data of the system CO₂ (1) + CH₄ (2) + [bmim][Tf₂N] (3), where x_1 is the mole fraction of CO₂, x_2 is the mole fraction of CH₄, p the bubble-point pressure, T the temperature and $u(i)$ the standard uncertainties.^a

x_1	x_2	T / K	p / MPa	x_1	x_2	T / K	p / MPa	x_1	x_2	T / K	p / MPa
25-75 mixture											
0.014	0.040 ^b	303.25	1.872	0.037	0.110 ^c	303.43	6.045	0.053	0.158 ^d	303.23	10.053
0.014	0.040	313.22	1.972	0.037	0.110	313.43	6.326	0.053	0.158	313.25	10.468
0.014	0.040	323.19	2.062	0.037	0.110	323.40	6.606	0.053	0.158	323.19	10.854
0.014	0.040	333.19	2.147	0.037	0.110	333.19	6.846	0.053	0.158	333.21	11.199
0.014	0.040	343.19	2.227	0.037	0.110	343.38	7.086	0.053	0.158	343.19	11.544
0.014	0.040	353.25	2.292	0.037	0.110	353.32	7.316	0.053	0.158	353.20	11.835
0.014	0.040	363.22	2.362	0.037	0.110	363.34	7.517	0.053	0.158	363.30	12.105
50-50 mixture											
0.040	0.039 ^b	303.25	1.981	0.103	0.102 ^c	303.53	6.230	0.144	0.143 ^d	303.19	10.349
0.040	0.039	313.20	2.086	0.103	0.102	313.41	6.570	0.144	0.143	313.17	10.915
0.040	0.039	323.18	2.191	0.103	0.102	323.32	6.881	0.144	0.143	323.18	11.430
0.040	0.039	333.18	2.306	0.103	0.102	333.33	7.231	0.144	0.143	333.19	11.946
0.040	0.039	343.20	2.407	0.103	0.102	343.30	7.551	0.144	0.143	343.20	12.406
0.040	0.039	353.22	2.512	0.103	0.102	353.29	7.831	0.144	0.143	353.19	12.866
0.040	0.039	363.20	2.602	0.103	0.102	363.19	8.112				
75-25 mixture											
0.108	0.037 ^b	303.21	2.237	0.189	0.064 ^e	303.25	4.500	0.252	0.085 ^d	303.26	6.860
0.108	0.037	313.22	2.407	0.189	0.064	313.20	4.856	0.252	0.085	313.20	7.401
0.108	0.037	323.21	2.582	0.189	0.064	323.22	5.581	0.252	0.085	323.23	7.942
0.108	0.037	333.24	2.758	0.189	0.064	323.26	5.221	0.252	0.085	333.24	8.527
0.108	0.037	343.21	2.933	0.189	0.064	343.22	5.941	0.252	0.085	343.20	9.067
0.108	0.037	353.23	3.108	0.189	0.064	353.22	6.307	0.252	0.085	353.26	9.612
0.108	0.037	363.27	3.288	0.189	0.064	363.27	6.672	0.252	0.085	363.28	10.147

^a $u(x_i) = 0.004$, $u(T) = 0.01$ K and $u(p) = 0.005$ MPa

^b $(x_2/x_3) = 0.043$, ^c $(x_2/x_3) = 0.129$, ^d $(x_2/x_3) = 0.201$, ^e $(x_2/x_3) = 0.086$

solubility increases with pressure and decreases with increasing temperature. Figures 4.2 to 4.10 also show the PR EoS modeling results using only binary interaction parameters. The predicted bubble-point pressures are in good agreement with the experiments for low pressures (< 50 bar) and low CH₄/IL ratios. As the CH₄/IL ratio and the pressure increases the PR EoS modeling results start to deviate from the experimental data, which is likely due to three-body interactions in the ILs. The three-body interactions are more likely to occur at higher gas concentrations (i.e., higher CH₄/IL ratios) and at higher pressures. The modeling results for the CO₂-CH₄-[emim][dep] system are in good agreement with the experimental data for all the investigated CH₄/IL ratios, but this is mainly due to the relatively low molar

Table 4.3: Bubble point data of the system CO₂ (1) + CH₄ (2) + [emim][dep] (3), where x_1 is the mole fraction of CO₂, x_2 is the mole fraction of CH₄, p the bubble-point pressure, T the temperature and $u(i)$ the standard uncertainties.^a

x_1	x_2	T / K	p / MPa	x_1	x_2	T / K	p / MPa	x_1	x_2	T / K	p / MPa
25-75 mixture											
0.007	0.020 ^b	303.42	1.733	0.011	0.032 ^c	303.40	2.892	0.016	0.046 ^d	303.43	4.455
0.007	0.020	313.38	1.813	0.011	0.032	313.38	3.042	0.016	0.046	313.41	4.620
0.007	0.020	323.34	1.893	0.011	0.032	323.42	3.142	0.016	0.046	323.40	4.795
0.007	0.020	333.35	1.964	0.011	0.032	333.38	3.263	0.016	0.046	333.43	4.975
0.007	0.020	343.32	2.034	0.011	0.032	343.36	3.363	0.016	0.046	343.50	5.130
0.007	0.020	353.31	2.084	0.011	0.032	353.37	3.463	0.016	0.046	353.53	5.280
0.007	0.020	363.32	2.144	0.011	0.032	363.35	3.563	0.016	0.046	363.53	5.415
50-50 mixture											
0.020	0.020 ^b	303.25	1.793	0.032	0.031 ^c	303.20	2.997	0.045	0.045 ^d	303.43	4.554
0.020	0.020	313.18	1.903	0.032	0.031	313.20	3.152	0.045	0.045	313.39	4.785
0.020	0.020	323.17	2.003	0.032	0.031	323.18	3.312	0.045	0.045	323.37	5.055
0.020	0.020	333.16	2.094	0.032	0.031	333.18	3.468	0.045	0.045	333.37	5.266
0.020	0.020	343.19	2.169	0.032	0.031	343.24	3.608	0.045	0.045	343.35	5.486
0.020	0.020	353.21	2.249	0.032	0.031	353.21	3.743	0.045	0.045	353.30	5.686
0.020	0.020	363.22	2.329	0.032	0.031	363.25	3.878	0.045	0.045	363.34	5.886
75-25 mixture											
0.056	0.019 ^b	303.44	2.024	0.087	0.030 ^c	303.40	3.358	0.122	0.041 ^d	303.20	5.164
0.056	0.019	313.44	2.194	0.087	0.030	313.40	3.623	0.122	0.041	313.21	5.539
0.056	0.019	323.35	2.355	0.087	0.030	323.37	3.893	0.122	0.041	323.21	5.980
0.056	0.019	333.45	2.515	0.087	0.030	333.38	4.159	0.122	0.041	333.23	6.395
0.056	0.019	343.43	2.675	0.087	0.030	353.35	4.699	0.122	0.041	343.25	6.820
0.056	0.019	353.40	2.835	0.087	0.030	343.36	4.424	0.122	0.041	353.20	7.246
				0.087	0.030	363.36	4.964				

^a $u(x_i) = 0.004$, $u(T) = 0.01 \text{ K}$ and $u(p) = 0.005 \text{ MPa}$

^b $(x_2/x_3) = 0.020$, ^c $(x_2/x_3) = 0.033$, ^d $(x_2/x_3) = 0.049$

fraction of the dissolved gases. Moreover, the deviation between the modeling and the experiments increases for increasing CO₂ concentrations in the gas phase (e.g., 75-25 mixture) at a fixed CH₄/IL ratio. At these conditions the predicted bubble-point pressures are higher than the experimental data, which suggests that CO₂ is lowering the pressure required for dissolving a fixed amount of CH₄. The three-body interactions between CO₂, CH₄ and IL are not accounted for in the modeling, which leads to an overestimation of the bubble-point pressures. Note that the 25-75 mixture, which is mostly relevant for the natural gas sweetening process (e.g., natural gas typically contains up to 10% CO₂), is adequately modeled by the PR EoS even at high pressures and high CH₄/IL ratios.

Table 4.4: Bubble point data of the system CO₂ (1) + CH₄ (2) + [thtdp][dca] (3), where x_1 is the mole fraction of CO₂, x_2 is the mole fraction of CH₄, p the bubble-point pressure, T the temperature and $u(i)$ the standard uncertainties.^a

x_1	x_2	T / K	p / MPa	x_1	x_2	T / K	p / MPa
25-75 mixture							
0.026	0.077 ^b	302.16	1.517	0.035	0.104 ^c	303.23	2.198
0.026	0.077	312.26	1.602	0.035	0.104	313.23	2.313
0.026	0.077	322.49	1.682	0.035	0.104	323.27	2.439
0.026	0.077	332.48	1.767	0.035	0.104	333.24	2.533
0.026	0.077	342.26	1.842	0.035	0.104	343.27	2.628
0.026	0.077	352.36	1.903	0.035	0.104	353.58	2.728
0.026	0.077	362.52	1.972	0.035	0.104	363.40	2.818
0.047	0.141 ^d	303.39	3.139	0.064	0.192 ^e	303.60	4.731
0.047	0.141	312.63	3.302	0.064	0.192	313.95	4.996
0.047	0.141	322.73	3.488	0.064	0.192	323.19	5.211
0.047	0.141	332.58	3.643	0.064	0.192	333.18	5.421
0.047	0.141	342.67	3.803	0.064	0.192	343.24	5.636
0.047	0.141	352.74	3.918				
0.047	0.141	362.69	4.034				
50-50 mixture							
0.074	0.073 ^b	302.52	1.670	0.098	0.097 ^c	302.86	2.397
0.074	0.073	312.86	1.785	0.098	0.097	312.37	2.567
0.074	0.073	322.45	1.886	0.098	0.097	322.40	2.728
0.074	0.073	332.45	2.001	0.098	0.097	332.47	2.878
0.074	0.073	342.54	2.111	0.098	0.097	342.44	3.023
0.074	0.073	352.49	2.211	0.098	0.097	352.55	3.163
0.074	0.073	362.55	2.311	0.098	0.097	362.45	3.293
0.130	0.129 ^d	303.26	3.463	0.172	0.170 ^e	322.39	5.824
0.130	0.129	313.25	3.698	0.172	0.170	332.45	6.154
0.130	0.129	323.24	3.934	0.172	0.170	342.46	6.464
0.130	0.129	333.22	4.139	0.172	0.170	352.51	6.770
0.130	0.129	343.28	4.354	0.172	0.170	362.50	7.050
75-25 mixture							
0.190	0.064 ^b	303.63	2.174	0.241	0.082 ^c	303.21	3.029
0.190	0.064	312.58	2.354	0.241	0.082	313.16	3.299
0.190	0.064	322.58	2.573	0.241	0.082	323.13	3.585
0.190	0.064	332.59	2.769	0.241	0.082	333.23	3.860
0.190	0.064	342.58	2.960	0.241	0.082	343.20	4.145
0.190	0.064	352.61	3.145	0.241	0.082	353.40	4.420
0.190	0.064	362.74	3.325	0.241	0.082	363.53	4.685
0.304	0.103 ^d	302.57	4.309	0.377	0.128 ^e	302.57	6.402
0.304	0.103	312.44	4.709	0.377	0.128	312.44	7.007
0.304	0.103	322.56	5.139	0.377	0.128	322.56	7.662
0.304	0.103	332.55	5.530	0.377	0.128	332.55	8.283
0.304	0.103	342.56	5.925	0.377	0.128	342.56	8.893
0.304	0.103	352.60	6.330	0.377	0.128	352.60	9.483
0.304	0.103	362.67	6.715	0.377	0.128	362.67	10.064

^a $u(x_i) = 0.004$, $u(T) = 0.01 \text{ K}$ and $u(p) = 0.005 \text{ MPa}$

^b $(x_2/x_3) = 0.086$, ^c $(x_2/x_3) = 0.121$, ^d $(x_2/x_3) = 0.174$, ^e $(x_2/x_3) = 0.258$

Table 4.5: Bubble point data of the system CO₂ (1) + CH₄ (2) + [thtdp][phos] (3), where x_1 is the mole fraction of CO₂, x_2 is the mole fraction of CH₄, p the bubble-point pressure, T the temperature and $u(i)$ the standard uncertainties.^a

x_1	x_2	T / K	p / MPa	x_1	x_2	T / K	p / MPa
25-75 mixture							
0.035	0.103 ^b	302.44	1.051	0.061	0.183 ^c	304.01	2.176
0.035	0.103	312.63	1.113	0.061	0.183	312.58	2.266
0.035	0.103	322.63	1.176	0.061	0.183	322.64	2.417
0.035	0.103	332.66	1.237	0.061	0.183	332.61	2.527
0.035	0.103	342.64	1.297	0.061	0.183	342.62	2.647
0.035	0.103	352.75	1.362	0.061	0.183	352.70	2.777
0.035	0.103	362.81	1.414	0.061	0.183	362.72	2.897
0.086	0.255 ^d	303.29	3.483	0.099	0.295 ^e	303.16	4.427
0.086	0.255	313.18	3.698	0.099	0.295	313.17	4.688
0.086	0.255	323.21	3.923	0.099	0.295	323.23	4.999
0.086	0.255	333.22	4.103	0.099	0.295	333.28	5.259
0.086	0.255	343.20	4.298	0.099	0.295	343.30	5.463
0.086	0.255	353.19	4.483	0.099	0.295	353.16	5.703
0.086	0.255	363.29	4.678	0.099	0.295	363.26	5.944
50-50 mixture							
0.097	0.096 ^b	303.25	1.083	0.164	0.163 ^c	303.27	2.357
0.097	0.096	313.25	1.158	0.164	0.163	313.37	2.503
0.097	0.096	323.23	1.242	0.164	0.163	322.23	2.678
0.097	0.096	333.20	1.322	0.164	0.163	332.24	2.843
0.097	0.096	343.15	1.412	0.164	0.163	342.60	3.048
0.097	0.096	353.23	1.508	0.164	0.163	352.70	3.224
0.097	0.096	363.12	1.608	0.164	0.163	362.76	3.409
0.220	0.218 ^d	303.26	3.914	0.248	0.246 ^e	303.252	4.921
0.220	0.218	313.25	4.159	0.248	0.246	313.236	5.261
0.220	0.218	323.24	4.424	0.248	0.246	323.233	5.606
0.220	0.218	333.22	4.669	0.248	0.246	333.259	5.912
0.220	0.218	343.28	4.915	0.248	0.246	343.344	6.228
0.220	0.218	353.32	5.184	0.248	0.246	353.309	6.583
0.220	0.218	363.29	5.474	0.248	0.246	363.259	6.943
75-25 mixture							
0.240	0.081 ^b	303.19	1.492	0.365	0.124 ^c	303.32	3.278
0.240	0.081	313.08	1.632	0.365	0.124	313.19	3.583
0.240	0.081	323.31	1.777	0.365	0.124	323.26	3.948
0.240	0.081	332.52	1.917	0.365	0.124	333.19	4.203
0.240	0.081	342.08	2.074	0.365	0.124	343.17	4.563
0.240	0.081	351.97	2.239	0.365	0.124	353.15	4.854
0.240	0.081	362.74	2.443	0.365	0.124	363.16	5.194
0.452	0.153 ^d	303.31	5.305				
0.452	0.153	312.54	5.780				
0.452	0.153	322.81	6.370				
0.452	0.153	332.57	6.831				
0.452	0.153	342.71	7.396				
0.452	0.153	352.86	7.886				
0.452	0.153	362.97	8.442				

^a $u(x_i) = 0.004$, $u(T) = 0.01 \text{ K}$ and $u(p) = 0.005 \text{ MPa}$

^b $(x_2/x_3) = 0.120$, ^c $(x_2/x_3) = 0.242$, ^d $(x_2/x_3) = 0.387$, ^e $(x_2/x_3) = 0.488$

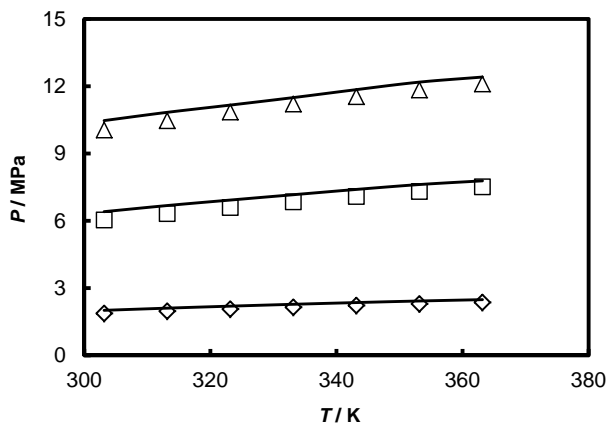


Figure 4.2: Bubble-point isopleths of the system $\text{CO}_2\text{-CH}_4\text{-[bmim][Tf}_2\text{N]}$ for different CH_4/IL molar ratios: 0.043 (diamonds), 0.129 (squares) and 0.201 (triangles). Ternary mixtures prepared using the 25-75 $\text{CO}_2\text{-CH}_4$ gas mixture. The lines are PR EoS modeling results.

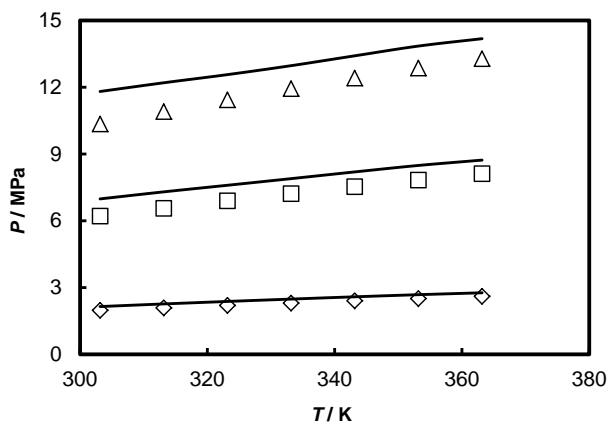


Figure 4.3: Bubble-point isopleths of the system $\text{CO}_2\text{-CH}_4\text{-[bmim][Tf}_2\text{N]}$ for different CH_4/IL molar ratios: 0.043 (diamonds), 0.129 (squares) and 0.201 (triangles). Ternary mixtures prepared using the 50-50 $\text{CO}_2\text{-CH}_4$ gas mixture. The lines are PR EoS modeling results.

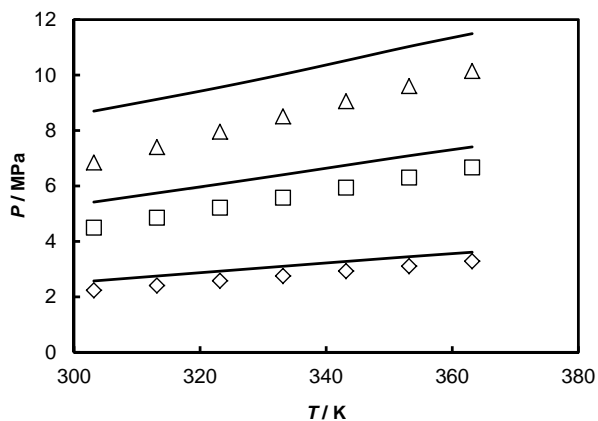


Figure 4.4: Bubble-point isopleths of the system CO₂-CH₄-[bmim][Tf₂N] for different CH₄/IL molar ratios: 0.043 (diamonds), 0.086 (squares) and 0.129 (triangles). Ternary mixtures prepared using the 75-25 CO₂-CH₄ gas mixture. The lines are PR EoS modeling results.

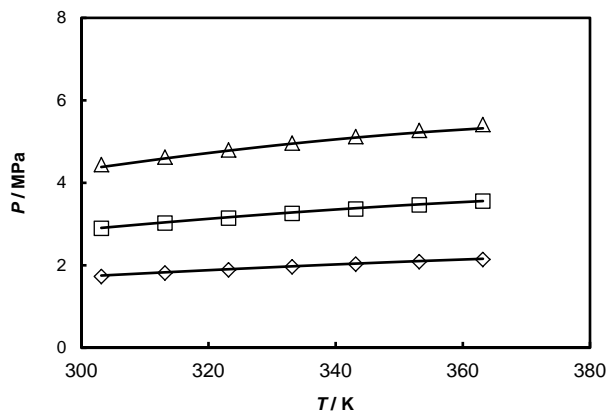


Figure 4.5: Bubble-point isopleths of the system CO₂-CH₄-[emim][dep] for different CH₄/IL molar ratios: 0.020 (diamonds), 0.033 (squares) and 0.049 (triangles). Ternary mixtures prepared using the 25-75 CO₂-CH₄ gas mixture. The lines are PR EoS modeling results.

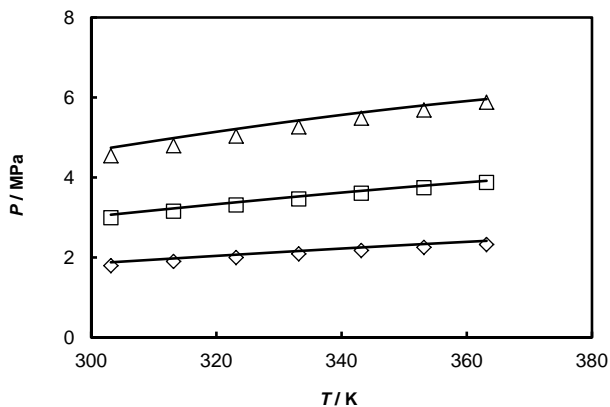


Figure 4.6: Bubble-point isopleths of the system CO₂-CH₄-[emim][dep] for different CH₄/IL molar ratios: 0.020 (diamonds), 0.033 (squares) and 0.049 (triangles). Ternary mixtures prepared using the 50-50 CO₂-CH₄ gas mixture. The lines are PR EoS modeling results.

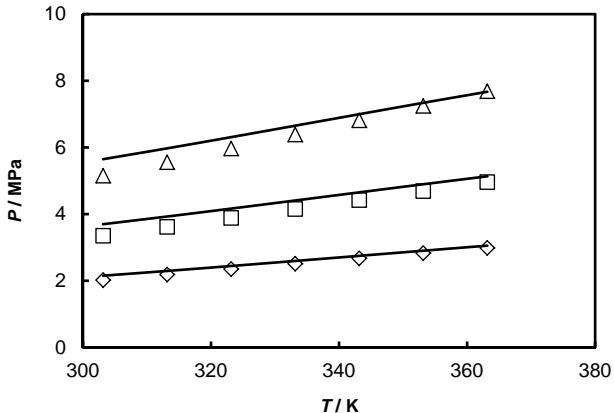


Figure 4.7: Bubble-point isopleths of the system CO₂-CH₄-[emim][dep] for different CH₄/IL molar ratios: 0.020 (diamonds), 0.033 (squares) and 0.049 (triangles). Ternary mixtures prepared using the 75-25 CO₂-CH₄ gas mixture. The lines are PR EoS modeling results.

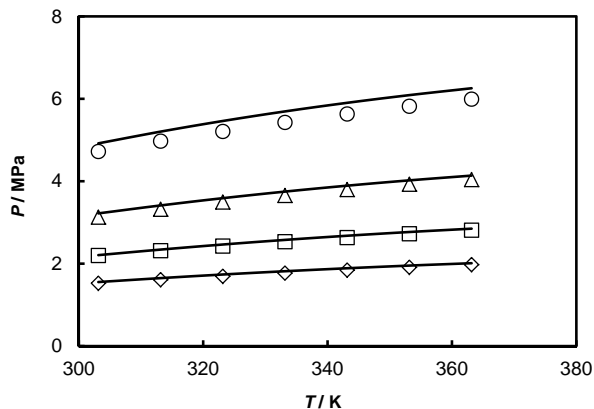


Figure 4.8: Bubble-point isopleths of the system CO₂-CH₄-[tthdp][dca] for different CH₄/IL molar ratios: 0.086 (diamonds), 0.121 (squares), 0.174 (triangles) and 0.258 (circles). Ternary mixtures prepared using the 25-75 CO₂-CH₄ gas mixture. The lines are PR EoS modeling results.

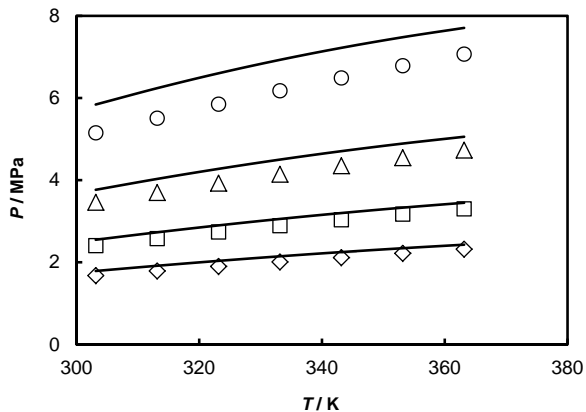


Figure 4.9: Bubble-point isopleths of the system CO₂-CH₄-[tthdp][dca] for different CH₄/IL molar ratios: 0.086 (diamonds), 0.121 (squares), 0.174 (triangles) and 0.258 (circles). Ternary mixtures prepared using the 50-50 CO₂-CH₄ gas mixture. The lines are PR EoS modeling results.

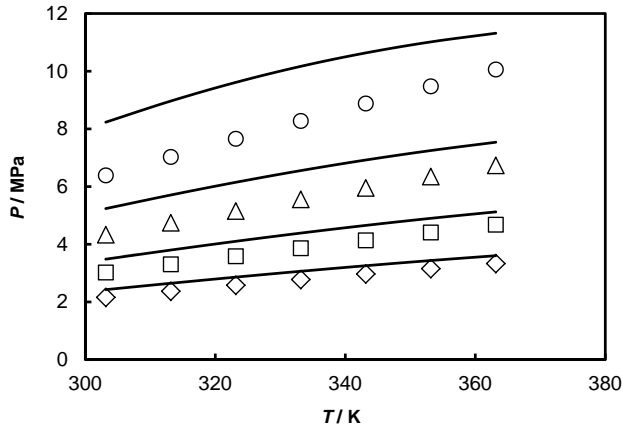


Figure 4.10: Bubble-point isopleths of the system $\text{CO}_2\text{-CH}_4\text{-[tthdp][dca]}$ for different CH_4/IL molar ratios: 0.086 (diamonds), 0.121 (squares), 0.174 (triangles) and 0.258 (circles). Ternary mixtures prepared using the 75-25 $\text{CO}_2\text{-CH}_4$ gas mixture. The lines are PR EoS modeling results.

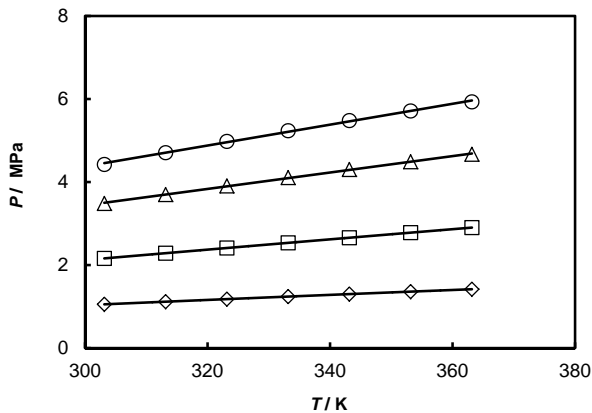


Figure 4.11: Bubble-point isopleths of the system $\text{CO}_2\text{-CH}_4\text{-[tthdp][phos]}$ for different CH_4/IL molar ratios: 0.120 (diamonds), 0.242 (squares), 0.387 (triangles) and 0.488 (circles). Ternary mixtures prepared using the 25-75 $\text{CO}_2\text{-CH}_4$ gas mixture. The lines are polynomial fits to guide the eye.

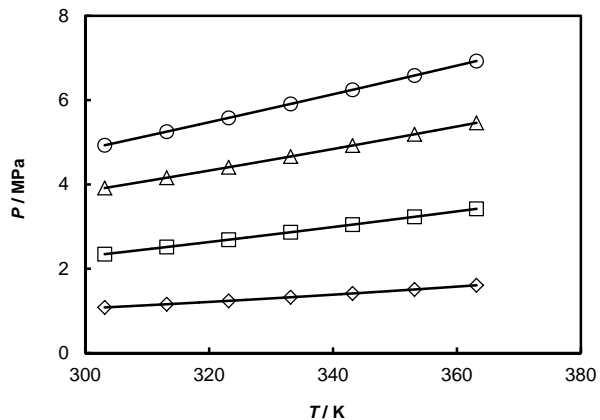


Figure 4.12: Bubble-point isopleths of the system CO₂-CH₄-[ttdp][phos] for different CH₄/IL molar ratios: 0.120 (diamonds), 0.242 (squares), 0.387 (triangles) and 0.488 (circles). Ternary mixtures prepared using the 50-50 CO₂-CH₄ gas mixture. The lines are polynomial fits to guide the eye.

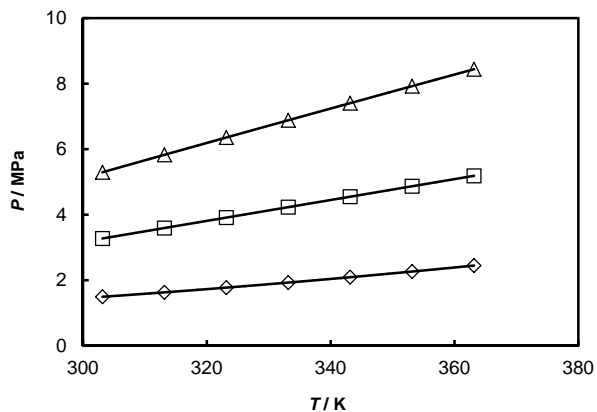


Figure 4.13: Bubble-point isopleths of the system CO₂-CH₄-[ttdp][phos] for different CH₄/IL molar ratios: 0.120 (diamonds), 0.242 (squares) and 0.387 (triangles). Ternary mixtures prepared using the 75-25 CO₂-CH₄ gas mixture. The lines are polynomial fits to guide the eye.

The modeling results for the ternary systems with a 50-50 or 75-25 gas mixture, which is typical for low quality/uneconomical natural gas reservoirs, are acceptable for low CH_4/IL ratios and for moderate pressures, but for high CH_4/IL ratios the deviation can be as high as 25 %. However, we are mainly concerned with the selectivities rather than solubilities. As mentioned earlier, it is not possible to obtain real selectivities directly from the reported VLE data, since a synthetic method was used for the experiments. Sampling and subsequent analysis of the phases is inevitable if one wish to obtain real selectivities directly from VLE experiments [373, 374]. However, real selectivities can also be obtained, though indirectly, using an EoS. Here, the PR EoS has been applied to obtain the real CO_2/CH_4 selectivity, $S_{\text{CO}_2/\text{CH}_4}^{\text{R}}$, defined as:

$$S_{\text{CO}_2/\text{CH}_4}^{\text{R}} = \left(\frac{y_{\text{CH}_4}/x_{\text{CH}_4}}{y_{\text{CO}_2}/x_{\text{CO}_2}} \right)_{p,T} \quad (4.1)$$

where y_i and x_i denote the gas-phase and liquid-phase composition of the corresponding components, respectively. The liquid-phase composition at bubble-point conditions is known from the experiments, while the gas-phase composition is obtained from the PR EoS. The calculated (real) selectivities in [bmim][Tf₂N], [emim][dep] and [thtdp][dca] are compared in Figures 4.14 to 4.16 with the ideal selectivities from the literature [345]. The ideal selectivities ($S_{\text{CO}_2/\text{CH}_4}^{\text{I}}$) were calculated as the ratio of the Henry constant of CH_4 over that of CO_2 , see Equation (3.7). We note that this definition of the ideal selectivity does not account for nonidealities, while Equation (4.1) for the real selectivity does consider these effects. The real CO_2/CH_4 selectivity in [bmim][Tf₂N] and [emim][dep] is approximately the same as the ideal selectivity, whereas the real selectivity in [thtdp][dca] is slightly lower than the ideal selectivity. The real selectivities are not influenced by the gas phase composition as it can be seen in Figures 4.14 to 4.16. It is surprising to observe ideal selectivities even for mole fractions of IL as high as 0.7. The reason for this is likely due to the structure/cavities of the ILs. Both solutes are hosted in well defined cavities of the ILs without having the opportunity to interact with each other at low/moderate pressures. This

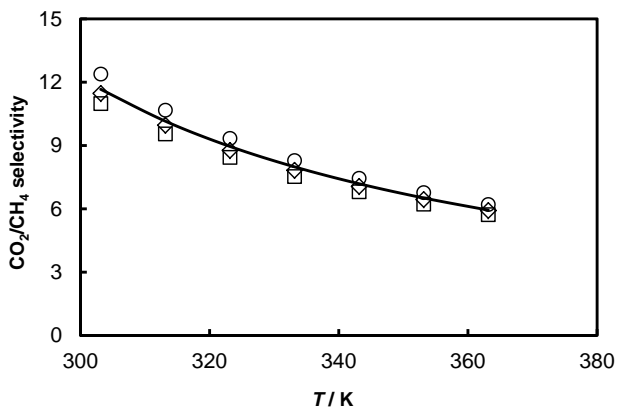


Figure 4.14: Comparison of the ideal and real CO₂/CH₄ selectivity in [bmim][Tf₂N]: ideal selectivity (line) and real selectivity; 25-75 mixture (squares), 50-50 mixture (diamonds) and 75-25 mixture (circles).

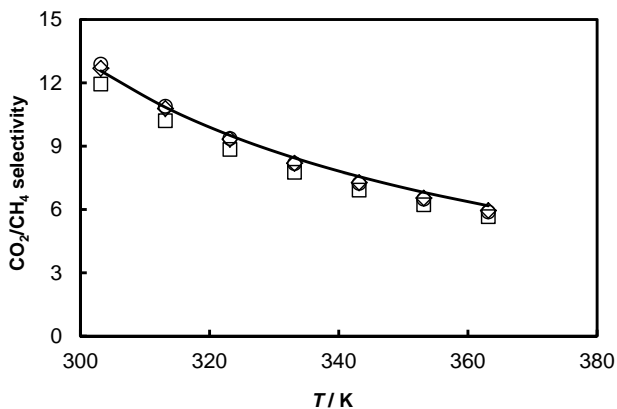


Figure 4.15: Comparison of the ideal and real CO₂/CH₄ selectivity in [emim][dep]: ideal selectivity (line) and real selectivity; 25-75 mixture (squares), 50-50 mixture (diamonds) and 75-25 mixture (circles).

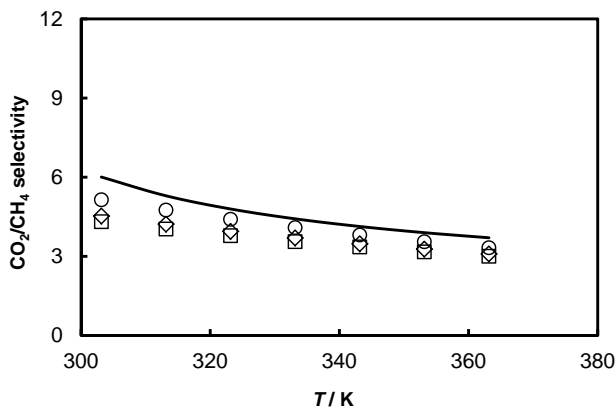


Figure 4.16: Comparison of the ideal and real CO_2/CH_4 selectivity in [thtdp][dca]: ideal selectivity (line) and real selectivity; 25-75 mixture (squares), 50-50 mixture (diamonds) and 75-25 mixture (circles).

explanation is merely a hypothesis, which will be tested in the future using molecular simulations. Recently, molecular simulations have been used to analyse the IL structure in terms of size, shape, and electrostatic potential of the cavities (i.e., free volume) and their effect on gas solubility/selectivity [99, 149, 375–377]. These studies clearly indicate a strong free volume contribution driving gas solubilities in ILs, but more research is required to reveal the solubility mechanism especially for gas mixtures.

The CO_2/CH_4 selectivities in the investigated ILs are comparable with those of conventional solvents like Selexol, Purisol and Rectisol [345]. However, the price/performance ratio of traditional solvents like Selexol and Purisol is better than of ILs considering their low volumetric capacity, high viscosity and cost [9, 378]. In conclusion, the real CO_2/CH_4 selectivity in the investigated ILs is, under the studied conditions, more or less equal to the ideal selectivity regardless of the gas phase composition. In the natural gas sweetening process, which typically contains up to 10% CO_2 in the feed, ideal CO_2/CH_4 selectivity can be expected even at the high operating pressure of the process.

4.5 Conclusions

The solubility of the binary gas mixtures containing carbon dioxide (CO₂) and methane (CH₄) has been measured in the following ionic liquids (ILs): 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium diethylphosphate, trihexyltetradecylphosphonium dicyanamide and trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate. The experiments involved bubble-point measurements for a temperature range of 303.15 - 363.15 K and for pressures up to 14 MPa using a synthetic method. The influence of the gas composition on the bubble-point pressure was investigated by using three gas mixtures containing 25 mole % CO₂-75 mole % CH₄, 50 mole % CO₂-50 mole % CH₄ and 75 mole % CO₂-25 mole % CH₄. The Peng-Robinson (PR) equation of state (EoS) in combination with van der Waals mixing rules was applied to predict the ternary vapor-liquid equilibrium data and to calculate the real CO₂/CH₄ selectivities. The real selectivity (i.e., the selectivity of CO₂ in the presence of CH₄ in the ternary mixture CO₂-CH₄-IL) does not differ significantly from the ideal selectivity (i.e., the ratio of the pure gas Henry constants) regardless of the gas phase composition. Therefore, in the natural gas sweetening process, which typically contains up to 10% CO₂ in the feed, ideal CO₂/CH₄ selectivity can be expected even at the high operating pressure of the process.

Chapter 5

Solubility of Natural Gas Species from Monte Carlo Simulations

This chapter is based on the paper: M. Ramdin, Q. Chen, S. P. Balaji, J. M. Vicent-Luna, A. Torres-Knoop, D. Dubbeldam, S. Calero, T. W. de Loos and T. J. H. Vlugt. Solubilities of CO₂, CH₄, C₂H₆, and SO₂ in ionic liquids and Selexol from Monte Carlo simulations. J. Comput. Sci. (2015) (in press).

5.1 Introduction

In the previous chapters, CO₂/CH₄ solubilities and selectivities in ILs were calculated assuming that only CO₂ and CH₄ are present in the feed. However, natural gas typically contains a large number of components (e.g., CO₂, CH₄, H₂S, N₂ and higher alkanes) [9] and the calculation of the selectivity requires solubility data of all the major components participating in the mixture. It is, therefore, practically impossible to experimentally determine the solubility of all these natural gas constituents and their mixtures

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 this chapter, Monte Carlo simulations are used to compute the solubility of natural gas components in ILs and Selexol, which is a mixture of poly(ethylene glycol) dimethyl ethers (PEGDME, $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_n\text{CH}_3$, where n is typically between 3 and 11) [354]. 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 [379, 380] 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 ($[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$, $n = 4, 6$), 1-ethyl-3-methylimidazolium diethylphosphate ($[\text{emim}][\text{dep}]$) and Selexol ($\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_n\text{CH}_3$, $n = 4, 6$) at 313.15 K and several pressures. The solubility of the gases obtained from the MC simulations are compared with available experimental data.

5.2 Simulation Details

Phase equilibria calculations using Monte Carlo simulations rely on insertions and deletions of molecules to and from a system [381]. Standard Monte Carlo methods are inefficient due to the low insertion and deletion probabilities especially for systems with a high density [382]. Therefore, advanced biasing/sampling methods have been devised (e.g., Configurational-bias Monte Carlo (CBMC) and gradual insertions) that can (partially) overcome this problem [383–385]. An example of such a method is the Continuous Fractional Component Monte Carlo (CFCMC) scheme developed by Shi and Maginn [379, 380]. 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 $\lambda \rightarrow 0$. The CFCMC scheme performs λ -moves in addition to the standard MC moves like translation, rotation and volume change [7, 386]. 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 [387]. The CFCMC scheme is more efficient than conventional MC and CBMC methods in particular for systems with a high density [388]. Details of the CFCMC method can be found in the original papers by Shi and Maginn [124, 172, 379, 380, 389], the excellent review by Dubbeldam et al. [383] and the recent publication by Torres-Knoop et al. [388]. 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. [380, 390, 391]. The TraPPE united-atom (TraPPE-UA) models were used for CO₂, CH₄, C₂H₆, SO₂ and Selexol [392–395]. The solute molecules were considered rigid in the simulations. The Lorentz-Berthelot combining rules were used for the LJ interactions between dissimilar atoms [396]. Long-range electrostatic interactions were taken into account by the Ewald method using a relative precision of 10^{-5} [385]. 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 [385, 397–399]. 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. A schematic representation of the osmotic ensemble is shown in Figure 5.1. Note that the Gibbs phase rule is not violated by disallowing IL molecules in the gas phase, because the number of equilibrium conditions and the number of intensive variables are both reduced by one [400]. Furthermore, the assumption that only solutes without solvent molecules are present in the gas phase is reasonable, since ILs and Selexol have a negligible vapor pressure [202]. 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 [340]. The CFCMC simulations were performed at 313.15 K and pressures up to 12 MPa using the molecular simulation software RASPA [401]. The following number of solvent molecules, 50, 50, 70, 75, and 70, were used in the simulations for $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$, $\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, $[\text{emim}][\text{dep}]$, $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_4\text{CH}_3$ and $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_6\text{CH}_3$, 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. Once we verified that the system has

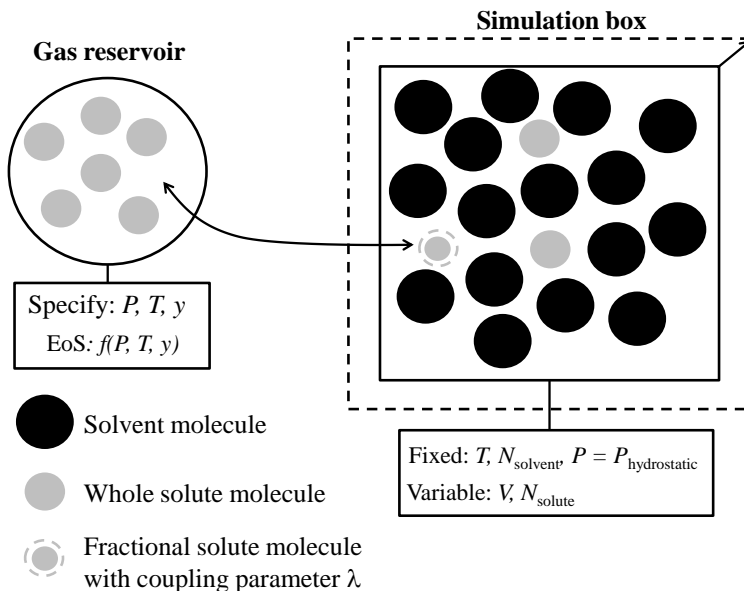


Figure 5.1: A schematic representation of the osmotic ensemble using the CFCMC method. The pressure (P), the temperature (T), and the composition (y) of the gas phase are specified and the fugacity of the gases (f) is calculated from the PR EoS. The number of solvent molecules (N_{solvent}) and the temperature of the simulation box (T) are fixed, while the number of solute molecules (N_{solute}) and the volume (V) fluctuate. The pressure of the gas (P) is equal to the hydrostatic pressure of the liquid ($P_{\text{hydrostatic}}$). In the CFCMC method, solute molecules are inserted gradually utilizing a parameter λ as explained in the text.

attained its equilibrium state, the solubility data is obtained from block averages and the uncertainty is calculated from the standard deviation.

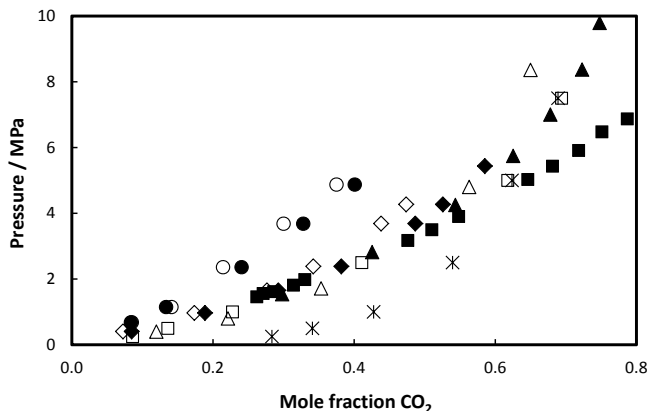


Figure 5.2: Solubility of CO_2 at 313.15 K in ILs and Selexol from experiments (closed symbols) and Monte Carlo simulations (open symbols). [hmim][Tf₂N], triangles; [bmim][Tf₂N], diamonds; [emim][dep], circles; $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_4\text{CH}_3$, squares; and only MC data for $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_6\text{CH}_3$, stars. Experimental data taken from Refs [97, 345, 370, 402].

5.3 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 ($[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$, $n = 4, 6$), [emim][dep], and poly(ethylene glycol) dimethyl ethers (PEGDME, $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_n\text{CH}_3$, $n = 4, 6$), which are the principle ingredients of Selexol. The Selexol solvent is a mixture of PEGDME with n ranging from 3 to 11 [354]. 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. In Figure 5.2, the solubility of CO_2 obtained from the simulations is compared with experimental absorption data. For the system CO_2 - $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_6\text{CH}_3$ only MC data is shown in Figure 5.2, since experimental data of this system is lacking in the literature. Clearly, the CO_2 solubility in the ILs is lower than the

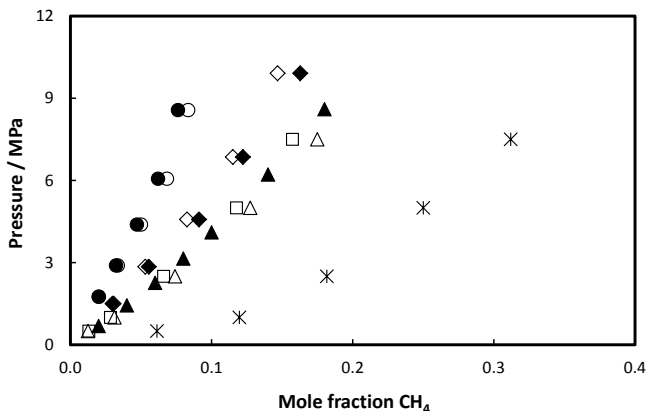


Figure 5.3: Solubility of CH_4 at 313.15 K in ILs and Selexol from experiments (closed symbols) and Monte Carlo simulations (open symbols). [hmim][Tf₂N], triangles; [bmim][Tf₂N], diamonds; [emim][dep], circles; $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_4\text{CH}_3$, squares; and only MC data for $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_6\text{CH}_3$, stars. Experimental data taken from Refs [345, 371, 403].

PEGDME solvents. Furthermore, the CO_2 solubility data obtained from the MC simulations are in quantitative agreement with the experimental results. In Figure 5.3, 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 $x_{\text{CH}_4} \rightarrow 0$) in $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_4\text{CH}_3$ 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 [353]. Figure 5.3 also shows that $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_6\text{CH}_3$ has a high affinity for CH_4 , which will cause product losses in the natural gas sweetening process. In Figure 5.4, 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

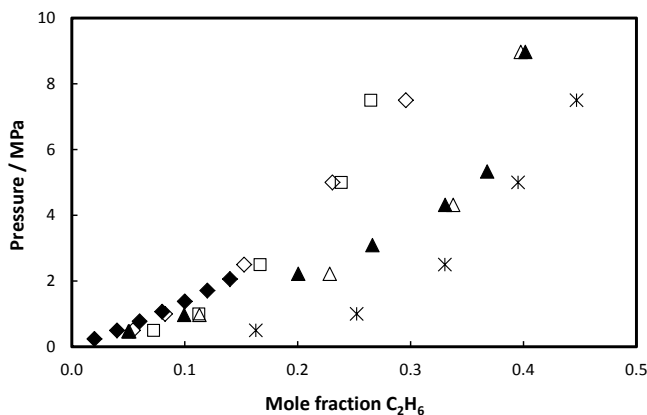


Figure 5.4: Solubility of C₂H₆ at 313.15 K in ILs and Selexol from experiments (closed symbols) and Monte Carlo simulations (open symbols). [hmim][Tf₂N], triangles; [bmim][Tf₂N], diamonds; CH₃O[CH₂CH₂O]₄CH₃, squares; and only MC data for CH₃O[CH₂CH₂O]₆CH₃, stars. Experimental data taken from Refs [98, 404].

results show that the PEGDME solvents possess a high C₂H₆ solubility. The solubility of hydrocarbons is increased as the nonpolar domains of the solvents are increased, which is due to nonpolar-nonpolar interactions [345]. 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 SO₂ is only computed for the solvents [C₆mim][Tf₂N] and CH₃O[CH₂CH₂O]₄CH₃, see Figure 5.5. The results show that SO₂ has an extremely high solubility in both the solvents, which means that SO₂ can selectively be removed in the presence of CO₂. A first estimate of the ideal SO₂/CO₂ selectivity can be obtained from the ratio of the Henry constant of CO₂ over that of SO₂. Note that a lower Henry constant implies a higher solubility. The Henry constants of CO₂ and SO₂ in [C₆mim][Tf₂N] at 313.15 K are respectively 4.3 MPa and 0.23 MPa, which yields an ideal SO₂/CO₂ selectivity of 19 [123, 151]. The Henry constants of CO₂ and SO₂ in CH₃O[CH₂CH₂O]₄CH₃ at 313.15 K are respectively 4.3 MPa and 0.037 MPa, which yields an ideal SO₂/CO₂

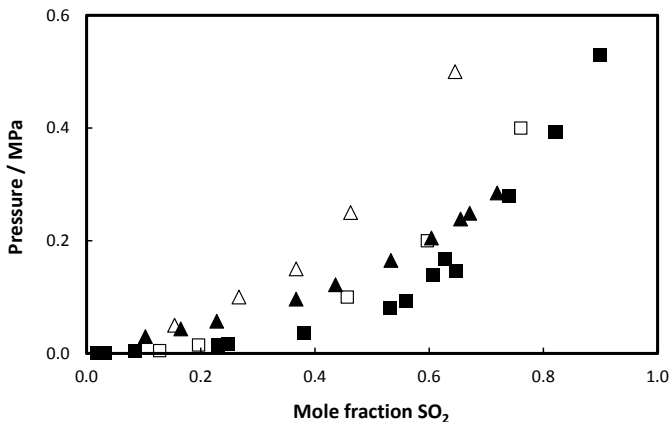


Figure 5.5: Solubility of SO₂ at 313.15 K in ILs and Selexol from experiments (closed symbols) and Monte Carlo simulations (open symbols). [hmim][Tf₂N], triangles and CH₃O[CH₂CH₂O]₄CH₃, squares. Experimental data taken from Refs [151, 405].

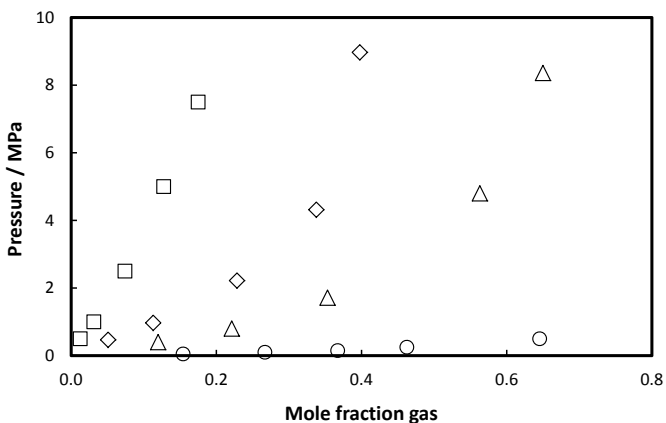


Figure 5.6: Solubility of the gases in [C₆mim][Tf₂N] at 313.15 K obtained from MC simulations. SO₂, circles; CO₂, triangles; C₂H₆, diamonds; and CH₄, squares.

selectivity of 116 [356, 405]. Clearly, $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_4\text{CH}_3$ is more selective towards SO_2 than $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$. 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 5.6, the solubility of the gases in $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ obtained from the MC simulations are compared. The following solubility trend, $\text{SO}_2 > \text{CO}_2 > \text{C}_2\text{H}_6 > \text{CH}_4$, is observed for all the investigated solvents.

5.4 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 ($[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$, $n = 4, 6$), $[\text{emim}][\text{dep}]$, and poly(ethylene glycol) dimethyl ethers (PEGDME, $\text{CH}_3\text{O}[\text{CH}_2\text{CH}_2\text{O}]_n\text{CH}_3$, $n = 4, 6$). The following gas solubility trend is observed in the experiments and simulations for all the solvents: $\text{SO}_2 > \text{CO}_2 > \text{C}_2\text{H}_6 > \text{CH}_4$. 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.

Chapter 6

Computing Bubble Points of Mixtures from Molecular Simulations

This chapter is based on the paper: M. Ramdin, S. P. Balaji, J. M. Vicent-Luna, A. Torres-Knoop, Q. Chen, D. Dubbeldam, S. Calero, T. W. de Loos and T. J. H. Vlugt. Computing bubble-points of CO₂/CH₄ gas mixtures in ionic liquids from Monte Carlo Simulations. Fluid Phase Equilib. (2015) (in press).

6.1 Introduction

Industrial processes often involve multicomponent gas mixtures, which have to be separated or purified to obtain the final product [406]. Solubility and selectivity data of the components in the mixture are required to properly design and operate separation processes [9]. 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 [407]. Therefore, accurate solubility data of gas mixtures are essential to describe this non-ideal

behavior [337]. Recently, we investigated the potential of ionic liquids (ILs) for CO₂ capture from natural gas using experiments and Monte Carlo simulations [7–9, 18, 345, 346, 386]. Bubble-point pressures of carbon dioxide (CO₂) and methane (CH₄) mixtures were measured in different ionic liquids using the Cailletet apparatus, which operates according to the visual synthetic method [8]. 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) [338]. 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 CH₄ (CO₂) on the solubility of CO₂ (CH₄) as both are simultaneously dissolved in an IL. This effect can be quantified by the so-called real CO₂/CH₄ selectivity as defined in Equation (4.1). The ideal selectivity can be defined in several ways, but for convenience the ratio of Henry constants (H_i) is used here, see Equation (3.7). The Henry constants, H_{ij} , of solute i in solvent j are calculated from Equation (3.8). 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 CO₂ and CH₄. From the data of the Cailletet experiments, it is not possible to calculate the real selectivity $S_{\text{CO}_2/\text{CH}_4}^{\text{R}}$, since only the bubble-point pressures of the CO₂-CH₄ 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, see Chapter 4. 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 [408]. We note that bubble-point calculations are extremely important for industrial separation processes [409]. 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 CO₂+CH₄+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 [410–416]. 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.* [417] and the Grand Equilibrium (GE) method proposed by Vrabec and Hasse [418] 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.* [417], and Vrabec and Hasse [418], 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 [385]. Simulations using the Continuous Fractional Component Monte Carlo (CFCMC) technique in the osmotic ensemble have been used to compute the solubilities of CO₂ and CH₄ gas mixtures in the ILs 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf₂N] 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 CO₂/CH₄ selectivities obtained from the MC simulations are compared with the PR EoS modeling results.

The chapter 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, conclusion are presented regarding the real CO₂/CH₄ selectivities in ILs.

6.2 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 [419]. 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 [337]:

$$y_s P \phi_s = x_s \gamma_s P_s^{\text{sat}} \quad (6.1)$$

$$y_i P \phi_i = x_i \gamma_i H_i \quad (6.2)$$

Here, P is the pressure, ϕ the fugacity coefficient, y the gas phase composition, x the liquid phase composition, H the Henry 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 (6.1) and (6.2). Since ILs have a negligible vapor pressure [202], Equation (6.1) cancels and after rearranging Equation (6.2) 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:

$$P = \frac{\sum_{i=1}^n x_i \gamma_i H_i}{\sum_{i=1}^n y_i \phi_i} \quad (6.3)$$

For a ternary system (e.g., $\text{CO}_2 + \text{CH}_4 + \text{IL}$) in which the IL is nonvolatile, Equation (6.3) reduces to:

$$P = \frac{x_{\text{CO}_2} \gamma_{\text{CO}_2} H_{\text{CO}_2} + x_{\text{CH}_4} \gamma_{\text{CH}_4} H_{\text{CH}_4}}{y_{\text{CO}_2} \phi_{\text{CO}_2} + y_{\text{CH}_4} \phi_{\text{CH}_4}} \quad (6.4)$$

For sufficiently low pressures and solubilities (i.e., $\phi_{\text{CO}_2} \approx \phi_{\text{CH}_4} \approx 1$ and $\gamma_{\text{CO}_2} \approx \gamma_{\text{CH}_4} \approx 1$), Equation (6.4) reduces to the following well-known equation [337]:

$$P = x_{\text{CO}_2} H_{\text{CO}_2} + x_{\text{CH}_4} H_{\text{CH}_4} \quad (6.5)$$

Equation (6.5) allows us to calculate the bubble-point pressure of a binary gas-mixture from the knowledge of pure component Henry constants assuming ideal mixing.

6.3 Simulation Details

We recall that the aim is to compute the gas composition (y_i) of a $\text{CO}_2 + \text{CH}_4 + \text{IL}$ 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. It turns out that 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 apriori 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 [417, 418, 420–424]. All of them require the computation of the liquid phase chemical potentials (e.g., using Widom test particle method or an equivalent method [385]), which are typically subjected to large uncertainties for complex dense liquid systems [385]. 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 ($f_i(P, T, y_i)$):

$$\left(\frac{\partial x_i}{\partial y_i}\right)_{T,P,\Sigma} = \frac{(\partial f_i/\partial y_i)_{T,P,\Sigma}}{(\partial f_i/\partial x_i)_{T,P,\Sigma}} \quad (6.6)$$

The differentiation in the left hand side of Equation (6.6) 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 molecules are considered nonvolatile, hence $y_{\text{CH}_4} = (1 - y_{\text{CO}_2})$. The numerator in Equation (6.6), $(\partial f_i/\partial y_i)$, 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., $k_{ij} = 0.1$ [369]) is used to calculate the fugacities as a function of pressure and gas composition [340]. 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 [392, 393]. Therefore, the gas fugacities computed with molecular simulations or the PR EoS will be almost identical. The denominator in Equation (6.6), $(\partial f_i / \partial x_i)$, 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 CO₂-CH₄-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:

$$y_i = y_{i0} + \left(\frac{\partial y_i}{\partial x_i} \right)_{T,P,\Sigma} (x_i - x_{i0}) \quad (6.7)$$

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 Figure 6.1, the procedure described above is explained graphically. Once the gas phase compositions are known from Equation (6.7), Equation (4.1) can be applied to calculate the real selectivities. The molecular simulation software RASPA [401] was used to perform the molecular simulations. The Continuous Fractional Component Monte Carlo (CFCMC) method in the

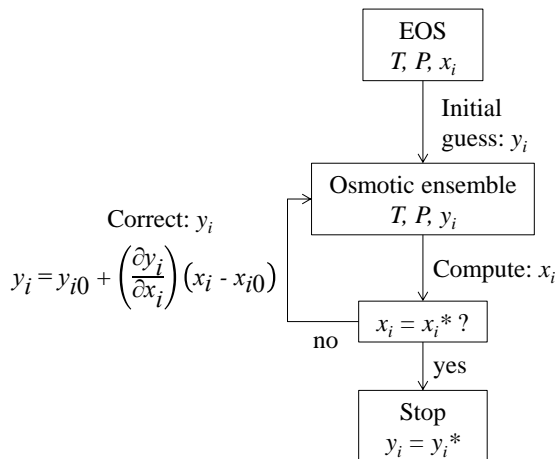


Figure 6.1: Graphical explanation of the procedure used for computing the bubble point of CO_2/CH_4 gas mixtures in ILs. The Peng-Robinson (PR) equation of state (EoS) is used to obtain an initial guess for the gas composition, y_i , by fitting the experimental bubble-point pressure of the $\text{CO}_2\text{-CH}_4\text{-IL}$ 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 (6.7). 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 $\text{CO}_2\text{-CH}_4\text{-IL}$ 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.

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 [379]. The method has been described in detail by Shi and Maginn [379, 389], and by Dubbeldam *et al.* [383] and Torres-Knoop *et al.* [388]. The method has been applied by Shi and Maginn [124, 172, 380] and Ramdin *et al.* [7, 18, 114, 386] to compute the solubility of several gases in ILs and conventional solvents. An ensemble of 50 and 70 IL molecules 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. The force field parameters of [bmim][Tf₂N] and [emim][dep] were taken from Maginn *et al.* [390, 391]. The TraPPE models were used for CO₂ and CH₄ [392, 393]. The Lennard-Jones (LJ) interactions between different atoms were described by the Lorentz-Berthelot combining rules [385]. The electrostatic interactions were taken into account by the Ewald sum method using a relative precision of 10^{-5} [396]. The LJ interaction was 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 molecule [385, 397–399, 425]. 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 [387]. The CFMCMC simulations were started with an equilibration run of 50000 MC cycles, followed by a production run of 0.5 to 1 million 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.

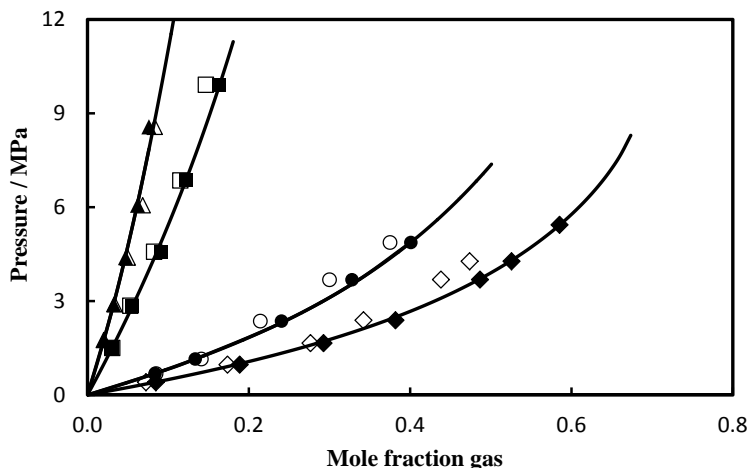


Figure 6.2: Solubility of pure CO_2 and CH_4 in $[\text{bmim}][\text{Tf}_2\text{N}]$ and $[\text{emim}][\text{dep}]$ at 313.15 K from experiments (closed symbols) and Monte Carlo simulations (open symbols). CO_2 (diamonds) and CH_4 (squares) in $[\text{bmim}][\text{Tf}_2\text{N}]$. CO_2 (circles) and CH_4 (triangles) in $[\text{emim}][\text{dep}]$. Lines are Peng-Robinson equation of state modeling results [7, 345]. Data taken from Ramdin *et al.* [18, 114].

6.4 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 $[\text{bmim}][\text{Tf}_2\text{N}]$ and $[\text{emim}][\text{dep}]$ at 313.15 K and 333.15 K. In our previous study, the solubility of the pure gases CO_2 and CH_4 in $[\text{bmim}][\text{Tf}_2\text{N}]$ and $[\text{emim}][\text{dep}]$ at 313.15 K and 333.15 K was computed from Monte Carlo simulations [7, 114]. The computed isotherms of the pure gases were in quantitative agreement with experimental data measured using the Cailletet technique, see Figure 6.2. Therefore, the MC simulations are expected to yield reasonable results for CO_2/CH_4 gas mixtures as well. In Table 6.1, the MC simulation results are compared with the experimental data and PR EoS modeling results reported in Ramdin *et al.* [8]. In the Cailletet experiments, three different gas mixtures

initially containing 25 % CO₂ - 75 % CH₄ (25-75 mixture), 50 % CO₂ - 50 % CH₄ (50-50 mixture), and 75 % CO₂ - 25 % CH₄ (75-25 mixture) were investigated [8]. 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 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, $y_{\text{CO}_2}^{\text{PR}}$ in Table 6.1, was estimated from the PR EoS by fitting the experimental bubble-point pressure [8]. In our MC simulations, the composition of the gas phase is obtained iteratively by substitution of Equation (6.6) into Equation (6.7). The method is illustrated in Figure 6.3 at a pressure of 1.97 MPa and 313.15 K, for the first data point in Table 6.1, using three different gas compositions. Similar diagrams can be constructed for the other solutes in a multicomponent system. Note that for the ternary system CO₂-CH₄-IL, it is not necessary to draw a diagram for CH₄, since the gas-phase composition of CH₄ can be obtained from the constraint $y_{\text{CH}_4} = (1 - y_{\text{CO}_2})$. 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 ($y_{\text{CO}_2}^{\text{sim.}}$) and the PR EoS modeling ($y_{\text{CO}_2}^{\text{PR}}$) 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.* [8] for the modeling results. Therefore, the gas composition obtained from the PR EoS is unreliable for the 75-25 gas mixture. Subsequently, the real CO₂/CH₄ selectivity is calculated from Equation (4.1). The ideal selectivity, which is defined in Equation (3.7) as the ratio of the Henry constants, is also reported in Table 6.1. 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 6.1, the bubble-point pressure of the system CO₂+CH₄+[bmim][Tf₂N] predicted by Equation (6.5) 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

Table 6.1: Bubble-point compositions of the system $\text{CO}_2 + \text{CH}_4 + [\text{bmim}][\text{Tf}_2\text{N}]$ obtained from MC simulations (sim.) and Peng-Robinson (PR) equation of state at a given temperature (T) and bubble-point pressure ($P^{\text{exp.}}$). $P^{\text{pred.}}$ is the bubble-point pressure predicted by Equation (6.5). The gas composition (y_i), which is in equilibrium with the experimental liquid composition (x_i), is obtained from Equation (6.7). Real and ideal selectivities are obtained from Equation (4.1) and Equation (3.7), respectively. The Henry constants of CO_2 in $[\text{bmim}][\text{Tf}_2\text{N}]$ at 313.15 K and 333.15 K computed from the MC data are 5.4 MPa and 7.1 MPa, respectively [114]. The Henry constants of CH_4 in $[\text{bmim}][\text{Tf}_2\text{N}]$ at 313.15 K and 333.15 K computed from the MC data are 50.7 MPa and 53.7 MPa, respectively [114]. The experimental Henry constants of CO_2 (CH_4) in $[\text{bmim}][\text{Tf}_2\text{N}]$ at 313.15 K and 333.15 K are 4.9 MPa (49.3 MPa), and 6.6 MPa (52.4 MPa), respectively [370, 371].

T/K	x_{CO_2}	x_{CH_4}	$P^{\text{exp.}}/\text{MPa}$	$P^{\text{pred.}}/\text{MPa}$	$y_{\text{CO}_2}^{\text{PR}}$	$y_{\text{CO}_2}^{\text{sim.}}$	$S_{\text{CO}_2/\text{CH}_4}^{\text{R}}$	$S_{\text{CO}_2/\text{CH}_4}^{\text{I}}$
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

in Equation (6.5). As it becomes evident from Equation (6.4), 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.* [8] for the experimental details. It is, therefore, possible that ideal CO_2/CH_4 selectivities are observed due to the low CO_2 concentrations in the liquid

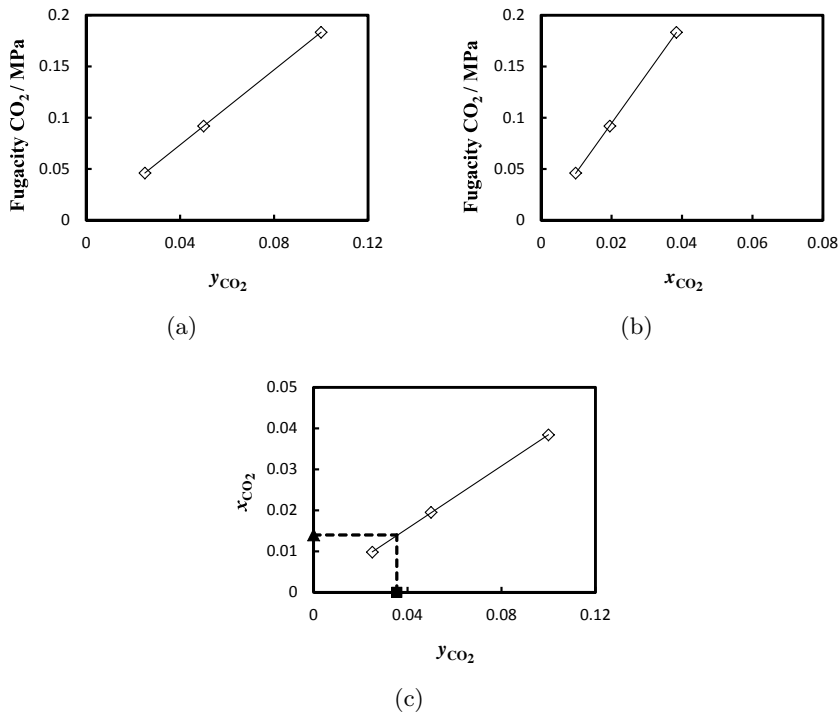


Figure 6.3: (a) Fugacity of CO₂ as a function of CO₂ composition at a constant pressure of 1.970 MPa and 313.15 K calculated with the PR EoS. (b) The solubility of CO₂ in [bmim][Tf₂N] computed with MC simulations in the osmotic ensemble at CO₂ fugacities corresponding to Figure 6.3(a). (c) Combination of Figures 6.3(a) and 6.3(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 (6.7).

phase. We have used MC simulations in the osmotic ensemble to investigate the effect of CO₂ concentration in the liquid phase on the CO₂/CH₄ selectivity, see Table 6.2 and Figure 6.4. The following can be concluded from Tables 6.1 and 6.2 and Figure 6.4: (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 rela-

Table 6.2: CO₂/CH₄ solubilities and selectivities in [bmim][Tf₂N] from MC simulations in the osmotic ensemble at a given T , P , and y_i . The experimental Henry constants of CO₂ and CH₄ in [bmim][Tf₂N] at 313.15 K are 4.9 MPa and 49.3 MPa, respectively [370, 371]. The Henry constants of CO₂ and CH₄ in [bmim][Tf₂N] at 313.15 K computed from the MC data are 5.4 MPa and 50.7 MPa, respectively [18, 114]. The ideal CO₂/CH₄ selectivities computed from the experiments and MC data as a ratio of the Henry constants are 10.1 and 9.5, respectively.

T/K	P/MPa	y_{CO_2}	y_{CH_4}	x_{CO_2}	x_{CH_4}	$S_{\text{CO}_2/\text{CH}_4}^{\text{R}}$
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

tively low pressures and low CO₂ concentrations in the liquid phase, (4) the real selectivity deviates from the ideal selectivity for relatively high CO₂ concentrations in the liquid phase. Recently, Budhathoki *et al.* [426] used Gibbs ensemble Monte Carlo simulations to compute CO₂/CH₄ selectivities in [bmim][Tf₂N]. These authors also observed ideal selectivity for low CO₂ concentrations in the liquid phase, but the selectivity was shown to decrease for relatively high CO₂ concentrations. This is in agreement with our simulation results.

In Table 6.3, the MC results for the system CO₂-CH₄-[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 CO₂ concentrations, the real selectivity starts to deviate from the ideal selectivity. This is not unexpected, because

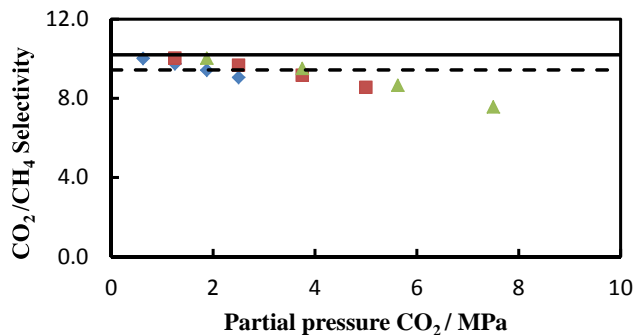


Figure 6.4: Effect of the CO₂ partial pressure on the real CO₂/CH₄ selectivity in [bmim][Tf₂N] at 313.15 K. 25-75 gas mixture (diamonds), 50-50 gas mixture (squares), and 75-25 gas mixture (triangles). The ideal selectivity computed from MC data (dashed line) and from experiments (solid line) are included.

the definition of the ideal selectivity (Equation (3.7)) does not account for the nonidealities in the mixture. Hert *et al.* [168] measured the simultaneous solubility of CO₂ and CH₄ in the IL 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf₂N]. These authors observed an enhancement of CH₄ solubility in the presence of CO₂ 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 CO₂ and CH₄ were lower than 0.1. Therefore, the data of Hert *et al.* should be treated with caution until substantiated further [113].

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 (6.6). However, providing a poor initial guess for the gas composition will require more than two independent simulations in order to accurately evaluate Equation (6.7). An educated guess for the gas composition can always be obtained from an

Table 6.3: CO₂/CH₄ solubilities and selectivities in [emim][dep] from MC simulations in the osmotic ensemble at a given T , P , and y_i . The Henry constants of CO₂ 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 [114]. The Henry constants of CH₄ 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 [114].

T/K	P/MPa	y_{CO_2}	y_{CH_4}	x_{CO_2}	x_{CH_4}	$S_{\text{CO}_2/\text{CH}_4}^{\text{R}}$
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

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.

6.5 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 $\text{CO}_2\text{-CH}_4$ gas mixtures in the ILs [bmim][Tf₂N] 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][Tf₂N] 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][Tf₂N] and [emim][dep] is computed and compared with the ideal selectivity, which is defined as the ratio of the Henry 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.

Chapter 7

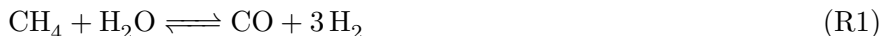
Solubility of Pre-combustion Gases from Monte Carlo Simulations

This Chapter is based on the paper: M. Ramdin, S. P. Balaji, J. M. Vicent-Luna, J. J. Gutiérrez-Sevillano, S. Calero, T. W. de Loos and T. J. H. Vlugt. Solubility of the Precombustion Gases CO₂, CH₄, CO, H₂, N₂, and H₂S in the Ionic Liquid [bmim][Tf₂N] from Monte Carlo Simulations. J. Phys. Chem. C, 118 (2014) 23599-23604.

7.1 Introduction

The previous chapters focused on the application potential of ILs for CO₂ capture in the natural gas sweetening process. In this chapter, the potential of ILs for CO₂ capture in the pre-combustion process is investigated. The pre-combustion process involves a reaction of the fuel with air/oxygen and steam to produce syngas, which is a mixture of carbon monoxide (CO) and hydrogen (H₂). In the case of natural gas as fuel, the syngas is produced

via the steam-reforming reaction [6]:



In a next step, the CO is converted according to the water-gas-shift (WGS) reaction to CO₂ and more H₂:



After separating the CO₂ from H₂, the hydrogen-rich fuel can be used in many applications like gas turbines for electricity production, engines, fuel cells, and chemical synthesis such as ammonia, methanol and Fischer-Tropsch fuels [4]. The advantage of pre-combustion CO₂ capture is the relatively high partial pressure of CO₂ after the WGS reaction allowing for less expensive separation methods including physical absorption/adsorption and membranes [427, 428]. Several existing solvents (e.g., amines, Selexol and Rectisol) and new materials (e.g., zeolites and metal-organic frameworks (MOFs)) have been considered for pre-combustion CO₂ capture [429–432]. The reader is referred to the recent work of Liu *et al.* [4] for an excellent state-of-the-art review of technologies used for hydrogen/syngas production and purification.

The focus of this chapter is the separation of CO₂ from syngas, either before or after the WGS reaction, using the IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf₂N]. The equilibrium reactions (R1) and (R2) yield a mixture of reactants and products, which will require a separation step downstream of the process. The relevant separation selectivities are CO₂/CH₄, CO₂/CO, CO₂/H₂, CO₂/N₂ if air instead of pure oxygen is used, and CO₂/H₂S if the syngas is not desulfurized prior to CO₂ removal. The selectivity of one gas over the other can be calculated from solubility data of the corresponding gases in the IL. Unfortunately, solubility data of sparingly soluble gases (e.g., H₂, N₂ and CH₄) or toxic gases (e.g., CO and H₂S) are scarcely reported in the literature. An alternative tool for these difficult to conduct experiments is provided by means of molecular simulations. Here, Monte Carlo simulations using a classical force field have been used to predict the solubility of the gases CO₂, CH₄, CO, H₂, N₂

and H₂S in the IL [bmim][Tf₂N] and whenever possible a comparison with experimental data is provided.

7.2 Simulation Details

The recently developed Continuous Fractional Component Monte Carlo (CFCMC) method in the osmotic ensemble has been used to compute absorption isotherms of the pre-combustion gases CH₄, CO₂, CO, H₂, N₂, and H₂S in the IL [bmim][Tf₂N] [379, 380]. A brief description of the CFCMC method can be found in Chapter 5 and for more details the reader is referred to the original publication by Shi and Maginn and the recent work by Torres-Knoop *et al.* [379, 383, 388].

A classical force field including bond-stretching, bond-bending, torsion, Lennard-Jones and electrostatic interactions was used for the IL molecules in our simulations. The force field parameters for the IL [bmim][Tf₂N] have been taken from Liu and Maginn [390]. The molecular models used for the gases contain one or more LJ interaction sites with or without partial charges and/or dipoles. All the gases have been treated as rigid in the simulations. The standard TraPPE model was used for the gases CH₄, CO₂ and N₂ [392]. The CO model, which includes a dipole moment, has been adopted from Martín-Calvo *et al.* [433]. For H₂, the two-center LJ model of Cracknell has been applied [434]. For H₂S, three different models have been used; the three-site (3S) model of Kamath *et al.* [435], the four-site (4S) model of Kristóf and Lizi [436], and the five-site (5S) model of Gutiérrez-Sevillano *et al.* [437]. The Lorentz-Berthelot mixing rules were adopted for the LJ interactions between unlike atoms [396]. The values of all force field parameters are listed in the Supporting Information of Ref. [7]. The Ewald method with a relative precision of 10⁻⁵ was applied to account for the long range electrostatic interactions. The LJ interactions were truncated and shifted at 12 Å and no tail corrections were applied. All the simulations were performed in the osmotic ensemble, see Chapter 5 for more details. The fugacity of the gases was obtained from the Peng-Robinson (PR) equation of state (EoS) [340]. The λ moves were biased using the Wang-Landau

sampling scheme, which enforces the system to visit all the possible λ states and to achieve a flat histogram for λ [387]. The configurational-bias Monte Carlo (CBMC) scheme was used to sample the internal degrees of freedom of the IL molecules [385, 397–399].

The CFCMC simulations were executed at a temperature of 333.15 K using an ensemble of 50 IL molecules. All the MC simulations were performed using the molecular simulation tool RASPA [401]. In order to reduce the simulation time, however, the IL structure was first equilibrated using Molecular Dynamics (MD) simulations in GROMACS [438, 439]. After an energy minimization step, an ensemble of 50 IL molecules were simulated for 2 ns in the NPT ensemble. In a subsequent step, the atomic positions and velocities of the equilibrated ensemble were transferred to RASPA to perform the actual CFCMC simulations. The CFCMC simulations were started with an equilibration run of 50000 MC cycles, where the number of MC steps in a cycle equals the total number of molecules in the simulation box. In this equilibration run, the weights of the various MC moves are adjusted to obtain 50 % acceptance rates. The production runs consisted of 0.5 to 1 million cycles, where the exact number was dictated by the convergence characteristics of the system. The reported data were obtained from block averages, and the standard deviation was used to calculate the uncertainty.

7.3 Results and Discussion

7.3.1 Solubility

The solubility of CO₂, CH₄, CO, H₂, N₂ and H₂S in the IL [bmim][Tf₂N] was obtained from MC simulations in the osmotic ensemble at a temperature of 333.15 K and pressures up to 15 MPa. In Figure 7.1 and Tables 7.1 to 7.4, the solubility of CO₂, CH₄, CO and H₂ obtained from the MC simulations is, respectively, compared with the experimental data of Raeissi *et al.* [370, 371, 440, 441]. The experimental uncertainty is typically 0.003 in the mole fractions, whereas the uncertainty in the simulations is typically lower than 0.002 in the mole fractions (i.e., smaller than the symbol size).

Table 7.1: Solubility of CO₂ (1) in the IL [bmim][Tf₂N] (2) at a temperature of 333.15 K and different pressures.

p/MPa	$x_1^{\text{exp.}}$	$x_1^{\text{sim.}}$	difference/%
0.569	0.085	0.082	3.3
1.373	0.189	0.182	3.7
2.392	0.293	0.278	4.8
3.469	0.382	0.361	5.3
5.396	0.487	0.462	5.0
6.159	0.526	0.495	5.8
7.908	0.585	0.550	6.1

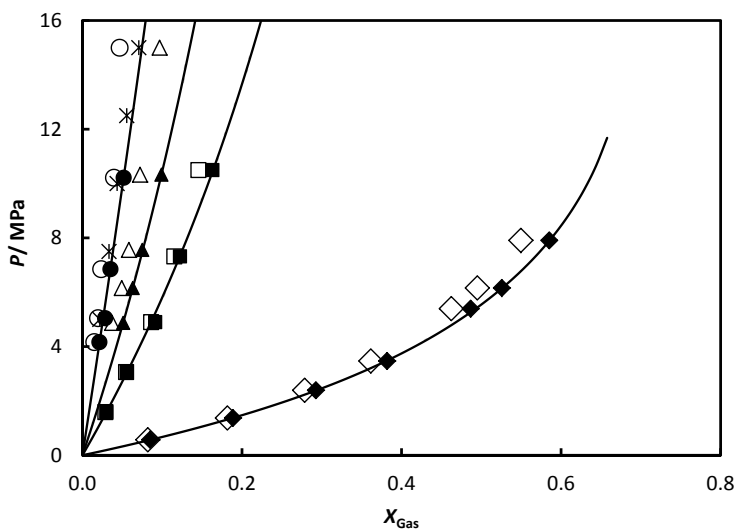


Figure 7.1: Solubility of CO₂, CH₄, CO, H₂ and N₂ in [bmim][Tf₂N] from MC simulations (open symbols) and experiments (filled symbols) at a temperature of 333.15 K. CO₂ experiments (filled diamonds) and MC data (open diamonds); CH₄ experiments (filled squares) and MC data (open squares); CO experiments (filled triangles) and MC data (open triangles); H₂ experiments (filled circles) and MC data (open circles), and MC data of N₂ (stars). Lines are Peng-Robinson equation of state modeling results [8, 340].

Table 7.2: Solubility of CH₄ (1) in the IL [bmim][Tf₂N] (2) at a temperature of 333.15 K and different pressures.

p/MPa	$x_1^{\text{exp.}}$	$x_1^{\text{sim.}}$	difference/%
1.591	0.030	0.029	3.8
3.063	0.056	0.055	1.5
4.900	0.091	0.086	5.6
7.320	0.122	0.115	5.9
10.497	0.163	0.145	10.7

Table 7.3: Solubility of CO (1) in the IL [bmim][Tf₂N] (2) at a temperature of 333.15 K and different pressures.

p/MPa	$x_1^{\text{exp.}}$	$x_1^{\text{sim.}}$	difference/%
4.871	0.051	0.037	27.1
6.153	0.063	0.049	21.8
7.558	0.075	0.058	22.4
10.326	0.099	0.072	27.1
15.000	-	0.097	-

Table 7.4: Solubility of H₂ (1) in the IL [bmim][Tf₂N] (2) at a temperature of 333.15 K and different pressures.

p/MPa	$x_1^{\text{exp.}}$	$x_1^{\text{sim.}}$	difference/%
4.167	0.0212	0.015	30.3
5.047	0.0283	0.019	31.3
6.849	0.035	0.023	33.0
10.216	0.0516	0.039	23.7
15.000	-	0.047	-

The uncertainty of the simulations will only be reported if this is higher than the experimental uncertainty. The MC simulations slightly underpredict the solubility of CO and H₂, but the agreement is excellent for the gases CO₂ and CH₄ even at higher pressures. The simulation results for N₂ solubility in [bmim][Tf₂N] are reported in Table 7.5 and depicted in Figure 7.1. For the N₂ system no experimental data has been reported, but the predicted solubilities are in between that of H₂ and CO, which is

Table 7.5: Solubility of N₂ (1) in the IL [bmim][Tf₂N] (2) at a temperature of 333.15 K and different pressures.

p/MPa	$x_1^{\text{sim.}}$
5.00	0.022
7.50	0.033
10.00	0.043
12.50	0.056
15.00	0.071

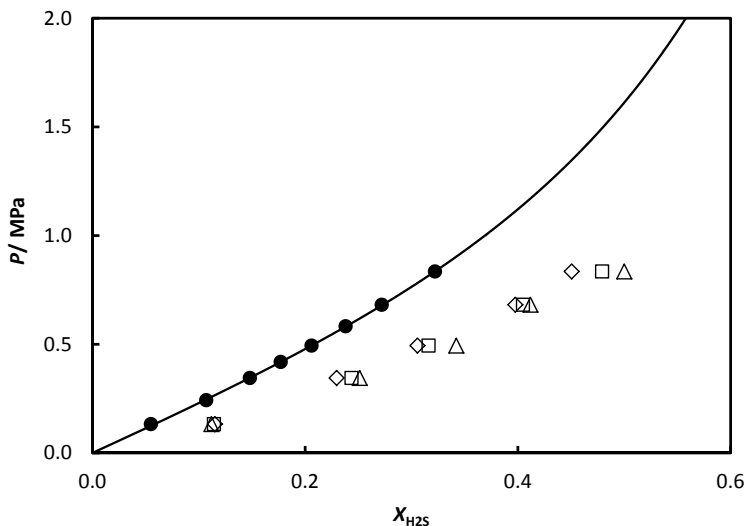


Figure 7.2: Solubility of H₂S in [bmim][Tf₂N] at a temperature of 333.15 K. Experiments (filled circles) and MC data: 3S H₂S model (open squares), 4S H₂S model (open diamonds) and 5S H₂S model (open triangles). Line is Peng-Robinson equation of state modeling result [8, 340].

consistent with the trend observed in other ILs [9, 123, 157, 158]. The H₂S solubilities obtained from MC simulations using the three different H₂S models are compared with the experimental data of Jalili *et al.* [442] in Figure 7.2 and Table 7.6. The MC simulations highly overpredict the H₂S solubility, regardless of the used H₂S model, compared to the experimental

Table 7.6: Solubility of H₂S (1) in the IL [bmim][Tf₂N] (2) at a temperature of 333.15 K and different pressures.

H ₂ S model	p/MPa	$x_1^{\text{exp.}}$	$x_1^{\text{sim.}}$	difference/%
H ₂ S ^a	0.133	0.055	0.115	109.2
	0.345	0.148	0.230	55.1
	0.494	0.206	0.306	48.3
	0.682	0.272	0.398	46.2
	0.835	0.322	0.451	39.9
H ₂ S ^b	0.133	0.055	0.114	107.7
	0.345	0.148	0.244	64.6
	0.494	0.206	0.316	53.4
	0.682	0.272	0.405	48.8
	0.835	0.322	0.479	48.8
H ₂ S ^c	0.133	0.055	0.112	103.5
	0.345	0.148	0.251	69.8
	0.494	0.206	0.342	66.1
	0.682	0.272	0.412	51.4
	0.835	0.322	0.500	55.3

^a Three-site model of Kamath *et al.* [435].

^b Four-site model of Kristóf and Lizi [436].

^c Five-site model of Gutiérrez-Sevillano *et al.* [437].

data of Jalili *et al.* The 3S model of Kamath *et al.* and the 4S model of Kristóf and Lizi are slightly in better agreement with the experimental data than the 5S model of Gutiérrez-Sevillano *et al.* Differences can be attributed to the used force field, but the simulation results are acceptable considering that none of the interaction parameters used in this study were fitted to the experimental solubility data of [bmim][Tf₂N]. Moreover, the MC simulations correctly predict the experimental solubility trend, which obeys the following order: H₂S > CO₂ > CH₄ > CO > N₂ > H₂. These results show that molecular simulation is a promising tool for predicting gas solubilities in complex systems like ionic liquids.

Table 7.7: Henry constants of CO₂, CH₄, CO, H₂, N₂, and H₂S in Selexol and the IL [bmim][Tf₂N] at a temperature of 333.15 K.

solute	$H_{\text{Selexol}}^{\text{exp.}}/\text{MPa}$	$H_{\text{IL}}^{\text{exp.}}/\text{MPa}$	$H_{\text{IL}}^{\text{sim.}}/\text{MPa}$	difference/%
CO ₂	6.81 ^a	6.56	7.10	8.2
CH ₄	40.13 ^a	52.4	53.7	2.5
CO	-	95	125.9	33.0
H ₂	193 ^b	199	271.7	36.3
N ₂	151 ^b	-	225.7	-
H ₂ S (3S)	1.01 ^c	2.17	1.15	47.0
H ₂ S (4S)	1.01	2.17	1.16	46.5
H ₂ S (5S)	1.01	2.17	1.17	46.1

^a Taken from Rayer *et al.* [354, 355].

^b Calculated from Gainar *et al.* [443].

^c Taken from Xu *et al.* [263].

7.3.2 Selectivity

The separation performance of a real process is not governed by the solubility, but the key parameter is the selectivity of a target component with respect to the other components in the mixture [8, 345]. This means that a good solvent for CO₂ capture at pre-combustion conditions should have a high CO₂ solubility, but at the same time a low capacity for the other gases (e.g. CH₄). The ideal selectivity can be calculated in many different ways from the pure gas solubility data [345]. Here, the ratio of the Henry constants is used to quantify the ideal selectivity ($S_{i/j}^I$), where i is the target component and j the undesired component, see Equation (3.7). The Henry constants of the solutes i in the solvent j , [bmim][Tf₂N], are calculated from Equation (3.8). The Henry constants derived from the MC data are compared with the experimental data in Table 7.7. The agreement between the MC data and the experiments is excellent for the gases CO₂ and CH₄. For the other gases the absolute deviation between the predicted and experimental Henry constants can be as high as 40%. However, the sparingly soluble gases (CO, H₂ and N₂) are generally difficult to measure and consequently the uncertainty in the experimental Henry constant is

Table 7.8: Selectivity of CO₂, CH₄, CO, H₂, N₂, and H₂S in Selexol and the IL [bmim][Tf₂N] at a temperature of 333.15 K.

separation	$S_{\text{Selexol}}^{\text{exp.}}$	$S_{\text{IL}}^{\text{exp.}}$	$S_{\text{IL}}^{\text{sim.}}$	difference/%
CO ₂ /CH ₄	5.9 ^a	8.0	7.6	5.3
CO ₂ /CO	-	14.4	17.7	23.0
CO ₂ /H ₂	25 ^b	30.4	38.3	26.0
CO ₂ /N ₂	20 ^b	-	31.8	-
CO ₂ /H ₂ S	0.15 ^c	0.33	0.16	51.0
CO ₂ /H ₂ S	0.15	0.33	0.16	50.6
CO ₂ /H ₂ S	0.15	0.33	0.16	50.2

^a Calculated from Rayer *et al.* [354, 355].

^b Calculated from Gainar *et al.* [443].

^c Calculated from Xu *et al.* [263].

often large (e.g. in some cases up to 50%) [9]. The relevant selectivities for the pre-combustion process were calculated using Equation (3.7) and are compared with experimental data in Table 7.8. The absolute deviation between the predicted and experimental selectivities are of the same order as for the Henry constants. It is important to note that the high CO₂/CH₄, CO₂/CO, CO₂/N₂ and CO₂/H₂ selectivities indicate a great potential of [bmim][Tf₂N] for CO₂ removal from the pre-combustion process. However, the syngas should be desulfurized before the CO₂ removal step, because CO₂ can not be removed selectively in the presence of H₂S. A comparison of the Henry constants and the selectivities of the gases in [bmim][Tf₂N] and the widely used solvent Selexol is provided in Table 7.7 and Table 7.8, respectively. Clearly, the Henry constants and the selectivities in both solvents are very similar, hence considering the price/performance ratio the Selexol solvent outperforms the costly IL [bmim][Tf₂N].

7.4 Conclusions

Monte Carlo simulations were used to predict the solubility of the single gases CO_2 , CH_4 , CO , H_2 , N_2 and H_2S in the ionic liquid (IL) 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf₂N]. Simulations in the osmotic ensemble were performed to compute absorption isotherms at a temperature of 333.15 K using the versatile continuous fractional component Monte Carlo (CFCMC) method. The predicted gas solubilities and Henry constants are in good agreement with the experimental data. The MC simulations correctly predict the observed solubility trend, which obeys the following order: $\text{H}_2\text{S} > \text{CO}_2 > \text{CH}_4 > \text{CO} > \text{N}_2 > \text{H}_2$. The CO_2/CH_4 , CO_2/CO , CO_2/N_2 , CO_2/H_2 and $\text{CO}_2/\text{H}_2\text{S}$ selectivities relevant for the pre-combustion CO_2 capture process were calculated from the ratio of pure gas Henry constants. The results indicate that [bmim][Tf₂N] can effectively capture CO_2 at pre-combustion conditions, but the syngas should be desulfurized prior to CO_2 removal, because H_2S is three times more soluble than CO_2 . Moreover, we have shown that molecular simulations can be used to predict gas solubilities in complex systems like ionic liquids.

Chapter 8

Monte Carlo Simulations of CO₂ and Monoethanolamine

This chapter is based on the paper: S. P. Balaji, S. Gangarapu, M. Ramdin, A. Torres-Knoop, H. Zuilhof, E. L. V. Goetheer, D. Dubbeldam, and T. J. H. Vlugt. Simulating the reactions of CO₂ in aqueous monoethanolamine solution by Reaction Ensemble Monte Carlo using the Continuous Fractional Component method. J. Chem. Theory. Comput., 11 (2015) 2661-2669.

8.1 Introduction

As explained in Chapter 2, CO₂ capture at post-combustion conditions demands a chemical solvent. Typically, the removal of CO₂ from flue gas streams is carried out using liquid amine solvents [33]. Monoethanolamine-containing (MEA) solutions were among the first alkanolamine based solvents used in the capture of CO₂. This system remains one of the most important solvents in the post combustion CO₂ capture [257]. Some of the advantages of using MEA solutions for CO₂ capture are the high CO₂ absorption capacity and reaction rates and low cost of solvent [257, 444]. In order to regenerate the solvent back, heat must be supplied [257, 444, 445].

Some of the disadvantages of using MEA solution as solvents include the high energy demand to regenerate the solvent and emissions of MEA solvents as aerosol [446, 447]. MEA solutions are also susceptible to oxidative and thermal degradation [446–448]. The mechanism of CO₂ absorption in MEA solutions is chemical in nature. CO₂ reacts with MEA solution forming stable carbamates [33, 257, 386, 445, 449]. To study the chemisorption of CO₂ in MEA solutions and to reduce the heat required to regenerate the alkanolamine after CO₂ capture, it is necessary to study the chemical reactions that take place in the solution [449]. There are several possible mechanisms explaining how CO₂ reacts with alkanolamines [445, 449–451]. CO₂ reacts through an acid-base buffer mechanism with the alkanolamines to form protonated amines. CO₂ also reacts with some primary and secondary alkanolamines to form carbamates and reacts with tertiary alkanolamines to form bicarbonates [445, 449, 450]. To design a CO₂ amine treating process, it is important to understand the chemical equilibrium as well as the kinetics of the different reactions. There are many studies in the literature about the CO₂-MEA system [9, 33, 446, 452]. Sartori and Savage obtained the equilibrium constants for carbamate formation [453]. Batt *et al.* [454] and Maddox *et al.* [455] qualitatively investigated the reactions occurring in the MEA system. Poplsteinova *et al.* [456] have studied systems containing MEA and N-methyl-diethanolamine using NMR spectroscopy. Hasse and co-workers [445] have studied the chemical equilibria of CO₂ in aqueous alkanolamines using online NMR spectroscopy. Chemical equilibria and kinetics of CO₂-alkanolamine solutions are difficult to study experimentally at a molecular level because of the extremely fast reaction rates and the different reaction mechanisms. Molecular simulations play an important role in bridging the gap between our understanding of the reaction phenomena on a molecular level and the experimental observations on a macroscopic scale [385]. The impact of individual reactions and reaction mechanisms on the chemical equilibrium of the system can be studied using molecular simulations. Quantum chemical methods are widely applied to compute stationary points on the potential energy surface like transition states and activation barriers. Time dependent ab-initio methods like Car-Parrinello molecular dynamics [457] can be used to model the reactions directly. These

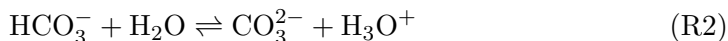
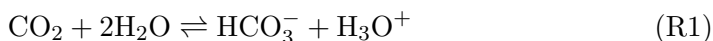
methods scale poorly with system size and are sometimes difficult to apply to liquid phases. A classical based approach developed by Van Duin *et al.* uses “Reactive” force fields (ReaxFF) that are parameterized to study the chemical reactions of a few systems using classical molecular dynamics simulations [458]. ReaxFF treats the intermolecular interactions between the atoms and molecules through a classical force field which have been parameterized from experimental data or quantum simulations [458]. Another classical based approach called the Reaction Ensemble Monte Carlo (RxMC) for studying chemical reactions in equilibrium ignores transient events like bond breaking and formation (reaction mechanism in general). This approach is ideal to study the equilibrium distributions of the reacting species, since the effect of the intermolecular interactions with the surrounding molecules are taken into account. It is important to realize that equilibrium speciation is determined by thermodynamics of the system, and classical molecular simulations are a suitable tool to study this. The Reaction Ensemble Monte Carlo (RxMC) was developed independently by Johnson *et al.* [459] and Smith and Triska [460]. An important feature of Reaction Ensemble Monte Carlo (RxMC) is the actual reaction and its transition path is not simulated, but that only the equilibrium configurations of the molecules before and after the reaction are sampled. The forward and backward reactions are sampled using stochastic trial moves. In case of a forward reaction, the reactant molecules are chosen at random and are deleted from the simulation box while the product molecules are inserted randomly according to the stoichiometry of the reaction. This RxMC method requires the input of stoichiometric coefficients of the reactants and products and the ideal gas partition functions of isolated reactant and product molecules along with the intermolecular potential parameters to describe the interactions between the molecules. These ideal gas partition functions of isolated molecules can be obtained from thermophysical tables or quantum mechanical calculations [461–463]. The partition function of ideal gas molecules depend on the volume of the simulation box and this must be taken into account in the acceptance rules of the RxMC algorithm (see the Supporting Information of Ref. [19] for details). Previous research pertaining to RxMC has focused on small molecules with fixed internal

degrees of freedom [459, 460, 464–467]. Lisal and co-workers [468, 469] have developed the Reaction Ensemble Monte Carlo for systems with flexible internal degrees of freedom to study the synthesis of Methyl-*tert*-butyl-ether (MTBE) from isobutene and methanol. The acceptance rules for the reaction move derived by Lisal and co-workers also include the change in energy due to intramolecular contributions. Intermolecular interactions are counted twice in their derivation of the acceptance rules, which is incorrect [463, 468, 469]. Rosch *et al.* [463] have derived the correct acceptance rules. Keil *et al.* [461, 462] have studied propene metathesis reactions within confined environments. These authors have combined the Configurational-Bias Monte Carlo (CBMC) approach with the Reaction Ensemble Monte Carlo for linear alkanes and alkenes. The Configurational-Bias Monte Carlo algorithm is useful for simulating larger molecules as inserting these large molecules in confined systems is extremely difficult. To the best of our knowledge, application of the Reaction Ensemble Monte Carlo for complex molecules and reactions in a dense liquid phase has not been studied. A reaction in the Reaction Ensemble involved the deletion of reactants and the insertion of the reaction products. These so-called "insertions" and "deletions" are accepted in such a way that the correct equilibrium distribution is sampled. The efficiency and accuracy of these simulations depend on the probability of successful insertions and deletions of molecules. At high densities typically encountered in a liquid phase, the probability of successful insertions and deletions is very low due to a large number of overlaps with the existing molecules in the simulation box [379, 385, 388]. To increase the efficiency of the successful insertions and deletions, Maginn *et al.* [379, 389] have developed the Continuous Fractional Component Monte Carlo (CFCMC) method to insert/delete molecules in a more gradual manner. Torres-Knoop *et al.* [388] have combined the CBMC with the CFCMC to obtain higher computational efficiencies. Other works have been published proposing methods that try to increase the efficiency of insertion and deletion in dense liquids [470–472]. Rosch *et al.* have extended the CFCMC method for the Reaction Ensemble, coupling the CFCMC for inserting the product molecules and deleting the reactant molecules based on their respective stoichiometry [463]. In this work, we use the Reaction Ensemble Monte

Carlo using the Continuous Fractional Component (RxMC/CFC) method to study the chemical equilibrium of CO₂ in MEA solution and determine the equilibrium concentrations of the different species in the system. The results are compared to experimental results from literature. We study the effects of different reaction mechanisms on the equilibrium concentrations of the various species. The rest of this paper is organized as follows: Section 2 deals with simulating the reactions of CO₂ in MEA solution along with the derivation of the acceptance rules for the RxMC/CFC algorithm. Section 3 contains the different results and discussions and our findings are summarized in Section 4.

8.2 Simulating the reactions of CO₂ in MEA solution

The reactions of CO₂ with primary and secondary amine solutions usually takes place through an acid-base buffer mechanism which results in the formation of stable carbamates and bicarbonate followed by the subsequent protonation of the amine [455]. Non-hindered primary and secondary amines react rapidly with CO₂ to form carbamate ions and the addition of water increases the absorption capacity and rate. Tertiary amines react with CO₂ via the bicarbonate pathway to form bicarbonate ion and the ammonium salt of the amine. Since monoethanolamine (HOCH₂CH₂NH₂) is a primary amine, the reactions take place via the carbamate ion pathway [449, 450]:



These reactions are generally described in the literature [445, 449, 450, 456]. It is important to note that in the reactions mentioned above, the appearance of H₃O⁺ is to avoid the presence of H⁺ in the system, as H⁺ does not obey the Born-Oppenheimer approximation for classical simulations [385].

Some other additional reactions have also been described in the literature [445]. MEA is also able to form 2-oxazolidone which is a heterocyclic component [445, 473]. Other amine degradation reaction mechanisms are also possible [473, 474]. In spite of the different possible reaction mechanisms, the aim of all modeling and experimental studies is to obtain the equilibrium concentrations of the different species. In this regard, Reactions R1, R3 and R4 may be combined to result in a simplified Reaction R5 which is given by,



8.2.1 RxMC/CFC Algorithm

To obtain the equilibrium concentrations of the different species in a reacting mixture, the Reaction Ensemble Monte Carlo (RxMC) [459, 461, 462, 475] is used. The RxMC algorithm samples the reactions directly and bypasses transition states. The RxMC algorithm only requires the stoichiometric coefficients of the reactions as an input and the partition functions of the isolated molecules or ions, along with the force field parameters to compute the intermolecular interactions. Therefore, the RxMC method allows for a systematic study of the effect of the medium (or solvent) on the reaction equilibrium constant. The reaction trial move within the RxMC framework involves choosing the forward or reverse reaction at random. If the forward reaction is chosen, the reactant molecules are deleted and the product molecules are inserted according to their stoichiometries. For dense systems, these insertions and deletions of molecules, if performed in a single step, often lead to overlaps with the surrounding molecules. The probabilities of successful insertions/deletions of the molecules are very low. To circumvent this problem, Maginn *et al.* [379, 389] have developed the Continuous Fractional Component Monte Carlo method. Fractional molecules of the reactants and products are introduced into the system. By controlling the interactions of these fractional molecules with the surrounding molecules, the reactants/products are gradually inserted or removed. This is controlled

by a pseudocoupling factor, λ . Changes in λ will gradually insert or delete the molecules appropriately. The reaction ensemble is best described by taking the osmotic ensemble as the starting point, since most chemical reactions take place in a system at constant pressure. Let N_i denote the number of molecules of type i , P the imposed hydrostatic pressure, V the volume and μ_i the chemical potential of the species i . For an expanded osmotic ensemble, the partition function for a system of n species can be expressed as [463]

$$\begin{aligned} \Xi_{\text{biased}}(\mu_1, \dots, \mu_n, p, T) = & \beta P \int_0^1 d\lambda \sum_{N_i=0}^{\infty} \cdots \sum_{N_n=0}^{\infty} \int \exp \left[\beta \sum_{i=1}^n N_i \mu_i \right. \\ & - \sum_{i=1}^n \ln N_i! + \sum_{i=1}^n N_i \ln(\hat{q}_i(T)V) - \beta PV \\ & \left. - \beta U(s^N, \omega^N, \lambda) \right] \exp[\eta(\lambda)/k_B T] \\ & \times ds^{N_1} d\omega^{N_1} \cdots ds^{N_n} d\omega^{N_n} dV \end{aligned} \quad (8.1)$$

where s^{N_i} are the configurations of the N_i molecules of type i , ω^{N_i} are the orientations and internal configurations of N_i molecules of type i and $U(s^N, \omega^N, \lambda)$ is the potential energy of the system. $\beta = 1/k_B T$, $\hat{q}_i(T)$ is the temperature dependent term in the molecular partition function for the molecule of type i . $\eta(\lambda)$ are the biasing factors introduced to improve the probabilities of transitions in λ . The reader is referred to the Supporting Information of Ref. [19] for a detailed explanation on the molecular partition functions and partition functions of the osmotic ensemble. From (8.1), it follows that the probability that the system is in a certain state is

$$\begin{aligned} p_{\text{biased}} \sim & \exp \left[\beta \sum_{i=1}^n N_i \mu_i - \sum_{i=1}^n \ln N_i! + \sum_{i=1}^n N_i \ln(\hat{q}_i(T)V) \right. \\ & \left. - \beta PV - \beta U(s^N, \omega^N, \lambda) \right] \exp[\eta(\lambda)/k_B T] \end{aligned} \quad (8.2)$$

This equation can be used to derive the acceptance rules in our Monte Carlo algorithm.

Reaction Ensemble Monte Carlo using the Continuous Fractional Component algorithm

Let us consider a reaction involving c species in a system consisting of n molecule types. For the species not involved in the reaction, the stoichiometric coefficient ν_i is set to 0 by definition. If a reaction takes place in the forward or reverse direction, there will be a change in the molecules of each component. The state before the reaction takes place is now denoted by old state “o”, while the state after the reaction takes place is denoted by new state “n”. Since the reaction has taken place, we know how the number of molecules of each component changes:

$$N_{i,n} = N_{i,o} + \nu_i \quad (8.3)$$

The probabilities to exist in states “o” and “n” can be obtained from Eq. (8.2). Substituting Eq. (8.3) in (8.2) for the new state, the expressions for the probabilities to exist in the old and the new states are,

$$p_{o,\text{biased}} \sim \exp \left[\beta \sum_{i=1}^n N_{i,o} \mu_i - \sum_{i=1}^n \ln N_{i,o}! + \sum_{i=1}^n N_{i,o} \ln(\hat{q}_i(T) V_o) - \beta P V_o - \beta U_o(s^{N,o}, \omega^{N,o}, \lambda_o) \right] \exp[\eta(\lambda_o)/k_B T] \quad (8.4)$$

$$p_{n,\text{biased}} \sim \exp \left[\beta \sum_{i=1}^n \nu_i \mu_i + \beta \sum_{i=1}^n N_{i,o} \mu_i - \sum_{i=1}^n \ln(N_{i,o} + \nu_i)! + \sum_{i=1}^n N_{i,o} \ln(\hat{q}_i(T) V_n) + \sum_{i=1}^n \nu_i \ln(\hat{q}_i(T) V_n) - \beta P V_n - \beta U_n(s^{N,n}, \omega^{N,n}, \lambda_n) \right] \exp[\eta(\lambda_n)/k_B T] \quad (8.5)$$

Acceptance rules in RxMC/CFC

Averages in the Boltzmann ensemble (denoted by $\langle \dots \rangle$) follow directly from biased averages (denoted by $\langle \dots \rangle_{\text{biased}}$) according to [396]

$$\langle A \rangle = \frac{\langle A \exp[-\eta(\lambda)] \rangle_{\text{biased}}}{\langle \exp[-\eta(\lambda)] \rangle_{\text{biased}}} \quad (8.6)$$

In the Reaction Ensemble Monte Carlo using Continuous Fractional Component method, there are four types of trial moves possible:

1. Change the position of a randomly selected molecule (either a regular or a fractional molecule)
2. Change the orientation of a randomly selected molecule (either a regular or a fractional molecule)
3. Change the volume of the system
4. Change the coupling parameter λ of a randomly selected reaction. The reactions are chosen with equal probability. This can be further divided into 3 cases ($\Delta\lambda$ is the change in λ):

(a) $0 \leq \lambda + \Delta\lambda \leq 1$

(b) $\lambda + \Delta\lambda < 0$

(c) $\lambda + \Delta\lambda > 1$

The first two Monte Carlo moves are trivial and have the same acceptance rules as the ones derived previously [385, 396]. For the Volume Change Monte Carlo trial move, random walks are made in $\ln(V_n/V_{\text{ref}})$ [385] in which V_{ref} is an arbitrary reference volume. The probabilities of existing in

the old state “o” and the new state “n” are

$$p_{\text{o,baised}} \sim \beta P V_{\text{o}} \exp \left[\beta \sum_{i=1}^n N_{i,\text{o}} \mu_i - \sum_{i=1}^n \ln N_{i,\text{o}}! + \sum_{i=1}^n N_{i,\text{o}} \ln(\hat{q}_i(T) V_{\text{o}}) - \beta P V_{\text{o}} - \beta U_{\text{o}}(s^N, \omega^N, \lambda) \right] \exp[\eta(\lambda_{\text{o}})/k_B T] \quad (8.7)$$

$$p_{\text{n,baised}} \sim \beta P V_{\text{n}} \exp \left[\beta \sum_{i=1}^n N_{i,\text{o}} \mu_i - \sum_{i=1}^n \ln N_{i,\text{o}}! + \sum_{i=1}^n N_{i,\text{o}} \ln(\hat{q}_i(T) V_{\text{n}}) - \beta P V_{\text{n}} - \beta U_{\text{n}}(s^N, \omega^N, \lambda) \right] \exp[\eta(\lambda_{\text{n}})/k_B T] \quad (8.8)$$

For random walks in $\ln(V_{\text{n}}/V_{\text{ref}})$, $\lambda_{\text{o}} = \lambda_{\text{n}}$ and $\eta(\lambda_{\text{o}}) = \eta(\lambda_{\text{n}})$. The acceptance rule is therefore

$$\text{acc}(o \rightarrow n) = \min \left(1, \left(\frac{V_{\text{n}}}{V_{\text{o}}} \right)^{N+1} \exp[-\beta P(V_{\text{n}} - V_{\text{o}})] \times \exp[-\beta(U_{\text{n}}(s^N, \omega^N, \lambda) - U_{\text{o}}(s^N, \omega^N, \lambda))] \right) \quad (8.9)$$

This expression is the same as the acceptance rule derived previously [385]. We now consider the reaction move as a change in λ of the system. For the reaction move, $V_{\text{o}} = V_{\text{n}}$. Looking into more detail at the three different cases when λ is changed, we have: **First case (a)**, where $0 \leq \lambda + \Delta\lambda \leq 1$, is the case where there is no addition or deletion of molecules. The old state is denoted by “o” and λ_{o} is the old coupling factor of the reaction. The new state is denoted by “n” and $\lambda_{\text{n}} = \lambda_{\text{o}} + \Delta\lambda$. From Eq. (8.2), we can obtain the probabilities to exist in old and new states. As the number of molecules in the system remain the same for the old and the new configurations, the acceptance rule is

$$\text{acc}(o \rightarrow n) = \min \left(1, \exp[-\beta(U_{\text{n}}(s^N, \omega^N, \lambda_{\text{n}}) - U_{\text{o}}(s^N, \omega^N, \lambda_{\text{o}}))] \times \exp[(\eta(\lambda_{\text{n}}) - \eta(\lambda_{\text{o}}))/k_B T] \right) \quad (8.10)$$

Second case (b), where $\lambda + \Delta\lambda > 1$, is the case of a reverse reaction. The λ of the old fractional reactant and product molecules are set to 1 and 0 respectively. New fractional reactant molecules are inserted into the system with $\lambda_n = (\lambda_o + \Delta\lambda) - 1$. Random product molecules are selected from the system and their λ is set from 1 to $1 - \lambda_n$. **Third case (c)**, where $\lambda + \Delta\lambda < 0$, is when there is a forward reaction. The λ of the old fractional reactant and product molecules are set to 0 and 1 respectively. New fractional product molecules are inserted into the system with $\lambda_n = (\lambda_o + \Delta\lambda) - 1$. Random reactant molecules are selected from the system and their λ is set to $1 - \lambda_n$. In cases two and three, the reaction has proceeded, either in the forward direction or the backward direction. For a reaction involving n species, equilibrium is achieved when

$$\sum_{i=1}^n \nu_i \mu_i = 0 \quad (8.11)$$

Substituting Eq. (8.11) in Eq. (8.5) since the reaction takes place at equilibrium, the expression for the acceptance rule for the forward/reverse reaction (cases (b) and (c)) is

$$\begin{aligned} \text{acc}(o \rightarrow n) = \min & \left(1, \prod_{i=1}^n \left(\frac{N_i^o!}{(N_i^o + \nu_i)!} (\hat{q}_i(T)V)^{\nu_i} \right) \right. \\ & \times \exp[-\beta(U_n(s^N, \omega^N, \lambda_n) - U_o(s^N, \omega^N, \lambda_o))] \\ & \left. \times \exp[(\eta(\lambda_n) - \eta(\lambda_o))/k_B T] \right) \quad (8.12) \end{aligned}$$

The acceptance rule for the RxMC derived above for one reaction can be generalized easily to include many reactions in the same system. It is important to note that in the acceptance rule (Eq. (8.12)), the volume term is included explicitly, since during the simulation the volume of the system changes. It is instructive to consider the case of a reaction in a mixture of

ideal gases. In that case, the acceptance rule of Eq. (8.12) reduces to

$$\text{acc}(o \rightarrow n) = \min \left(1, \prod_{i=1}^n \left(\frac{N_i^{o!}}{(N_i^o + \nu_i)!} (\hat{q}_i(T)V)^{\nu_i} \right) \right) \quad (8.13)$$

If the total number of molecules does not change during the reaction ($\sum_{i=0}^n \nu_i = 0$), it is well known from classical thermodynamics that the equilibrium constant is only a function of the molecular partition functions [476]. From Eq. (8.13), it can also be observed that there will be no dependence on the volume of the system when $\sum_{i=0}^n \nu_i = 0$ as the volume term V cancels out in Eq. (8.13) and the expression reduces to

$$\text{acc}(o \rightarrow n) = \min \left(1, \prod_{i=1}^n \left(\frac{N_i^{o!}}{(N_i^o + \nu_i)!} (\hat{q}_i(T))^{\nu_i} \right) \right). \quad (8.14)$$

If there is a change in the number of molecules during the reaction ($\sum_{i=0}^n \nu_i \neq 0$), the acceptance rule will now depend on the volume of the system, as can be seen from Eq. (8.13). It is important to consider the volume dependent term of the partition function explicitly in the acceptance rules since in many cases, the number of molecules during the reaction changes ($\sum_{i=0}^n \nu_i \neq 0$). It is unclear whether or not this volume term was taken into account correctly in previous studies from literature. Of course, the final results will not be affected if the simulations consider reactions where the number of molecules does not change due to the reaction [461–463].

8.2.2 Simulation Details

Two different sets of reactions are studied to obtain the equilibrium speciations by including: (1) Reactions R1-R4 (2) only Reaction R5. All simulations are performed in the Reaction Monte Carlo Ensemble (RxMC) in the constant temperature, constant pressure ensemble. The hydrostatic pressure of the system equals 1 bar. The effect of temperatures on the equilibrium compositions of the mixture is also studied. Different loadings of CO₂ have also been investigated. The initial concentration of MEA in

the aqueous MEA solution is 30 weight percent. Boettinger *et al* [445] measured the speciations at different loadings higher than 0.5 mole CO₂/mol MEA using online NMR spectroscopy. To achieve high loadings of CO₂ in experiments, the partial pressure of CO₂ ranged from 5 bar to 25 bar. In our simulations, a system with a fixed number of CO₂ molecules is simulated and only the hydrostatic pressure of the system needs to be specified. As the properties of a liquid phase do not depend much on the hydrostatic pressure and the total loading of CO₂ is specified, one can safely assume a hydrostatic pressure of 1 bar. Quantum mechanical simulations using GAUSSIAN 09 [477] are performed to obtain the partition functions \hat{q}_i of the isolated molecules required for the RxMC/CFC molecular simulations. All molecular species involved in the reaction were optimized with a second order Møller-Plesset perturbation method (MP2) in combination with a 6-311+G(2d,2p) basis set at different temperatures (293 K, 333 K, 353 K). A frequency analysis was performed on the optimized geometries to confirm the true minima on the potential energy surface and to obtain partition functions of all the molecules. All the calculations were performed with GAUSSIAN 09 [477]. Mulliken atomic charges were obtained from population analysis of self-consistent field density matrix. The individual contributions of translational, vibrational, rotational and electronic motions are considered for the calculation of the partition function for every molecule. [478]. The partition functions were split into a temperature dependent part and a volume dependent part (details are provided in the Supporting Information of Ref. [19]). The values of the computed partition functions of the molecules at different temperatures are listed in the Supporting Information of Ref. [19]. Force fields for the MEA have been taken from the OPLS force field [479]. Intermolecular potential parameters and intramolecular potential parameters for MEACOO⁻ and MEAH⁺ have also been taken from the OPLS force field. Force field parameters for CO₂ have been taken from the TraPPE force field [392] and for water from the Tip4p water model has been used [480]. The force field parameters for H₃O⁺ are taken from Vacha *et al.* [481] The force field parameters for the HCO₃⁻ and CO₃²⁻ have been taken from the OPLS database. Water, MEA, MEA⁺, MEACOO⁻, H₃O⁺, HCO₃⁻ and CO₃²⁻ are modeled as rigid molecules. The

partial charges for HCO₃⁻, CO₃²⁻, MEACOO⁻ and MEAH⁺ have been computed from quantum mechanical simulations in GAUSSIAN 09 [477]. The force field parameters for all the species are specified in the Supporting Information of Ref. [19]. Electrostatic interactions were handled by the Ewald summation algorithm [482] with a relative precision of 10⁻⁵. The cutoff radius was set at 12 Å for the Lennard-Jones interactions. σ and ϵ are the Lennard-Jones (LJ) parameters [401]. The Lorentz-Berthelot mixing rules were used to calculate the Lennard-Jones parameters between different atoms (σ_{ij} and ϵ_{ij}). Monte Carlo simulations in the RxMC/CFC ensemble were performed using RASPA, [401] a program for Monte Carlo and Molecular dynamics simulations. Monte Carlo simulations of 1 million cycles were performed for equilibration and production runs of 2 million cycles were performed, where one MC cycle is equal to the total number of molecules in the system. The probabilities of selecting a translation move, a rotation move, a partial reinsertion move and a reaction move were all 0.245. The probability of selecting a volume change move was 0.02. Simulations were performed with 444 water molecules, 56 MEA molecules and the appropriate number of CO₂ molecules depending on the loading. The size of the simulation box varied around 27 Å. By switching off electrostatics and intermolecular van der Waals interactions, the effect of electrostatics and intermolecular interactions on the reaction equilibrium was studied. At the start of the simulation, fractional molecules were assigned for all reacting species for both reactants and products in the Reactions R1-R4. The net charge of the fractional molecules (both the reactants and products) of all the Reactions R1-R4) is not zero. It is important to note that if we sum Reactions R1, R2, R3, and R4, the total net charge of the reactants equals -1. Similarly, the total net charge of products of the summed reactions also equals -1. To keep the simulation box charge neutral independent of the value of λ for each reaction, two H₃O⁺ fractional molecules, one as a reactant and the other as a product in Reaction R2, were added to the simulation box. This ensures that during the reaction the simulation box is always charge neutral. For the RxMC/CFC, the Lennard-Jones parameters as well as the partial charges are scaled with a pseudo coupling factor which is changed during the reaction move. The scaled Lennard-Jones and

electrostatic potentials are specified in detail in the Supporting Information of Ref. [19].

8.3 Results and Discussion

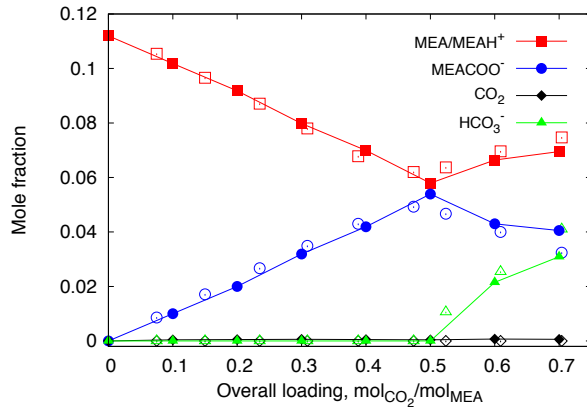
8.3.1 Effect of Electrostatics and intermolecular van der Waals interactions

When there are no intermolecular interactions between molecules, the system behaves as an ideal gas. For an ideal gas system, the equilibrium constant can be written directly in terms of the molecular partition functions of the individual species [483] which can be calculated from quantum simulations. A detailed derivation of this is provided in the Supporting Information of Ref. [19]. To observe the effect of intermolecular interactions, the intermolecular van der Waals interactions and the electrostatics were "switched off" *i.e.*, all the intermolecular Lennard-Jones parameters and electrostatics were set to zero. From the simulations, it was observed that forward reactions did not take place when including (1) reactions R1-R4 and (2) only reaction R5. Equilibrium constants for these ideal gas reactions calculated from quantum simulations are specified in the Supporting Information of Ref. [19]. The equilibrium constants for the forward reaction are extremely low. Equilibrium concentrations of the species for the ideal gas system can be obtained by solving the non-linear expressions for the equilibrium constants. The analytical solutions yield extremely low concentrations of carbamates and protonated amines. This is consistent with the results obtained from simulations performed when the intermolecular van der Waals interactions and the electrostatic are set to zero. It can be observed from the results of the simulations and analytical solutions that intermolecular interactions are necessary to compute the equilibrium concentrations of the species. Equilibrium speciations cannot be obtained by only performing quantum simulations as the system cannot be treated as an ideal gas. As expected, the solvation of ions in the solution is essential for the different reactions to take place. Classical simulations take into account the intermolecular interactions between the species and this is necessary

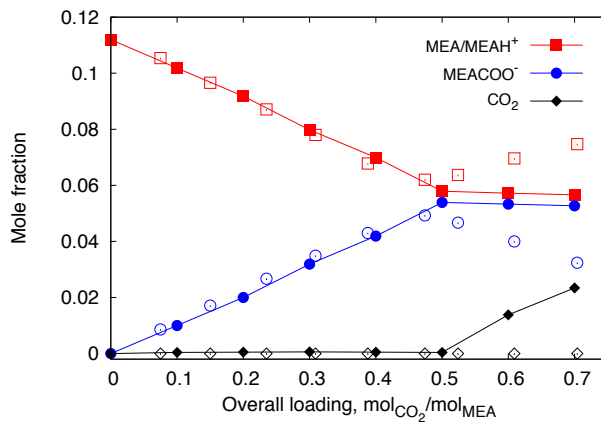
to compute the equilibrium concentrations of the species. If the reaction occurs in the ideal gas phase, the ions are not solvated and energetically this is very unfavorable.

8.3.2 Chemical Equilibrium of reactions R1+R2+R3+R4 and R5

The equilibrium mole fractions of the different species were obtained at different temperatures (293 K, 333 K, 353 K) and at a hydrostatic pressure of 1 bar for different loadings of CO₂ (mol CO₂/mol MEA) by performing Monte Carlo simulations in the Reaction Ensemble using the Continuous Fractional Component method. In Figures 8.1,8.2 and 8.3, the equilibrium mole fractions of the species MEA, MEAH⁺, MEACOO⁻, CO₂ and HCO₃⁻ are compared to experimental data [445, 456]. Poplsteinova *et al.* [456] and Boettinger *et al.* [445] measured the equilibrium speciation of CO₂-MEA-H₂O system using NMR spectroscopy. Boettinger *et al.* [445] report the sum of equilibrium concentrations of MEA and MEAH⁺, since it was impossible to distinguish between the protonated and the unprotonated MEA experimentally. In order to obtain the individual equilibrium concentrations of MEA and MEAH⁺, these authors have used a thermodynamic model (see below). Figure 8.1a shows the speciation of the CO₂+MEA solution for different loadings of CO₂ (mol CO₂/mol MEA) at 293 K and 1 bar when the reactions R1-R4 are used. The equilibrium concentration of the different species of CO₂+MEA solution exhibits the typical behavior of the primary amines. At low loadings until 0.5 mol CO₂/mol MEA, all CO₂ molecules react with the MEA molecules forming the carbamate and the protonated amine products. The concentrations of the carbamate and the protonated MEA increase as the loading of CO₂ increases until 0.5 mol CO₂/mol MEA, while the concentration of MEA decreases. At the loading of CO₂ of 0.5 mol CO₂/mol MEA, all the MEA has now reacted with the CO₂. Beyond loadings of CO₂ of 0.5 mol CO₂/mol MEA, the concentrations of the carbamate start to decrease and the concentrations of the protonated MEA increase. Beyond the loadings of CO₂ of 0.5 mol/mol MEA, bicarbonate ions were observed. The simulation results are in excellent agreement



(a)



(b)

Figure 8.1: The mole fractions of the different species MEA/MEA⁺ (squares), MEACOO⁻ (circles), CO₂ (diamonds) and HCO₃⁻ (triangles) for 30 wt. % aqueous MEA solutions at $T = 293$ K. The open symbols are results from experiments [445]. The closed symbols are the results obtained from the RxMC/CFC simulations (a) including reactions R1-R4 (b) including only reaction R5. The lines are a guide to the eye.

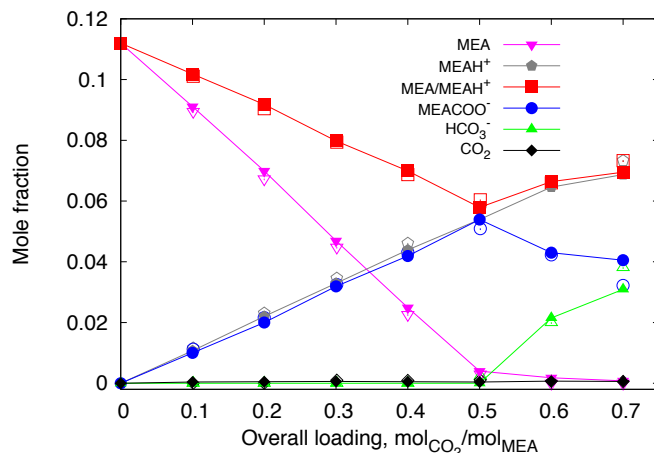
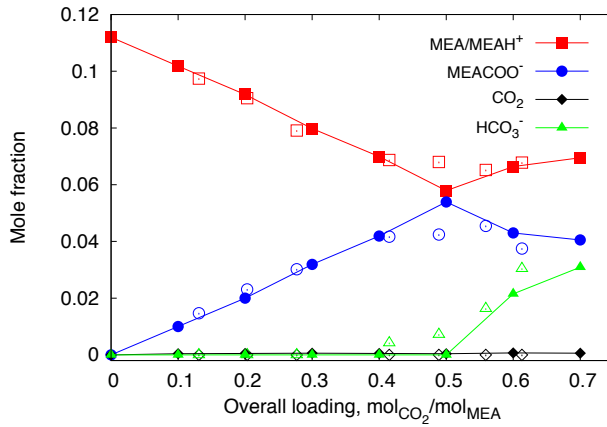
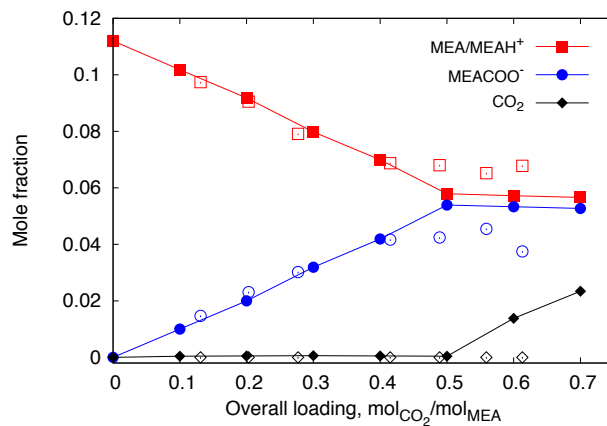


Figure 8.2: The mole fractions of the different species MEA (inverted triangles), MEAH⁺ (pentagons), MEA/MEA⁺ (squares), MEACOO⁻ (circles), CO₂ (diamonds), HCO₃⁻ (triangles) for 30 wt. % aqueous MEA solutions at $T = 293$ K. The open symbols are results from the thermodynamic model combined with experimental data [445]. The closed symbols are results obtained from the RxMC/CFC simulations including reactions R1-R4. The lines are a guide to the eye.

with the experimental results of Boettinger *et al.* [445]. Figure 8.1b shows the equilibrium concentrations of MEA, MEAH⁺, MEACOO⁻ and CO₂ for different loadings of CO₂ (mol CO₂/mol MEA) at 293 K and 1 bar when only the reaction R5 is considered. The results of equilibrium speciations obtained from simulating only reaction R5 follow the same trends for the concentrations of MEA, protonated MEA and the carbamate when we include all reactions R1-R4. Until loadings of 0.5 mol CO₂/mol MEA, the concentrations of the carbamate and the protonated MEA increase and the concentration of free MEA decreases. Beyond loadings of 0.5 mol CO₂/mol MEA, typically all the MEA has reacted with the CO₂. The concentrations of MEA, protonated MEA and MEACOO⁻ remain constant, while concentration of unreacted CO₂ increases for loadings higher than 0.5 mol CO₂/mol MEA. Boettinger *et al.* [445] also used a thermodynamic model to study the CO₂-MEA-H₂O system and obtained the individual equilibrium

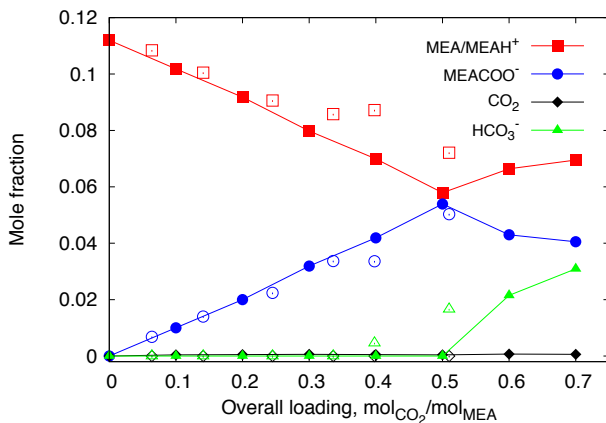


(a)

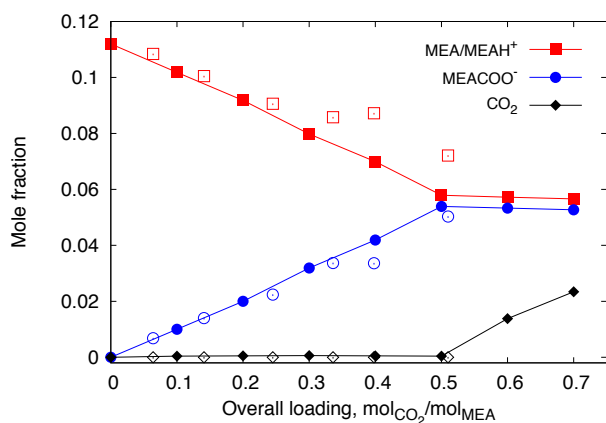


(b)

Figure 8.3: The mole fractions of the different species MEA/MEA⁺ (squares), MEACOO⁻ (circles), CO₂ (diamonds) and HCO₃⁻ (triangles) for 30 wt. % aqueous MEA solutions at $T = 333$ K. The open symbols are results from experiments [445]. The closed symbols are the results obtained from the RxMC/CFC simulations (a) including reactions R1-R4 (b) including only reaction R5. The lines are a guide to the eye.



(a)



(b)

Figure 8.4: The mole fractions of the different species MEA/MEA⁺ (squares), MEACOO⁻ (circles), CO₂ (diamonds) and HCO₃⁻ (triangles) for 30 wt. % aqueous MEA solutions at $T = 353$ K. The open symbols are results from experiments [445]. The closed symbols are the results obtained from the RxMC/CFC simulations (a) including reactions R1-R4 (b) including only reaction R5. The lines are a guide to the eye.

concentrations of the different species: MEA, MEA^+ , MEACOO^- , CO_2 , HCO_3^- . These authors have developed the model by simultaneously taking into account the chemical reactions and the vapor-liquid equilibria of the CO_2 -MEA- H_2O mixture into consideration. Figure 8.2 compares our simulation results of the individual equilibrium concentrations including MEA and MEA^+ with the results from the thermodynamic model of Boettinger *et al.* We find an excellent agreement with the model. It is important to note that we obtain individual concentrations of all the species in the mixture directly from simulations and we need not use any iterative modeling technique which requires binary interaction parameters, activity coefficients of molecular and ionic species, equilibrium coefficients, etc. as input. Figures 8.3 and 8.4 show the results of the speciations for different temperatures 333 K and 353 K at 1 bar. It can be observed that an increase in temperature does not significantly affect the equilibrium concentrations of the species. For Figure 8.4, there is no experimental data beyond loadings of 0.5 mol CO_2 /mol MEA. This is again in excellent agreement with the experimental results of Boettinger *et al.* [445] who also observe that the speciations of the CO_2 +MEA solution are only very weakly temperature dependent.

8.4 Conclusions

Monte Carlo simulations in the Reaction Ensemble using a Continuous Fractional Component method provide an excellent description of the equilibrium concentrations of all relevant species in the chemisorption of CO₂ in MEA water solutions. The simulations were performed at different temperatures and the results from simulation are in excellent agreement with the experimental results. Equilibrium concentrations of MEA, MEAH⁺, MEACOO⁻, CO₂ from Reactions R1-R4 and R5 are identical for loadings up to 0.5 mol CO₂/mol MEA and beyond that, they are different. To obtain the accurate results for loadings in excess of 0.5 mol CO₂/mol MEA, reactions R1-R4 must be included in the simulation. This RxMC/CFC methodology opens up possibilities to investigate the effect of the solvents in the reactions. Chemisorption of CO₂ in different solvents can be studied computationally to obtain the equilibrium concentrations. Only the thermodynamics need to be considered and the different transition states or reaction pathways can be ignored. This method may also investigate the effect of the chemistry of the amines, for example adding different functional groups [449, 451].

Chapter 9

CO₂/CH₄ Solubility: ILs versus Conventional Solvents

This chapter is based on the paper: M. Ramdin, S. P. Balaji, A. Torres-Knoop, D. Dubbeldam, T. W. de Loos and T. J. H. Vlugt. Solubility of Natural Gas Species in Ionic liquids and Commercial Solvents: Experiments and Monte Carlo Simulations. J. Chem. Eng. Data (2015) (in press).

9.1 Introduction

The price/performance ratio of ILs with respect to the traditional solvents is crucial for their potential application as gas sweetening agents. In this chapter, we assess the potential of ILs for CO₂ removal from natural gas. The performance of ILs in terms of CO₂ and CH₄ solubilities/selectivities are compared with respect to the commercial solvents Selexol, Purisol, Rectisol, propylene carbonate, and sulfolane. The principal ingredients in the solvents Selexol, Purisol, and Rectisol are mixtures of poly(ethylene glycol) dimethyl ethers, n-methylpyrrolidone, and methanol, respectively [9, 11]. The solubilities of the gases are compared on mole fraction, molality, and volume basis to eliminate the effect caused by the high molecular weight

of the ILS. The availability of CO₂ and in particular CH₄ solubility data in the conventional solvents is in contrast to the ILS and despite their wide application interest relatively poor. The focus here is mainly on CO₂/CH₄ solubilities and selectivities.

9.2 Results and Discussion

9.2.1 CO₂ Solubility

The solubilities of CO₂ and CH₄ are compared on mole fraction, molality, and volume (molarity) basis to remove the effect caused by the high molecular weight of ILS. In Chapter 3, we have reported CO₂ and CH₄ solubilities in 10 different ILS composed of several classes of cations and anions [8, 345, 346]. Figure 9.1 shows the mole fraction based solubility of CO₂ in several ILS in comparison with the widely used solvents Selexol, Purisol, Rectisol, propylene carbonate, and sulfolane. Clearly, some of the ILS (e.g., the alkyl-phosphonium-based ILS) have a higher CO₂ capacity on mole fraction basis than the conventional solvents like Selexol, Purisol propylene carbonate, and sulfolane. The solubility of CO₂ seems to be higher in Rectisol than the other solvents, but this is mainly due to the low operating temperature (i.e., around - 25 °C) of the process. However, a careful analysis of the data shows that the solubility increases with an increasing molecular weight of the IL [345]. Therefore, the solubility should be compared on molality or volume basis, which are more practical units from a process point of view. Figure 9.2 shows the same comparison, but now the solubility is expressed in moles per mass solvent or molality. Remarkably, the IL data tend to collapse on a universal solubility curve proposed by Carvalho and Coutinho [125]. The solubility data of CO₂ in conventional solvents do not obey the solubility curve. Clearly, the CO₂ solubility is strongly affected by the high molecular weight of the ILS. As explained in Chapter 3, the dissolution of CO₂ in ILS is a free volume effect, which effectively means that the CO₂ molecules are hosted in the cavities of the IL structure [149, 248]. It is, therefore, also interesting to compare the solubility on a volume basis. A comparison for the CO₂ solubility in ILS and

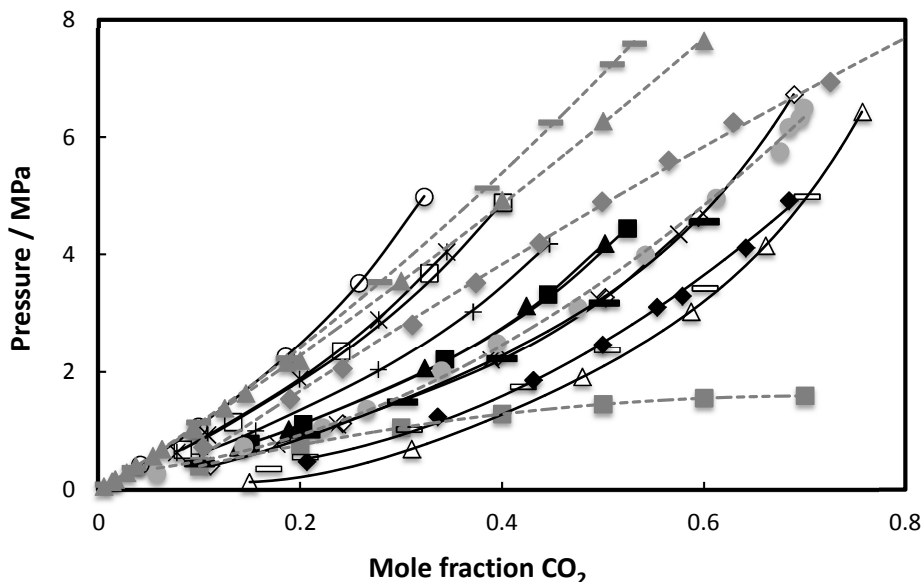


Figure 9.1: Solubility of CO_2 on mole fraction basis in ILs and commercial solvents (gray symbols). All data except for Rectisol are obtained at 313.15 K. The Rectisol process operates at low temperatures, therefore the reported data is at 248.15 K. ILs: trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate, open triangles; trihexyltetradecylphosphonium dicyanamide, open diamonds; 1-ethyl-3-methylimidazolium diethylphosphate, open squares; 1-allyl-3-methylimidazolium dicyanamide, open circles; 1-butyl-3-methylpyrrolidinium dicyanamide, stars; 1,2,3-tris(diethylamino)cyclopropenylum dicyanamide, pluses; methyltrioctylammonium bis(trifluoromethylsulfonyl)imide, black diamonds; 1-butyl-3-methyl-piperidinium bis(trifluoromethylsulfonyl)imide, black squares; 1,2,3-tris(diethylamino)cyclopropenylum bis(trifluoromethylsulfonyl)imide, crosses; triethylsulfonium bis(trifluoromethylsulfonyl)imide, black triangles; trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide, open rectangles; and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, black rectangles. Commercial solvents: Selexol (Genosorb 1753), gray circles; propylene carbonate, gray triangles; Rectisol, gray squares; Purisol, gray diamonds; and sulfolane, gray rectangles. Lines are polynomial fits to guide the eye. Data for the ILs can be found in Ramdin et al. [345] and the references cited therein. Data of the commercial solvents can be found in Refs [354, 358, 484–486].

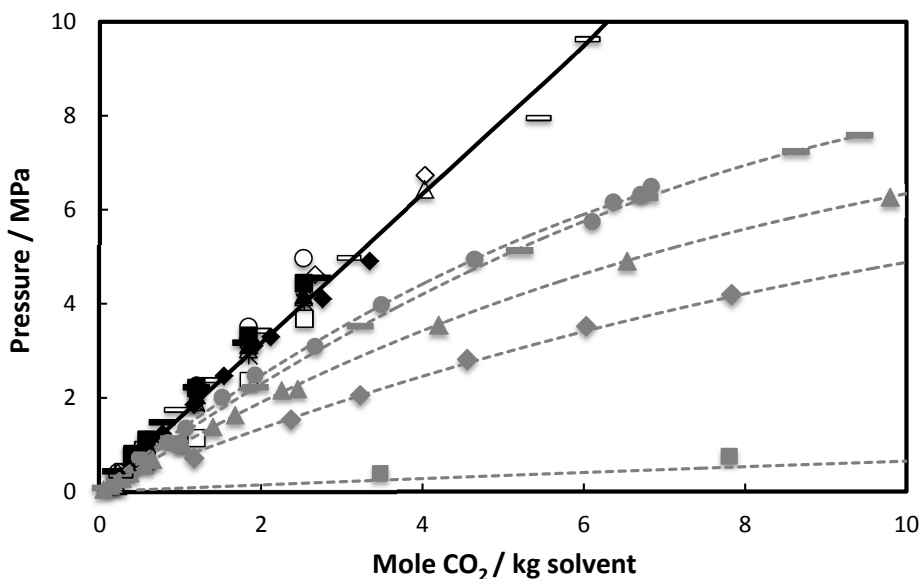


Figure 9.2: Solubility of CO₂ on molality basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 9.1. Solid line is calculated using the correlation of Carvalho and Coutinho [125] at 313.15 K and dashed lines are polynomial fits to guide the eye. All data except for Rectisol, which is at 248.15 K, are obtained at 313.15 K.

in conventional solvents on a molarity (i.e., kilomoles of gas per volume of solvent) basis is provided in Figure 9.3. The difference in solubility between the different ILs on a volume basis is also minimized. Figures 9.2 and 9.3 clearly show that conventional solvents are superior to ILs in terms of mass or volume based solubilities of CO₂.

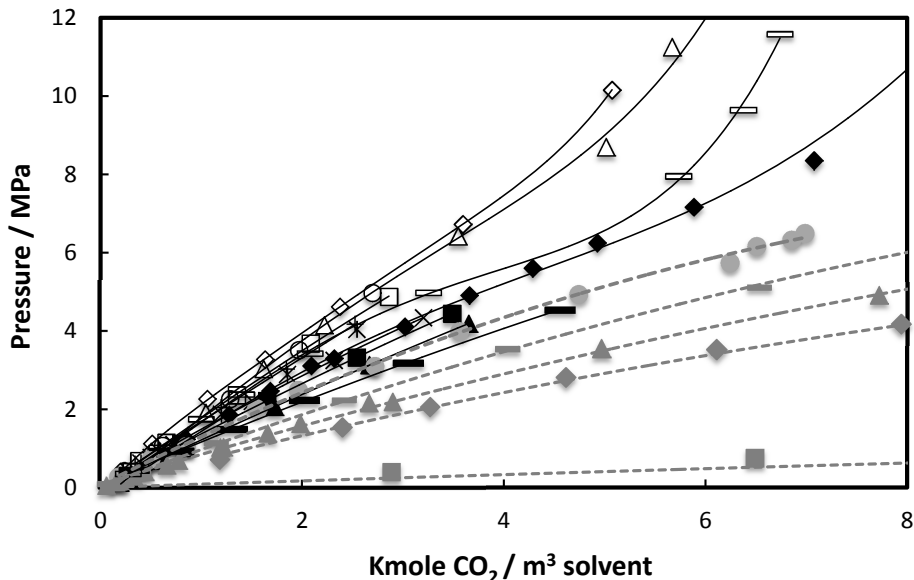


Figure 9.3: Solubility of CO_2 on volume basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 9.1. Lines are polynomial fits to guide the eye. All data except for Rectisol, which is at 248.15 K, are obtained at 313.15 K.

9.2.2 CH_4 Solubility

The mole fraction based solubility of CH_4 is shown in Figure 9.4 for several ILs and commercial solvents. The solubility trend for CH_4 is similar to that of CO_2 : the solubility of CH_4 increases also with an increasing IL molecular weight. However, the molality based solubility data of CH_4 do not collapse on a universal curve as in the case of CO_2 , see Figure 9.5. The volume based solubility trend for CH_4 is not much different from the observed solubility trend on molality basis, see Figure 9.6. Furthermore, solubility of CH_4 in conventional solvents are lower than those ILs previously characterized as promising for CO_2 capture. One exception is the 1-ethyl-

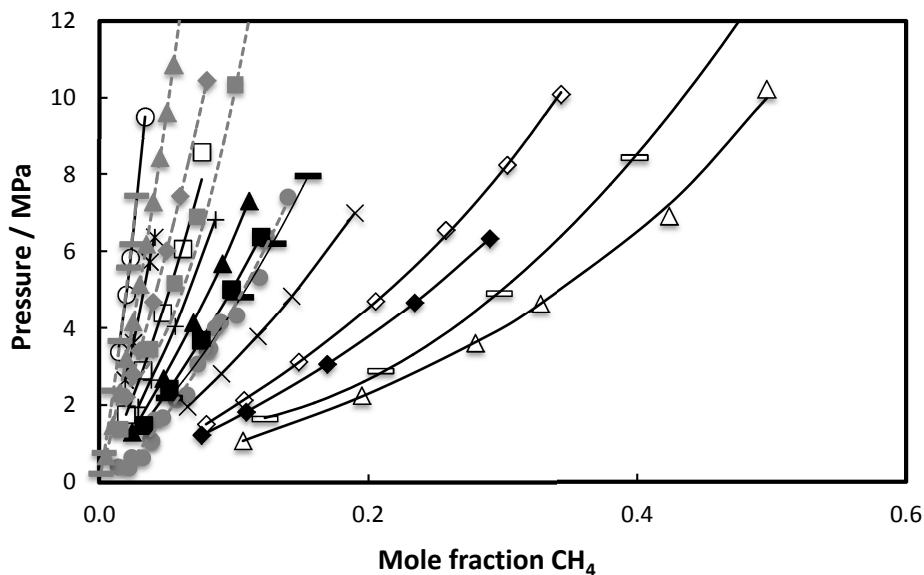


Figure 9.4: Solubility of CH₄ on mole fraction basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 9.1. Lines are polynomial fits to guide the eye. All data except for Rectisol, which is at 248.15 K, are obtained at 313.15 K. Data of commercial solvents can be found in Refs [355, 358, 362, 487, 488].

3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [emim][FAP] IL, which has a comparable CO₂ and CH₄ solubility as Selexol even on a mass or volume scale. A suitable solvent for natural gas sweetening should not only have a high CO₂ solubility, but at the same time a low CH₄ solubility to avoid valuable product losses.

9.2.3 Selectivity

As mentioned earlier, not the solubility, but rather the selectivity is the key parameter for judging the separation performance of an absorption process. In Chapter 3, we showed that the ideal CO₂/CH₄ selectivity

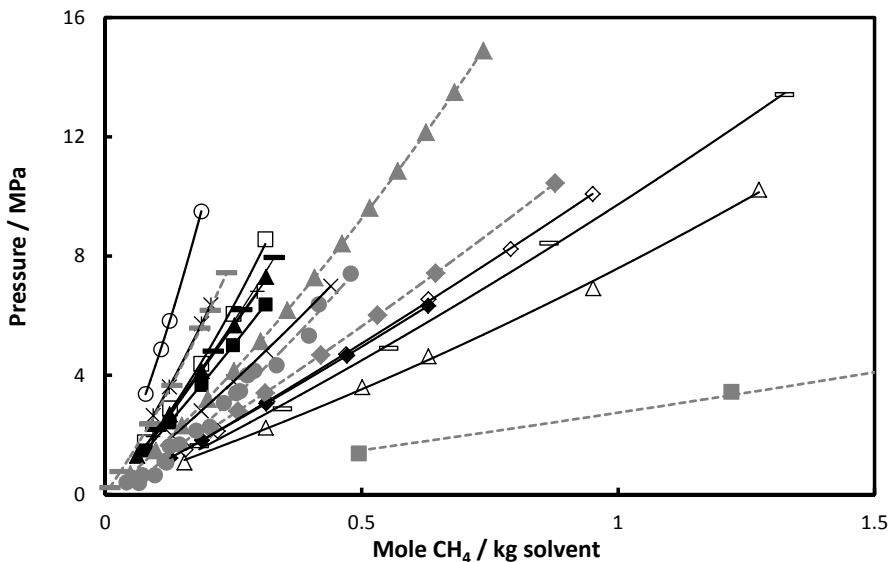


Figure 9.5: Solubility of CH_4 on molality basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 9.1. Lines are polynomial fits to guide the eye. All data except for Rectisol, which is at 248.15 K, are obtained at 313.15 K.

in ILs is comparable to that of commercial solvents like Selexol, Purisol, Rectisol, propylene carbonate, and sulfolane [345]. In Chapters 4 and 6, we showed that the ideal selectivity is approximately the same as the real selectivity. The ideal CO_2/CH_4 selectivity in ILs and conventional solvents was also shown to decrease dramatically with increasing temperature [345]. Therefore, the process should operate at low temperature to have a high CO_2/CH_4 selectivity. The viscosity of existing ILs at low temperatures are an order of magnitude higher than that of conventional solvents, which forms a serious barrier for their application in the natural gas process.

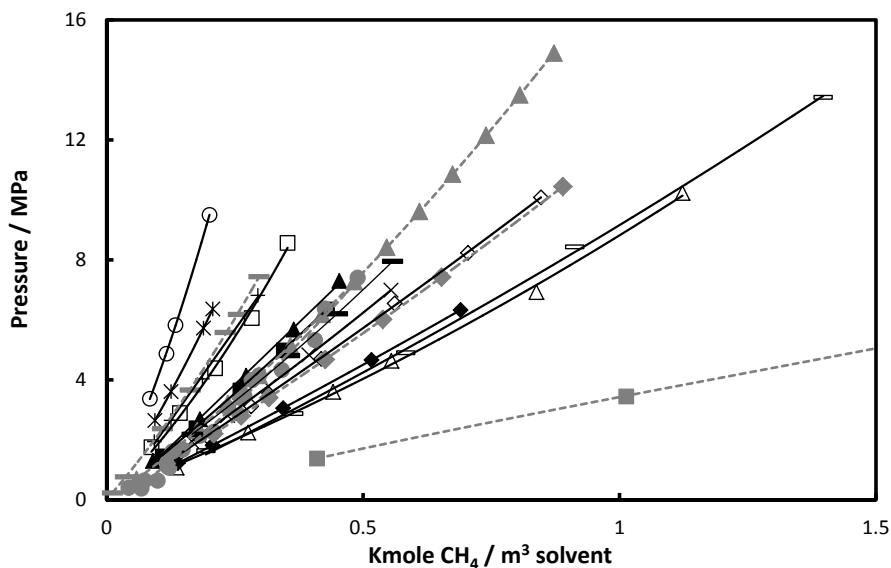


Figure 9.6: Solubility of CH₄ on volume basis in ILs and commercial solvents (gray symbols). Symbols have the same meaning as in Figure 9.1. Lines are polynomial fits to guide the eye. All data except for Rectisol, which is at 248.15 K, are obtained at 313.15 K.

9.3 Conclusions

A detailed comparison for the solubility/selectivity of carbon dioxide (CO₂) and methane (CH₄) in ionic liquids (ILs) and commercial solvents Selexol, Purisol, Rectisol, propylene carbonate, and sulfolane is presented. The solubilities are compared on mole fraction, molality, and volume basis to avoid the effect caused by the high molecular weight of ILs. Conventional solvents are superior to ILs when CO₂ and CH₄ solubilities are compared on a mass or volume basis. Although the CO₂/CH₄ selectivity in ILs are similar to that of commercial solvents, the high price and viscosity of ILs may limit their application in the natural gas sweetening process.

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Summary

Carbon dioxide (CO_2) is considered the main greenhouse gas, and is inevitably produced in large quantities by fossil-fuel based industries. Therefore, it is essential to limit CO_2 emissions into the atmosphere. One of the tools to achieve this goal is carbon dioxide capture and storage (CCS). However, due to the extremely large scale of the problem, the capture part of the CCS process turns out to be very challenging in terms of energy efficiency and cost. The currently used amine-based solvents for CO_2 capture, at post-combustion conditions, have several drawbacks including their volatility, corrosivity, and high regeneration cost. CO_2 is captured by a chemical reaction with the amines, which requires a huge amount of heat to release the CO_2 from the solvent. This is the main motivation for research on energy efficient processes and the search for environment friendly materials for CO_2 capture. An alternative for the post-combustion process is the pre-combustion process, which is associated with the integrated gasification combined cycle (IGCC). In this process, a fuel is gasified to produce syngas, which is subsequently shifted in a water-gas-shift reactor to produce a mixture containing predominantly hydrogen (H_2) and CO_2 . After removing CO_2 , the hydrogen can be used in several applications. The pre-combustion process operates at high pressures, which allows the use of physical sorbents for CO_2 removal.

CO_2 capture is not only relevant from an environmental perspective, but it has a major application in the natural gas sweetening process. Natural gas is typically contaminated with several impurities including the sour gases CO_2 and hydrogen sulfide (H_2S). These sour gases need to be

removed to avoid technological problems during transportation and to meet customer specifications. CO₂ is typically removed in an absorber-stripper configuration utilizing a physical solvent, a chemical solvent, or a mixture of both solvent types (hybrid solvent) depending on the type and concentration of the impurities. Despite the inherent high pressure of the sweetening process, which is favorable for physical absorption purposes, the majority of the units in the field utilize chemical solvents (e.g., monoethanolamine (MEA)). The use of physical solvents (e.g., Purisol, Rectisol, Selexol, etc.) is not uncommon in the natural gas industry and is in fact preferred over chemical solvents at high acid gas partial pressures.

In this thesis, we investigate the potential of ionic liquids (ILs), which are salts with melting points lower than 100 °C, for CO₂ capture at pre-combustion and natural gas sweetening conditions. ILs exhibit very interesting properties like a very low vapor pressure, a high thermal and chemical stability, a high tunability, a low flammability, and a relatively high acid gas capacities. These properties of ILs can be used to overcome some of the problems associated with the conventional solvents. Only physical ILs are considered here, which are suitable for the high pressure pre-combustion and the natural gas sweetening process. Experiments have been used to measure the solubility of natural gas components in many different kinds of ILs. In addition, molecular simulations have been used to predict the solubility of gases in ILs at pre-combustion and natural gas sweetening conditions. A detailed comparison of the performance of ILs in terms of gas solubilities and selectivities with respect to conventional solvents is provided.

In Chapter 2, a detailed overview of the recent achievements and difficulties that has been encountered in finding a suitable ionic liquid for CO₂ capture from flue-gas streams is presented. A major part of this review focuses on experimental data of CO₂ solubility, selectivity and diffusivity in different ionic liquids. The effect of anions, cations and functional groups on the CO₂ solubility, biodegradability and toxicity of the ionic liquids are highlighted. Recent developments on task-specific ionic liquids and supported ionic liquid membranes are also discussed. Scarcely available results of molecular simulations, which is a valuable tool in designing and evaluating ionic liquids, are also reviewed.

In Chapter 3, the potential of ILs for natural gas sweetening was investigated. A synthetic method has been used to measure the solubility of CO₂ and CH₄ in many different kinds of ILs. The solubility data has been reduced by calculating the Henry constants of CO₂ and CH₄ in all the ILs, from which the ideal CO₂/CH₄ selectivities are obtained (i.e., from the ratio of the Henry constants). The ideal CO₂/CH₄ selectivities of the investigated ILs are compared with that of the conventional solvents like Selexol, Purisol, Rectisol, Fluor Solvent, and sulfolane. The ideal CO₂/CH₄ selectivities in ILs are similar to that of the conventional solvents. The ideal CO₂/CH₄ selectivity decreases with increasing temperature and increasing IL molecular weight. Therefore, a low molecular weight IL should be used if a high selectivity is desired.

In Chapter 4, the solubility of CO₂/CH₄ gas mixtures in ILs has been measured experimentally. The aim was to investigate the effect of the presence of one gas (e.g., CO₂) on the solubility of the other gas (e.g., CH₄) when both are simultaneously being dissolved in a single IL. In other words, the objective was to obtain real CO₂/CH₄ selectivities from the VLE data. It was not possible to directly obtain the CO₂/CH₄ selectivities from the VLE data, since only bubble-point pressures of the mixtures were measured. Sampling of the phases was not possible in the experiments and thus the compositions of the phases required for calculating the real selectivity were unknown. The Peng-Robinson (PR) equation of state (EoS) was used to calculate the gas phase compositions. Under the investigated conditions, the real CO₂/CH₄ selectivities were approximately the same as the ideal CO₂/CH₄ selectivities.

In Chapter 5, the Continuous Fractional Component Monte Carlo method (CFCMC) in the osmotic ensemble have been used to predict the solubility of the natural gas components CO₂, CH₄, C₂H₆, and SO₂ in ILs, and Selexol, which is a mixture of poly(ethylene glycol) dimethyl ethers (PEGDME). The following gas solubility trend is observed in the experiments and simulations for all the solvents: SO₂ > CO₂ > C₂H₆ > CH₄. The solubility of SO₂ is substantially higher than that of CO₂, which indicates that SO₂ can be removed selectively in the presence of CO₂. However, the PEGDME solvents are more selective towards SO₂ than the ILs. Furthermore, the

solubility of CH_4 and C_2H_6 are higher in PEGDME than in the ILs, which is a well-known drawback of these Selexol solvents. Overall, the solubility data obtained from the MC simulations were in very good agreement with available experimental data.

In Chapter 6, CFMCM simulations in the osmotic ensemble were used to compute the bubble-points of CO_2/CH_4 gas mixtures in ILs. Standard ensembles (e.g., Gibbs, osmotic, etc.) commonly used for phase equilibria calculations cannot be applied directly to compute bubble-point pressures. 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. A method is outlined where 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 effect of temperature, pressure, and gas phase composition on the real CO_2/CH_4 selectivity was investigated. The computed real selectivities were 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 was only marginally different from the ideal selectivity, which was defined as the ratio of the Henry constants.

In Chapter 7, the potential of ILs for CO_2 capture at pre-combustion conditions was investigated. Monte Carlo simulations were used to compute the solubility of the pure gases CO_2 , CH_4 , CO , H_2 , N_2 and H_2S in the IL [bmim][Tf₂N]. Simulations in the osmotic ensemble were performed to compute absorption isotherms at a temperature of 333.15 K using the versatile Continuous Fractional Component Monte Carlo (CFMCM) method. The predicted gas solubilities and Henry constants were in good agreement with the experimental data. The Monte Carlo simulations correctly predict the observed solubility trend, which obeys the following order: $\text{H}_2\text{S} > \text{CO}_2 > \text{CH}_4 > \text{CO} > \text{N}_2 > \text{H}_2$. Relevant separation selectivities for the pre-combustion process were calculated from the pure gas Henry constants and a comparison with experimental data was provided. The results indicated

that [bmim][Tf₂N] can effectively capture CO₂ at pre-combustion conditions, but the syngas should be desulfurized prior to CO₂ removal, because H₂S was three times more soluble than CO₂.

In Chapter 8, a novel Monte Carlo method in the Reaction Ensemble using the Continuous Fractional Component technique (RxMC/CFC) has been developed to study the reactions of CO₂ with aqueous monoethanolamine (MEA). The RxMC/CFC method was used to compute the equilibrium speciation of all relevant species formed during the chemisorption process of CO₂ with aqueous MEA solutions. The computed equilibrium speciation results were in excellent agreement with available experimental data. The RxMC/CFC method can be used to screen and design chemical solvents for CO₂ capture.

In Chapter 9, the performance of ILs in terms of CO₂/CH₄ solubilities and selectivities are compared with respect to the commercial solvents Selsol, Purisol, Rectisol, propylene carbonate, and sulfolane. The solubilities of the gases were compared on mole fraction, molality, and volume basis to demonstrate the effect caused by the high molecular weight of the ILs. The results indicate that conventional solvents are superior to ILs when CO₂ and CH₄ solubilities are compared on a mass or volume basis. Although the CO₂/CH₄ selectivity in ILs are similar to that of commercial solvents, the high price and viscosity of ILs may limit their application in the pre-combustion and natural gas sweetening process.

Samenvatting

Koolstofdioxide (CO_2) is het belangrijkste broeikasgas dat in grote hoeveelheden wordt geproduceerd door de industrie. Het is daarom noodzakelijk om CO_2 emissies te beperken. Een methode om dit te bereiken is door middel van koolstofdioxide opvang en opslag (CCS). Door de extreem grote schaal van het probleem is het CCS proces echter zeer uitdagend in termen van energie efficiëntie en kosten. De momenteel gebruikte amines voor CO_2 opvang bij post-combustion condities hebben meerdere nadelen, zoals een hoge volatiliteit, corrosiviteit en regeneratie kosten. CO_2 wordt opgevangen door middel van een chemische reactie met de amines. Een grote hoeveelheid energie is vereist om de gebonden CO_2 weer los te krijgen. Dit is de voornaamste reden voor onderzoek naar energie-efficiënte processen en milieuvriendelijke materialen voor CO_2 opvang. Een alternatief voor het post-combustion proces is het pre-combustion proces welke geassocieerd wordt met een zogenaamde "integrated gasification combined cycle". In dit proces wordt synthese gas geproduceerd door een brandstof te vergassen. Vervolgens wordt het synthese gas in een water-gas-shift reactor geconverteerd naar een mengsel van overwegend waterstof (H_2) en CO_2 . Na het verwijderen van CO_2 kan waterstof voor verschillende doeleinden gebruikt worden. Fysische oplosmiddelen kunnen gebruikt worden voor CO_2 opvang, omdat het pre-combustion proces bij hoge drukken opereert.

CO_2 opvang is niet alleen interessant vanuit een milieuoogpunt, maar het heeft ook een belangrijke toepassing in het zuiveringsproces van aardgas. Aardgas is doorgaans verontreinigd met verschillende onzuiverheden waaronder CO_2 en waterstofsulfide (H_2S). Deze gassen moeten verwijderd worden

om technologische problemen tijdens gastransport te voorkomen en om aan de specificatie van de klant te kunnen voldoen. CO₂ wordt, afhankelijk van het type en concentratie van de onzuiverheden, in een absorber-stripper configuratie door middel van een fysisch oplosmiddel, een chemische oplosmiddel, of combinatie van beide typen verwijderd. In de praktijk worden vaak chemische oplosmiddelen zoals monoethanolamine (MEA) gebruikt voor CO₂ opvang bij atmosferische druk, terwijl de hoge druk van het zuiveringsproces gunstig is voor CO₂ absorptie door middel van fysische oplosmiddelen. Het gebruik van fysische oplosmiddelen zoals Purisol, Rectisol, Selexol en dergelijke is gebruikelijk in de aardgas industrie. Fysische oplosmiddelen worden geprefereerd boven chemische oplosmiddelen indien de partiele drukken van de zwavelhoudende componenten en CO₂ hoog zijn.

In dit proefschrift wordt de potentie van ionic liquids (ILs) voor CO₂ opvang bij pre-combustion en aardgas zuivering condities onderzocht. ILs zijn zouten met een smeltpunt lager dan 100 °C en hebben interessante eigenschappen zoals een verwaarloosbare dampspanning, een hoge thermische en chemische stabiliteit, een hoge mate van afstembaarheid, een lage ontvlambaarheid, en een relatief hoge capaciteit voor zure gassen. Deze eigenschappen van ILs kunnen gebruikt worden om de nadelen van conventionele oplosmiddelen te vermijden. We concentreren voornamelijk op fysische oplosmiddelen welke geschikt zijn voor het hoge druk pre-combustion proces en het aardgas zuiveringproces. Experimenten zijn gebruikt om de oplosbaarheden van componenten in aardgas in verschillende ILs te meten. Daarnaast zijn moleculaire simulaties gebruikt om de oplosbaarheden van gassen in ILs te voorspellen. We vergelijken gas oplosbaarheden en selectiviteiten in ILs en conventionele oplosmiddelen.

In Hoofdstuk 2 presenteren we een gedetailleerd overzicht van recente onderzoek over het vinden van een geschikte IL voor CO₂ opvang. Een groot deel van dit hoofdstuk concentreert zich op experimentele data van CO₂ oplosbaarheid, selectiviteit, en diffusie in verschillende ILs. Het effect van anionen, cationen, en functionele groepen op de oplosbaarheid van CO₂, de biologische afbreekbaarheid en toxiciteit van ILs worden besproken. Recente ontwikkelingen op het gebied van 'task-specific' ILs en 'supported IL membranes' worden ook besproken. Resultaten van moleculaire simulaties,

welke een waardevol instrument is voor het ontwerpen en evalueren van ILs, worden kort besproken.

In Hoofdstuk 3 is de potentie van ILs voor aardgas zuivering onderzocht. Een synthetische methode is gebruikt om de oplosbaarheden van CO_2 en CH_4 in verschillende ILs te meten. De Henry coëfficiënten van CO_2 en CH_4 in alle onderzochte ILs zijn gemeten en daaruit zijn ideale CO_2/CH_4 selectiviteiten bepaald. De ideale CO_2/CH_4 selectiviteiten in ILs zijn vergeleken met die van conventionele oplosmiddelen zoals Selexol, Purisol, Rectisol, Fluor Solvent, en sulfolane. De ideale CO_2/CH_4 selectiviteiten in ILs zijn vergelijkbaar met die van de conventionele oplosmiddelen. De ideale CO_2/CH_4 selectiviteit neemt af bij toenemende temperatuur en IL moleculair gewicht. Een IL met een laag moleculair gewicht moet gebruikt worden als een hoge CO_2/CH_4 selectiviteit gewenst is.

In Hoofdstuk 4 presenteren we experimentele data betreffende oplosbaarheden van CO_2/CH_4 gasmengsels in ILs. Het doel was om het effect van de aanwezigheid van één gas op de oplosbaarheid van een ander gas te onderzoeken. In andere woorden, we waren geïnteresseerd in het verkrijgen van de werkelijke CO_2/CH_4 selectiviteit. Het was niet mogelijk om direct CO_2/CH_4 selectiviteiten uit de VLE data te bepalen, omdat alleen bubelpunten van de mengsels konden worden gemeten. De samenstelling van de gas- en vloeistof fase bij evenwicht is vereist voor het bepalen van de echte CO_2/CH_4 selectiviteit, maar het bemonsteren van de fasen is helaas niet mogelijk in de experimenten. De Peng-Robinson (PR) equation of state (EoS) is gebruikt om de samenstelling van het gas te bepalen. De echte CO_2/CH_4 selectiviteit blijkt ongeveer hetzelfde te zijn als de ideale CO_2/CH_4 .

In Hoofdstuk 5 hebben we de Continuous Fractional Component Monte Carlo (CFCMC) methode in het osmotische ensemble gebruikt om de oplosbaarheden van aardgas componenten CO_2 , CH_4 , C_2H_6 , en SO_2 in ILs en Selexol te voorspellen. De experimentele en simulatie resultaten voor de oplosbaarheid van de gassen laat de volgende trend zien: $\text{SO}_2 > \text{CO}_2 > \text{C}_2\text{H}_6 > \text{CH}_4$. Het is dus mogelijk om SO_2 in aanwezigheid van CO_2 selectief te verwijderen, omdat SO_2 een veel hogere oplosbaarheid heeft dan CO_2 . De resultaten laten ook zien dat Selexol selectiever is voor SO_2 dan de ILs. Het

nadeel van Selexol ten opzichte van de ILs is dat de oplosbaarheid van CH_4 en C_2H_6 ook hoger zijn. In het algemeen zijn de oplosbaarheden verkregen uit Monte Carlo simulaties in goede overeenkomst met de experimentele data.

In Hoofdstuk 6 hebben we de CFMCM methode in de osmotische ensemble gebruikt om bubbelpunten van CO_2/CH_4 gasmengsels in ILs uit te rekenen. De ensembles die standaard gebruikt worden om fase-evenwichten te voorspellen (b.v., Gibbs, osmotisch, enz.) kunnen niet direct toegepast worden. Deze ensembles vereisen de specificatie van de druk en/of de gassamenstelling welke bij voorbaat onbekend zijn en in de simulaties uitgerekend moeten worden. We presenteren een nieuwe methode waarbij de gassamenstelling iteratief aan de hand van de vloeistofsamenstelling kan worden bepaald. Hiervoor zijn twee simulaties in het osmotische ensemble nodig bij dezelfde druk, maar bij verschillende samenstellingen van de gasfase. De samenstelling van het gas dat in evenwicht is met de experimentele vloeistofsamenstelling wordt gevonden met een eerste-orde Taylor expansie. Het effect van temperatuur, druk, en gassamenstelling op de echte CO_2/CH_4 selectiviteit is onderzocht. De echte selectiviteiten verkregen uit de simulaties zijn vergeleken met de experimentele selectiviteiten. De echte CO_2/CH_4 selectiviteit neemt af bij toenemende temperatuur en druk, terwijl de gassamenstelling een gering effect heeft. De ideale selectiviteit, gedefinieerd als de ratio van de Henry constanten, is bij benadering gelijk aan de echte selectiviteit.

In Hoofdstuk 7 onderzoeken we de potentie van ILs voor CO_2 opvang bij pre-combustion condities. Monte Carlo simulaties in het osmotische ensemble bij een temperatuur van 333.15 K zijn gebruikt om de oplosbaarheden van de volgende gassen in de IL $[\text{bmim}][\text{Tf}_2\text{N}]$ uit te rekenen: CO_2 , CH_4 , CO , H_2 , N_2 , en H_2S . De voorspelde gas oplosbaarheden en Henry coëfficiënten zijn in goede overeenstemming met de experimentele data. De Monte Carlo simulaties voorspellen de volgende trend voor de oplosbaarheden (welke in overeenstemming is met experimenten): $\text{H}_2\text{S} > \text{CO}_2 > \text{CH}_4 > \text{CO} > \text{N}_2 > \text{H}_2$. De Henry coëfficiënten zijn gebruikt om relevante selectiviteiten voor het pre-combustion proces te bepalen. De resultaten tonen aan dat $[\text{bmim}][\text{Tf}_2\text{N}]$ potentieel gebruikt kan voor CO_2 opvang bij pre-combustion

condities. Echter, het synthese gas dient eerst ontzwaveld te worden, omdat H_2S drie keer beter oplost dan CO_2 .

In Hoofdstuk 8 hebben we een nieuwe Monte Carlo methode in het 'Reaction Ensemble' ontwikkeld die gebruikt maakt van de CFMC techniek (RxMC/CFC). Deze techniek is toegepast om de reacties tussen CO_2 en MEA in een waterige oplossing te bestuderen. De RxMC/CFC methode is gebruikt om de 'equilibrium speciation' van de relevante componenten die gevormd worden tijdens het chemisorptie proces van CO_2 met MEA te bestuderen. De uitgerekenende 'speciation' resultaten zijn in excellente overeenstemming met beschikbare experimentele data. De RxMC/CFC methode kan gebruikt worden om nieuwe chemische oplosmiddelen voor CO_2 opvang te ontwikkelen.

In Hoofdstuk 9 vergelijken we de CO_2/CH_4 oplosbaarheden en selectiviteiten in ILs en de commerciële oplosmiddelen Selexol, Purisol, Rectisol, propylene carbonate, en sulfolane. De oplosbaarheden van de gassen zijn op massa basis, volume basis, en mol basis vergeleken om het effect van de hoge moleculaire massa van ILs te demonstreren. De resultaten tonen aan dat conventionele oplosmiddelen zoals Selexol, Purisol en Rectisol superieur zijn ten opzichte van bestaande ionic liquids in termen van gasoplosbaarheid en prijs. De CO_2/CH_4 selectiviteiten in ILs zijn vergelijkbaar met die van de commerciële oplosmiddelen, maar de hoge prijs en viscositeit van ILs zal de toepassing ervan in de industrie beperken.

Curriculum Vitae

Mahinder Ramdin was born on the 31th of December 1985 in Nickerie, Suriname. At an age of 16 he moved with his family to the Netherlands. He obtained his B.Sc degree in Chemical Engineering in 2008 from the Hogeschool Rotterdam. Subsequently, he started a M.Sc. program at Delft University of Technology and obtained his M.Sc. degree in Chemical Engineering in 2010. At the end of 2010, he started a Ph.D. project in the Engineering Thermodynamics group headed by Prof.dr.ir. Thijs Vlugt at Delft University of Technology. During the project, which concentrated on CO₂ capture with ionic liquids, he was supervised by Prof.dr.ir. Thijs Vlugt and Dr.ir. Theo de Loos. He spent a vast majority of the time in the Thermolab to obtain high pressure solubility data of several gases in many different ionic liquids. In the last stage of his Ph.D. project, he performed Monte Carlo simulations to compute gas solubilities in physical solvents including ionic liquids. The experimental and simulation results are presented in this dissertation.

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