CO\textsubscript{2} capture using monoethanolamine solutions: Development and validation of a process model based on the SAFT-VR equation of state

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A thesis submitted for the degree of
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May 2013
Declaration

I hereby declare that all the material in this dissertation is own and has been otherwise appropriately referenced.

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Abstract

The development of a predictive model for an absorber-desorber process for the separation of carbon dioxide (CO$_2$) from a gas stream using an aqueous alkanolamine solution as a solvent is presented. Post-combustion carbon dioxide capture by absorption with aqueous amine solvents is likely to play an important role in climate change mitigation, by helping to reduce a significant fraction of CO$_2$ emissions from fossil fuel power plants. There are, however, a number of concerns with the large scale deployment of this technology, including energy requirements, solvent degradation and the environmental and health impact resulting from a potential loss of solvent and solvent degradation products. Modelling studies can play an invaluable and complementary role in addressing some of these issues, including the choice of solvent and operating conditions that yield optimal performance. The model presented here incorporates state-of-the-art SAFT-VR thermodynamics into a rate-based process model. A characteristic of the proposed approach is that all the reactions are treated within a thermodynamic description, assuming chemical equilibrium throughout. This greatly reduces the amount of experimental data required to model the behaviour of the absorber. Furthermore, in contrast with many treatments of reactive systems of this type, no enhancement factor is used in the process model. The absorber-desorber process model is implemented in the gPROMS software platform and validated using published pilot plant experimental data for the removal of CO$_2$ from an air and CO$_2$ stream using monoethanolamine (MEA) solutions. A scaling of the diffusivity in the liquid phase, that is found to be transferable to different operating conditions, is proposed. Reliable predictions are obtained for the temperature and composition profiles in the gas and liquid phases, including a good description of the temperature bulge which sometimes appears along the height of the absorber column. The same transferable model is used to describe both the absorber and the desorber columns. The influence of key parameters of the model for different operating conditions is assessed through a sensitivity analysis. The model developed in this study is applied to simulate a complete amine-based
carbon capture absorber-desorber process. Given the relatively simple modelling of the solvent/CO$_2$ interactions, in which the reactions are treated implicitly through a physical approach, the proposed model lends itself well to the investigation of other solvents.
Acknowledgements

The work presented in this thesis would not have been possible hadn’t it been for the contribution of a number of people. First and foremost, I would like to express my sincer gratitude to my supervisors Professors Claire Adjiman, Amparo Galindo and George Jackson for their academic support and personal involvement during this PhD. Thank you for sharing with me your knowledge in process modelling and thermodynamic.

Thanks to the members of the MSE group for the fun and the help during these years, in particular Niall, Frances, Tom, Carlos, Javier, Alex, Vassilis, Jens, Andrew, Nina, Roochi, Zara, Lara, Olga, Hendrick.

Thanks to my Father, Mother, Brother and Sisters for the regular support and the wise guidance.

I am grateful to Nicolas, Quentin, Pierre, Philippe, Frank, Benjamin, and Paul for sharing their advice and experience.

Thanks to you Sophie for your presence, you are of great importance to me.
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Chapter 1

Introduction

1.1 Motivation for CO₂ capture

Carbon dioxide (CO₂) emissions are generally considered to play a major role in climate change and particularly in global warming. Fossil fuel power plants are the major fixed point-source emitters of CO₂. In response to global warming, the Roadmap for 2050 set by the European Commission in 2011 suggested reducing greenhouse gas emissions in Europe by 25% by 2020 and by 80% by 2050 (European Union, 2011). In this context, the development of carbon capture systems must be addressed in the short term, and amine-based post-combustion capture processes are seen as the most promising near-term technology in terms of development and applicability. In this technique, absorption is achieved both physically and chemically, so that significant CO₂ removal can take place even at low partial pressures of the greenhouse gas. The major advantage of this technology is that it can be retrofitted to existing power plants (e.g., see Rao and Rubin (2002); Figueroa et al. (2008); Mac Dowell et al. (2010a)).

There are however several concerns with this technology, in particular the large energy requirements associated with solvent regeneration, the degradation of the solvent, which is exacerbated by the presence of oxygen in the flue gas, and the environmental and health
impact that may result from solvent losses and solvent degradation products. These issues are particularly important because of the scale of deployment required to have a meaningful impact on CO$_2$ emissions. There are significant experimental programmes to identify new solvents (Paul et al., 2008; Mangalapally et al., 2009; Bardow et al., 2010; Barzagli et al., 2012; Mangalapally et al., 2012; Salkuyeh and Mofarahi, 2012) and several pilot plant studies are under way (Tontiwachwuthikul et al., 1992; Dugas, 2006; Tobiesen et al., 2007; Gabrielsen et al., 2007; Godini and Mowla, 2008; Cottrell et al., 2009; Notz et al., 2012). Modelling studies can play an invaluable and complementary role in addressing some of these issues, including the choice of solvent and operating conditions that yield optimal performance.

A key challenge in realising the benefits of a model-based approach is the development of models that can accurately predict the behaviour of the process under different conditions and for a range of solvents. This is particularly difficult in CO$_2$ absorption due to the complex reaction chemistry that occurs and the large number of ionic species present in the process. For example, in the case of absorption of CO$_2$ using the most common solvent, an aqueous solution of monoethanolamine (MEA, HOC$_2$H$_4$NH$_2$), the key reactions, excluding the speciation of water, are (Astarita, 1967; Hikita et al., 1977; Danckwerts, 1979; Laddha and Danckwerts, 1981; Astarita et al., 1983; Penny and Ritter, 1983; Blauwhoff et al., 1984):

\[
\begin{align*}
\text{CO}_2 + \text{HOC}_2\text{H}_4\text{NH}_2 & \rightleftharpoons \text{HOC}_2\text{H}_4\text{NH}_3^+\text{CO}_2^- \quad (1.1) \\
\text{HOC}_2\text{H}_4\text{NH}_3^+\text{CO}_2^- + \text{HOC}_2\text{H}_4\text{NH}_2 & \rightleftharpoons \text{HOC}_2\text{H}_4\text{NHCO}_2^- + \text{HOC}_2\text{H}_4\text{NH}_3^+ \quad (1.2) \\
\text{HOC}_2\text{H}_4\text{NH}_3^+\text{CO}_2^- + \text{H}_2\text{O} & \rightleftharpoons \text{HOC}_2\text{H}_4\text{NHCO}_2^- + \text{H}_3\text{O}^+ \quad (1.3) \\
\text{HOC}_2\text{H}_4\text{NHCO}_2^- + \text{H}_2\text{O} & \rightleftharpoons \text{HOC}_2\text{H}_4\text{NH}_2 + \text{HCO}_3^- \quad (1.4) \\
\text{HOC}_2\text{H}_4\text{NH}_3^+\text{CO}_2^- + \text{H}_2\text{O} & \rightleftharpoons \text{HOC}_2\text{H}_4\text{NH}_3^+ + \text{HCO}_3^- \quad (1.5) \\
\text{CO}_2 + \text{OH}^- & \rightleftharpoons \text{HCO}_3^- \quad (1.6) \\
\text{HOC}_2\text{H}_4\text{NH}_3^+ + \text{H}_2\text{O} & \rightleftharpoons \text{HOC}_2\text{H}_4\text{NH}_2 + \text{H}_3\text{O}^+ \quad (1.7) \\
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad (1.8)
\end{align*}
\]
1. Introduction

The main reaction products are therefore the zwitterion (HOC$_2$H$_4$NH$_2^+$CO$_2^-$), the carbamate (HOC$_2$H$_4$NHCO$_2^-$ + HOC$_2$H$_4$NH$_3^+$), and bicarbonate (HCO$_3^-$). The elucidation and characterization of the speciation, reaction mechanism, equilibria and kinetics for mixtures relevant to CO$_2$ chemisorption typically requires extensive experimental investigations before a detailed model can be built. This presents a significant barrier to the rapid development of improved processes for carbon capture. There is a need to develop models that offer reasonable predictive capabilities without extensive reliance on thermodynamic and kinetic data, and that can provide quantitative insight into the behaviour of the process.

1.2 Objectives of this work

The aim of this work is to develop a reliable and predictive model of an amine based CO$_2$ absorber-desorber process, capable of screening a wide range of operating conditions, using different solvents in order to gain a good understanding of the process and reduce its energy penalty.

To realise this objective, a single thermodynamic approach is used to mediate both the phase and the chemical equilibrium, limiting the reliance on experimental data. An extensive validation of the proposed models of the different unit operations constituting the CO$_2$ capture process is performed using different pilot plant data (Tontiwachwuthikul et al., 1992; Tobiesen et al., 2008).

Insights on the behaviour of the process under different operating conditions and on the relative importance of the different model parameters are obtained via a sensitivity analysis.
1.3 Outline of thesis

This thesis is organised as follows:

- In chapter 2, a brief description of some of the most advanced CO$_2$ techniques are presented, comparing their characteristics and performances. The carbon capture processes using amine based solvent are presented in more detail. The different techniques to model these processes are described and compared. Different thermodynamic theories and mass transfer models are presented.

- Chapter 3 first focuses on the evolution of thermodynamic theories applicable to carbon capture. Then the SAFT-VR equation of state used in this thesis is introduced and the molecular model for the mixtures of MEA, CO$_2$, H$_2$O and N$_2$ is presented in detail.

- In chapter 4, a predictive model of a rate-based absorber column incorporating the SAFT-VR model is described. Due to the radically different approach followed in this study, all the equations of the model are presented explicitly.

- In chapter 5, the rate based model developed in chapter 4, incorporating the thermodynamic treatment introduced in chapter 3, is validated against pilot plant data. The key parameters of the model are identified and their impact assessed via a sensitivity analysis.

- In chapter 6, the modelling of the solvent regeneration unit, composed of a desorber, a reboiler, and a condenser, is presented. The absorber model previously developed is transferred to the desorber model. The equations that differ from those presented chapter 4 are listed explicitly. The models for the condenser and the reboiler are proposed.

- In chapter 7, the predictive capabilities of the solvent regeneration unit model developed in chapter 6 are assessed using pilot plant data. The key parameters of the
model are identified and their impact assessed via a sensitivity analysis.

- In chapter 8, the models developed in chapters 3, 4 and 6 are linked together to form a complete flowsheet of an absorber-desorber process. An initial study of the complete process is presented.

- Finally, in chapter 9, the conclusions of this work and suggestions for future work are presented.
Chapter 2

Techniques for CO\textsubscript{2} capture

In the introduction, it has been shown that carbon capture and storage (CCS) is a must to reduce CO\textsubscript{2} emissions and meet the target set by the European Union. The transport and storage of CO\textsubscript{2} are great challenges but nonetheless they are not insurmountable. In this study, the focus will be placed on the capture of CO\textsubscript{2} from flue gas. A carbon capture method should be carefully selected by taking into account its applicability, its industrial readiness, and its capital and operating costs. The environmental impact should be addressed too, as there is no point in swapping one pollutant for another. The fossil fuel used to produce electricity in power plant are either gas or coal. It is the combustion of these fossil fuels that results in the formation of CO\textsubscript{2}. The flue gas from a natural gas-fired power plant typically consists of 2-3\% CO\textsubscript{2} (Amrollahi et al., 2012), while a coal-fired one consists of 10-20\% CO\textsubscript{2} (Nogueira and Mamora, 2008). There are also H\textsubscript{2}O, O\textsubscript{2}, N\textsubscript{2} and, impurities like NOx and SOx. These components and their potential effects on the carbon capture process need to be considered when selecting a technology.

As explained previously, there are several carbon capture technologies, but only five of them will be presented subsequently as they are already being used or likely to be used by the industry. These key technologies are: calcium-looping, oxy-fuel combustion, pre-combustion gasification combined cycle, pressure-swing adsorption, and amine solvent
In the next section, the five technologies are described in detail. The following section is focused on amine solvent processes and presents the modelling effort to date.

2.1 \( \text{CO}_2 \) capture technologies

2.1.1 Calcium looping

Among the high temperature solid sorbents available for \( \text{CO}_2 \) capture, calcium oxide (CaO) really stands out. This material can be derived from natural limestone, which is widely available and comes at low cost. The process is often referred to as carbonate or calcium looping in the literature. It uses the solid-gas reversible reaction between calcium oxide and carbon dioxide to form calcium carbonate.

\[
\text{CaO(s)} + \text{CO}_2(\text{g}) \rightleftharpoons \text{CaCO}_3(\text{s})
\]  

(2.1)

The application of this process to carbon capture was first introduced by Shimizu et al. (1999). This process is suitable for large scale industrial applications and compared to other processes, the overall penalty efficiency is extremely competitive (Mac Dowell et al., 2010a). The major energy penalty of this technology is the desorption of the \( \text{CO}_2 \) that needs to be done at temperature as high as 1200 K (Blamey et al., 2010). Moreover, it is important to note that the sorbent derived from natural limestone loses its capacity to capture \( \text{CO}_2 \) after multiple capture and release cycles (Grasa et al., 2008). A side advantage of this process is the potential link to the cement industry which is an important \( \text{CO}_2 \) emitter (Hadlington, 2011). After multiple \( \text{CO}_2 \) absorption cycles, the spent CaO could be sold to the cement industry and thus suppress the need for this industry to
2. Techniques for CO$_2$ capture

produce it. The production of CaO is responsible for about half the CO$_2$ emissions from the cement industry, the coupling of these processes could de-carbonate both of them. This type of technology exists at pilot plant scale and is now moving to demonstration scale (Sánchez-Biezma et al., 2011). With positive feedback, this technology should be considered for practical deployment in the medium to long term.

2.1.2 Oxy-fuel combustion

In oxy-fuel combustion, coal is burned with a gas mixture of O$_2$ and recycled gas (CO$_2$ and H$_2$O) from the combustion (Abraham et al., 1982). The proportion of oxygen in this gaseous mixture is 30% (Buhre et al., 2005), significantly higher than that in air (21%) and the gas does not contain N$_2$. The exhaust gas of this combustion will be pure CO$_2$ and H$_2$O which can be recovered by condensation. This technology allows for nearly 100% of the CO$_2$ to be captured (Figueroa et al., 2008). The oxy-fuel combustor is similar to the traditional combustor using air (Wall et al., 2009). Thus, this process could easily be retrofitted to an existing power-plant. The major energy penalty comes from the separation of N$_2$ from the air to produce O$_2$. This penalty is comparable to that of an amine-based scrubbing process. Different technologies exist to produce the oxygen. The industry standard is currently cryogenic air separation, but the energy needed to produce cryogenic conditions is high (Buhre et al., 2005; Figueroa et al., 2008; Wall et al., 2009). Coal-fired oxy-fuel combustion was first introduced by Abraham et al. (1982) but received only mild interest. There has been a regain in interest for the last decade. Buhre et al. (2005) presented a review of oxy-fuel combustion technology for coal-fired power generation. They identified four issues for oxy-fuel combustion that need to be addressed before further development: the heat transfer in the gas; the environmental issues, namely the control of gaseous emissions of SO$_2$; the ash related issues and the control of the combustion, including the flame stability.
2. Techniques for CO₂ capture

2.1.3 Integrated gasification combined cycle

The integrated gasification combined cycle (IGCC) process consists of the gasification of coal (or another fossil fuel) into synthesis gas with a sub-stoichiometric amount of oxygen. The synthesis gas is composed of H₂ and CO. Water is added to this mixture and reacts with CO in the so-called water-gas shift reaction: CO+H₂O ⇌ CO₂+H₂. The CO₂ can then be separated, leaving a product rich in H₂. The current benchmark to remove the CO₂ at this point in the process is the Selexol process (Pennline et al., 2008; Figueroa et al., 2008). The major advantages of IGCC are the low energy penalty needed to separate the CO₂ from the H₂ and the fact that the volume of gas to handle in the combustor is small, as there is no nitrogen. However, there is still an energy penalty for the shift reaction. Compared to an amine based post-combustion process, the IGCC offers better performance in term of operating costs (Gibbins and Chalmers, 2008). Moreover, this process produces H₂ which can be either burnt directly to produce electricity or used for other applications (Holt et al., 2003; Minchener, 2005). However, this method could not be retrofitted to an existing power-plant and so the investment costs are higher than for post-combustion chemical absorption (Damen et al., 2006; Figueroa et al., 2008; Mac Dowell et al., 2010a), which is a major drawback. To deploy such a process, new power generation plants and more complex systems should be built. Many existing power plants are still to be used for decades. Since the target set by the European Union involves short term reductions, this pre-combustion method will not be considered in this work. Nevertheless, pre-combustion capture might be preferable over post-combustion as a long term solution.

2.1.4 Pressure swing adsorption

Pressure swing adsorption (PSA) is a gas separation process in which the adsorbent is regenerated by reducing the partial pressure of the adsorbed component. It was introduced first by Skarstrom (1958) and Guerin de Montgareuil and Domine (1957). The first
applications of this system to CO$_2$ capture showed only limited results on the product purity due to the low selectivity between CO$_2$ and CH$_4$ on activated carbon (Doong and Yang, 1986).

One of the key aspect in PSA is the choice of adsorbent (Yoo et al., 1995). There were originally three main adsorbent type that were used for this process: activated carbon, carbon molecular sieves and synthetic zeolites. The main characteristics of an adsorbent in this context are the selectivity, the effective adsorption amount, the mass transfer kinetics, and the heat of adsorption. Zeolites have high selectivity for CO$_2$, but also a higher heat of adsorption than carbon sorbent, thus rendering the desorption difficult (Kikkinides et al., 1993; Yoo et al., 1995; Siriwardane et al., 2001). Kikkinides et al. (1993) obtained a high purity of CO$_2$ (99.97%) from flue gas using activated carbon and concluded that this process was superior to the one using molecular sieves. Later on Yoo et al. (1995) compared activated carbon and synthetic zeolite 13X and concluded that zeolite 13X is a better adsorbent for bulk separation of CO$_2$ from flue gas. Although zeolite 13X is now considered as the benchmark sorbent for PSA (Sumida et al., 2012), a new family of sorbents has gained interest recently; the metal-organic frameworks (MOFs) (Deng et al., 2010; Britt et al., 2009; Yazaydin et al., 2009; Bae and Snurr, 2011; Sumida et al., 2012). Extensive research is ongoing towards the design of these new sorbents for the application in carbon capture using PSA.

Another crucial aspect in PSA processes is the operation procedure. A typical fixed-bed adsorption system is operated in a cyclic manner, undergoing different steps; pressurization, adsorption, blowdown, and desorption (Biegler et al., 2005). Several improvements to this basic cycle have been introduced. For example, Berlin (1996); Marsh et al. (1964); Wagner (1969) proposed a pressure equalization stage during which the beds are connected and the pressures in the two chambers are equating, resulting in a saving in overall process energy consumption since less mechanical energy is required.

The PSA systems are particularly suited for medium scale processes but existing systems are not suitable for large scale industrial carbon capture (Wang et al., 2011).
2. Techniques for \(\text{CO}_2\) capture

2.1.5 Chemical absorption

In amine-based \(\text{CO}_2\) capture, the \(\text{CO}_2\) rich flue gas is contacted with a liquid amine solvent in solution. The amine solvent reacts reversibly with the carbon dioxide and creates weak bonds resulting in the formation of water-soluble salts. This bond formation is explained in the next chapter. The solvent is then regenerated by heating, which breaks the bonds. A flowsheet of a typical amine-based carbon capture process is represented in figure 2.1. The flue gas is fed to the bottom of the absorber where it will travel upward and be in contact with the liquid solvent flowing downward. The gaseous \(\text{CO}_2\) is reacting with the liquid solvent and is transferred to the liquid phase. The cleaned flue gas escapes at the top of the absorber, while the solvent rich in \(\text{CO}_2\) leaves at the bottom. This solvent is fed to the top of the desorber, flowing downwards while in contact with a gaseous mixture of \(\text{H}_2\text{O}\) and \(\text{CO}_2\). At the bottom of the desorber there is a reboiler to heat up the rich solvent, separate the \(\text{CO}_2\) from the solvent and transfer it to the gas phase along with some \(\text{H}_2\text{O}\). This gas mixture is fed back to the desorber and flows upward along the column. The solvent leaving the reboiler is stripped from the \(\text{CO}_2\) and sent back to the absorber. At the top of the desorber column, there is a condenser to condense the \(\text{H}_2\text{O}\) back to the desorber and obtain a high \(\text{CO}_2\) content gas stream. Three main classes of amines could be used as chemical solvents. These are primary, secondary and tertiary amines, named after the number of hydrogen atoms substituted by an alkyl group on the amine group. The primary amines, such as monoethanolamine (MEA, \(\text{H}_2\text{N}(-\text{OH})\)), react strongly and quickly with \(\text{CO}_2\). They are most suitable for low partial pressures of \(\text{CO}_2\). However, these types of amines are subject to degradation due to the oxygen contained in the flue gas (Bello and Idem, 2006; Uyanga and Idem, 2007; Davidson, 2007). Secondary and tertiary amines such as diethanolamine (DEA, \(\text{HO}(-\text{N}(-\text{OH})\)) and methyl diethanolamine (MDEA, \(\text{HO}(-\text{N}(-\text{OH})\) respectively, have a lower reactivity (Laddha and Danckwerts, 1981; Blauwhoff et al., 1984; Barth et al., 1984) which eases the regeneration of the solvent as the association bonds are weaker. Less heating is needed in the desorber. Nevertheless, as the rate of absorption is lower for these types of amines, they are unsuitable to work
at low CO₂ partial pressure. In the context of carbon capture for power plant generation where low CO₂ partial pressures are involved, MEA is considered as the benchmark. The problem of degradation can be addressed by using additives to the solvent to prevent the reactions with oxygen (Bello and Idem, 2006; Sexton and Rochelle, 2009). An important advantage of amine-based CO₂ capture is its potential applicability to the majority of the existing large fixed point CO₂ emitters as it could be retrofitted to an existing power plant (Rao and Rubin, 2002; Figueroa et al., 2008; Mac Dowell et al., 2010a).

In addition to the ionic speciation equilibria due to the dissociation of CO₂ and the amines in aqueous solution, the principal reaction of interest between CO₂ and a primary or secondary amine (in water) is the formation of a carbamate:

\[
\text{CO}_2 + 2\text{R}_1\text{R}_2\text{NH} \rightleftharpoons \text{R}_1\text{R}_2\text{NCO}_2^- + \text{R}_1\text{R}_2\text{NH}_2^+ \tag{2.2}
\]

This reaction is the combination of the two chemical reactions 1.1 and 1.2 presented in chapter 1. It can be seen that the overall stoichiometry of the reaction is such that each molecule of CO₂ is eventually associated with two amine molecules.
The five technologies presented in this section show promising capacities for carbon capture and are all in constant development. Early work on solvent-based carbon capture processes date back from 1980, with notably the contributions from Hikita and Konishi (1983), Takahashi et al. (1984), Yonemoto et al. (1984), Takeshita and Kitamoto (1988). Rao and Rubin (2002) presented 4 reasons why the amine-based CO\textsubscript{2} absorption processes are the most suitable technologies for the short and medium term. (1) This technology is suitable for dilute CO\textsubscript{2} stream, a flue gas from a coal-fired plant typically contains 10-20 \% CO\textsubscript{2}. (2) It is a proven technology that is commercially used today. (3) Amine-based systems can be retrofitted to an existing power plant, in the same way as other end-of-pipe environmental control systems. (4) As can be seen by the high number of articles being published on the model development to improve this technology, one can expect future technological advances.

The different modelling approaches that have been developed for this technology are discussed in the remainder of this chapter.

2.2 Amine-based processes

2.2.1 Importance of the thermodynamic and the transport models

In order to design a process for carbon capture, one should develop a model which incorporates both the thermodynamics (Gani and O’Connell, 2001) and the transport phenomena (Taylor and Krishna, 1993) relevant to the process. Most non-trivial process models make use of physical properties, such as the chemical potential, density and enthalpy, which need to be determined accurately with a thermodynamic model. The choice of the thermodynamic model is of high importance as it is linked directly to the accurate determination of the vapour-liquid equilibrium that is the key to the description of the separation process. This choice is described subsequently. A model for the transport
phenomena then has to be developed to describe the exchange of mass and energy within and between the different phases. A goal of our process model development is to address concerns relating the large scale deployment of this technology, including energy requirements, solvent degradation and the environmental and health impact resulting from the loss of solvent and solvent degradation products. Modelling studies can play a useful role in addressing some of these issues and identifying the choice of solvent and operating conditions that yield the best performance. A key challenge is to develop models that can predict accurately the behaviour of the process and are robust enough to span the entire optimisation domain.

Any model considered for the design of CO₂ capture processes must be robust and predictive. The fluids comprising CO₂ absorbed in aqueous amine solvents considered in this study are highly complex, exhibiting extensive ionic speciation, intermolecular association via hydrogen bonds and chemical reactions. Thus, a model specifically designed for these reactive fluids is required. In this section, the methods typically used for modelling such fluids are reviewed, followed by a focus on the use of SAFT theory in process models.

There is an extensive body of literature concerning the process modelling and simulation of CO₂ absorption in packed columns. The modelling approaches that have been proposed to date differ in the choice of thermodynamic and kinetic models, and, where appropriate, heat- and mass-transfer models. Most of the effort has focused on the use of aqueous monoethanolamine solutions, due to their widespread industrial use and the availability of pilot plant data, although there have been some models developed for other solvents, notably aminomethylpropanol (AMP) (Aboudheir et al., 2006; Gabrielsen et al., 2006, 2007; Choi et al., 2009). The models presented here are applicable to the absorber column; the specificities of the models developed for the desorber column are presented in Chapter 6.
2. Techniques for CO\textsubscript{2} capture

2.2.2 Column description

The amine-based carbon capture process involves an absorber and a desorber (cf. Figure 2.1). The absorber and the desorber are countercurrent vapour-liquid multistage separation columns, with a liquid feed at the top stage and a vapour feed at the bottom stage. A vapour product comes off the top stage and a liquid product off the bottom stage. The inside of the column is filled with an inert packing material designed for maximum mass transfer between the vapour and the liquid and for low pressure drop. The vapour and liquid compositions vary continuously with packing height rather than discretely as in a tray column. The modelling of such columns could be either discrete or continuous in the vertical direction (Taylor and Krishna, 1993; Khoury, 2005; Gáspár and Cormo, 2011).

2.2.3 The concept of a stage

The column is usually divided into hypothetical stages, each representing a (sometimes infinitesimal) section of packing in the column (Taylor and Krishna, 1993; Khoury, 2005). A larger number of stages yields better results (Taylor and Krishna, 1993). Taken to the limit, using an infinite number of stages would be equivalent to modelling the column continuously. However, experience shows that above a certain number of stages, the difference in the results is negligible. A large number of segments needs more computational time, so a suitable compromise should be found. A discrete model of the column is sufficient to provide good predictive capability, compared to a more complex continuous model that would involve a significantly higher number of equations and differential equations. The use of discrete stages is the most common choice for the modelling of such processes (Taylor and Krishna, 1993; Khoury, 2005). Although both approaches could be used, the discrete model is chosen for this study.
2. Techniques for CO₂ capture

2.2.4 Rate-based vs Equilibrium models

Each stage can be modelled using either an equilibrium or a rate-based model. In an equilibrium model, vapour-liquid equilibrium is assumed on each stage, everywhere on the stage. A rate-based model accounts for limitations due to transport phenomena. For this model, the assumption is made that the two phases are distinct, and each phase is perfectly mixed on each stage. Figure 2.2 presents a diagram of a non-equilibrium stage. Vapour from the stage below is brought into contact with liquid from the stage above and the two phases exchange mass and energy through their common interface represented in the diagram by the wavy line. In a rate-based model, separate mass balances are written for each phase. The two phases are in contact through their interface where the material lost by the vapour phase is gained by the liquid phase and vice versa. The heat transfer is treated in a similar way. There is one energy balance in each phase, and the phases are linked together via the rate of energy transferred across the phase interface. The compositions of the two phases at the interface are determined assuming equilibrium conditions at the interface.

The rate-based model is a more precise representation of the physical process than the
equilibrium model. For chemisorption processes with fast reaction kinetics, as is the case for the process of interest (Blauwhoff et al., 1984; Ying and Eimer, 2013), a rate-based process is more reliable. Indeed, Lawal et al. (2009) compared the two approaches using the same physical property model and concluded that the rate-based model gave a better description of pilot plant (Dugas, 2006) temperature profiles.

2.2.5 Two film theory and enhancement factor

When using a rate-based approach, an important aspect in model development is the choice of approach to treat heat- and mass-transfer phenomena. The concentration and temperature profiles across hypothetical films in a two-film model can be imposed, taking into account the effect of chemical reactions on mass transfer with an enhancement factor, defined as the ratio of the amount of gas absorbed in a reacting liquid to the amount which would be absorbed if there were no reaction (Danckwerts, 1970; DeCoursey, 1982; van Swaaij and Versteeg, 1992). A liquid-gas interface between the two films is sketched in Figure 2.3, where the profiles for composition of component $i$, temperature and pressure are represented.

The enhancement factor varies along the length of the column and can often be adjusted to pilot plant data. This is the route followed in most models of CO$_2$ absorption (e.g., Pandya (1983); Tontiwachwuthikul et al. (1992); Pintola et al. (1993); Pacheco and Rochelle (1998); Tobiesen et al. (2007); Faramarzi et al. (2010); Lawal et al. (2010)). In an improvement over film theory, Tobiesen et al. (2007) developed a penetration model, where the two films at the interface are described continuously. This was found to describe their own pilot plant data well. A more rigorous approach is that followed by Kucka et al. (2003a), in which the Maxwell-Stefan formalism is used together with film discretisation to account for the effect of the chemical reaction on the mass transfer. This more detailed model leads to better predictions of concentration and temperature profiles at the pilot
Figure 2.3: A schematic of the two-film model of a column stage. \( \delta^V \) and \( \delta^L \) represent the thickness of the gas and liquid films, respectively. \( P^V, P^I, \) and \( P^L \) are the pressure in the bulk vapour phase, at the gas-liquid interface and in the bulk liquid, respectively. As can be seen an isobaric profile is assumed. The temperatures of the bulk vapour phase, at the gas-liquid interface, and of the bulk liquid are denoted by \( T^V, T^I, \) and \( T^L, \) respectively. Finally, \( y_i \) and \( x_i \) are the mole fractions of component \( i \) in the bulk vapour and liquid phases, respectively, and \( y'_i \) and \( x'_i \) are the mole fractions of component \( i \) at the vapour-liquid interface in the vapour and the liquid phases, respectively.
plant scale (Tontiwachwuthikul et al., 1992) than other models, without the need to fit any parameters to pilot plant data (Kucka et al., 2003a). However, in keeping with the objective of developing a simple model using an implicit treatment of the chemical reactions, this last approach is unnecessary.

2.2.6 Mass transfer correlations

In all rate-based models, empirical mass-transfer correlations are required to take into account the type of packing used and the operating conditions. The correlations of Onda et al. (1968a,b) and Bravo and Fair (1982) were developed specifically for random packing, whereas the correlations of Rocha et al. (1996) were developed for structured packing, but can be applied to random packing by using an equivalence relation linking the random packing characteristics to the structured packing ones. Correlations developed by Billet and Schultes (1999) are also available as they apply to both structured and random packing. In a detailed comparison applied to a model of a CO$_2$ capture pilot plant presented by Faramarzi et al. (2010), it appears that the main operating conditions to consider when choosing a mass-transfer correlation are the flowrates of the flue gas and the lean solvent.

2.2.7 Phase equilibrium and chemical reactions

Another important component in modelling CO$_2$ absorption is the representation of the chemical reactions and fluid phase equilibria of the mixture of MEA, CO$_2$ and H$_2$O. Most models proposed to date rely on the use of reaction kinetics derived from experimental data specific to each reaction (e.g., Austgen et al. (1989, 1991); Kucka et al. (2002); Noeres et al. (2003); Kenig et al. (2003); Kucka et al. (2003a,b)). In the earliest absorber models, the thermodynamics of the gas and liquid phases were described with the assumption of
ideal gas and ideal solution behaviour. This is the case for example of the model developed by Pandya (1983) and later used by Tontiwachwuthikul et al. (1992). However, this model was too simplified to describe the complex interactions between the CO$_2$ and the solvent, and might not be suitable when transferred to other solvents. The combination of the electrolyte-NRTL (eNRTL) approach (Chen and Evans, 1986; Austgen et al., 1989) with a Henry’s constant to describe CO$_2$ solubility is a method which has attracted much interest and is typically used in recent studies (Lawal et al., 2010). The eNRTL approach has recently been corrected for inconsistencies by Bollas et al. (2008). The major drawback of this method is that it contains a large number of parameters, requiring a great deal of experimental data for vapour-liquid equilibrium (VLE) and reaction kinetics, thus making it difficult to use with different solvents. A similar approach (Kucka et al., 2003a) is to combine the Soave-Rechlich-Kwong (SRK) equation of state (Poling et al., 2001) with the eNRTL model. Tobiesen et al. (2007) adapted an activity coefficient model from Hoff (2003) to fit VLE experimental data, using an experimentally-derived equilibrium constant (Weiland et al., 2004).

As an alternative to reduce the number of parameters to be fitted and the computational effort needed to solve the vapour-liquid equilibrium, Gabrielsen et al. (2005) developed their own thermodynamic model to determine the VLE of MEA, CO$_2$ and H$_2$O. They used a simple correlation derived from experimental data of CO$_2$ solubility in aqueous MEA. This correlation is valid only for MEA and over the conditions used in fitting: loading of CO$_2$ varying from 0 to 0.5 at two temperatures, 313K and 393K.

Although the combined reaction and activity coefficient models developed to date to represent the MEA + CO$_2$ + H$_2$O mixture provide an accurate representation of the behaviour of this complex mixture over the range of conditions of interest (Isaacs et al., 1980; Jou et al., 1982; Lal et al., 1985), they require extensive parametrisation and are clearly not transferable to other solvents.
2.2.8 Integration of SAFT into process models

Recently, an alternative approach to modelling the phase and chemical equilibria of mixtures of alkanolamines, CO\textsubscript{2} and water has emerged (Mac Dowell et al., 2010c; Rodríguez et al., 2012). The approach has been shown to offer good transferability from one alkanolamine to another (Rodríguez et al., 2012), thereby requiring limited experimental data as new solvents are investigated. It is based on a version of the molecular statistical associating fluid theory (SAFT) equation of state (Jackson et al., 1988; Chapman et al., 1989, 1990), in which a square-well intermolecular potential of variable range is used – this version is referred to as SAFT-VR (Gil-Villegas et al., 1997; Galindo et al., 1998; Kontogeorgis and Folas, 2010; McCabe and Galindo, 2010). In the SAFT formalism, the chemical reactions of the type seen in the mixtures of interest here can be mediated via short-range association sites incorporated in the molecular models, thanks to an inter-site interaction potential. In cases where chemical equilibrium holds, such an approach has been shown to be equivalent to the chemical models used to date in which the aggregated chemical species (e.g., carbamate, zwitterion) are modelled explicitly (Economou and Donohue, 1991). The SAFT family of equations has been successfully used for complex fluid phase equilibrium (Müller and Gubbins, 2001; Tan et al., 2008; McCabe and Galindo, 2010). Due to the strong basis of the equation of state in molecular thermodynamics and statistical mechanics, SAFT-VR parameters can often be transferred from one compound to another compound on the basis of similarities in molecular structure and the predictions obtained are valid over wide ranges of compositions, temperatures and pressures.

The use of the SAFT-VR thermodynamic approach within process models of CO\textsubscript{2} absorption has recently started being explored for high pressure physical absorption in alkanes (Pereira et al., 2011). In an early study (Mac Dowell, 2010; Mac Dowell et al., 2010b) the modelling of an amine-based absorption process was considered and explored in the context of solvent blend design. More recently, a dynamic model of a CO\textsubscript{2} absorber, that makes use of the SAFT-VR thermodynamic treatment, has been proposed (Mac Dowell et al., 2013) and has been used for control (Arce et al., 2012) and economic (Mac Dowell
and Shah, 2013) investigations of post-combustion CO$_2$ capture processes. Qualitative agreement with data from two pilot plant runs from (Tontiwachwuthikul et al., 1992) was found for the model used in these last three publications. The column profiles obtained by Mac Dowell et al. (2013) are somewhat difficult to interpret as the location of the plant data points as reported in the paper does not match the location of the sensors reported in the physical pilot plant. Nevertheless, the results from Mac Dowell et al. (2010b) and Mac Dowell et al. (2013) indicate that a physical approach to modelling the chemical and physical equilibria allows one to capture the process behaviour accurately with a limited number of parameters.

### 2.2.9 Summary of existing process models

The different absorber models cited in this section are listed in Table 2.1, together with a summary of their main characteristics. Overall, the models reported to date are able to represent the general behaviour of the absorber column. However, only the model of Tontiwachwuthikul et al. (1992) provides accurate descriptions of the temperature of the rich solvent at the outlet, and in all published models, the bulge in the temperature profile, which is a well-known characteristic of this absorption process (Kvamsdal and Rochelle, 2008), is reproduced qualitatively but not quantitatively. Existing models are able to reproduce either its magnitude or its location along the column, but not both.

### 2.2.10 Overview of available pilot plant

All the absorber models presented in this study rely on experimental data for their validation. There are only a few detailed sets of pilot plant data available for the capture of CO$_2$ in aqueous amine solutions. Some of the key contributions are listed in table 2.2.
Table 2.1: Overview of models of CO$_2$ absorber using MEA solutions.

<table>
<thead>
<tr>
<th>Source</th>
<th>Thermodynamic model</th>
<th>Mass transfer model</th>
<th>Validation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pandya (1983)</td>
<td>ideal gas and ideal solutions</td>
<td>Onda et al. (1968b)</td>
<td>Tontiwachwuthikul et al. (1992)</td>
</tr>
<tr>
<td>Faramarzi et al. (2010)</td>
<td>Gabrielsen et al. (2005)</td>
<td>Onda et al. (1968a,b); Rocha et al. (1996); Billet and Schultes (1999)</td>
<td>Tontiwachwuthikul et al. (1992)</td>
</tr>
</tbody>
</table>
Available pilot plant data for desorber columns are presented in Chapter 6. The first thing to consider is the size of these pilot plants. All of these absorbers have a packing height of the same order of magnitude (5m). This should be compared to an industrial scale absorber with height of tens of meters. These absorbers also have the same diameter, except for the one from Dugas (2006) which is larger. Once again, this is one order of magnitude smaller than future industrial scale CO$_2$ absorber. However, these pilot plants are among the largest available at the time of writing. Demonstration and industrial scale absorbers are being commissioned and to the best of our knowledge, no experimental data have been published yet. The second important factor is the type of packing used. A random packing is usually used on small installations and structured packing for larger scale processes. Although structured packing are more expensive than random packings, they have better pressure drop and mass transfer characteristics than random packings and are, therefore, more and more used in new columns or for revamping older columns to improve performance (Taylor and Krishna, 1993). It is highly probable that an industrial CO$_2$ absorber will have structured packing. The operating conditions at which these pilot plants are runs are also important factors. The pilot plants from Tontiwachwuthikul et al. (1992) and Dugas (2006) have a concentration of CO$_2$ in the flue gas around 15 to 20%, corresponding to the proportion in the flue gas from a coal-fired power plant. The pilot plants from Tobiesen et al. (2007) and Notz et al. (2012) have a much lower concentration of CO$_2$ in the flue gas at 2 to 3%, representing a gas-fired power plant. Once a model is validated, data from different pilot plant could be used to test the range of predictability of this model. The works from Tontiwachwuthikul et al. (1992) and Dugas (2006) are

Table 2.2: Experimental pilot plant data of CO$_2$ absorber using MEA solutions.

<table>
<thead>
<tr>
<th>Source</th>
<th>Packing</th>
<th>Height of packing (m)</th>
<th>Internal diameter (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tontiwachwuthikul et al. (1992)</td>
<td>Random</td>
<td>6.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Dugas (2006)</td>
<td>Structured; Random</td>
<td>6.1</td>
<td>0.43</td>
</tr>
<tr>
<td>Tobiesen et al. (2007)</td>
<td>Structured</td>
<td>4.36</td>
<td>0.15</td>
</tr>
<tr>
<td>Notz et al. (2012)</td>
<td>Structured</td>
<td>4.2</td>
<td>0.125</td>
</tr>
</tbody>
</table>
both well documented and most of all, there are values of temperature, and CO$_2$ concentration in the gas phase and the liquid phase all along the column. These values are essential to validate a model as the outlet values alone are not sufficient. Tobiesen et al. (2007) presented graphs of these results but did not publish tabulated values. Notz et al. (2012) present detailed measurement along the column but only two different runs are documented. Moreover, it was published after the development of the model used in this study. It should be considered as a reliable source of experimental data for future model development. Although the pilot plant used in the work presented by Dugas (2006) is larger than the other pilot plants, it should be treated with caution as there is reported inaccuracy in the measurements of the gas flow rate (Dugas, 2006; Kvamsdal and Rochelle, 2008). For this study, the results presented by Tontiwachwuthikul et al. (1992) are used.

2.2.11 Concluding remarks

In the present study, a rate-based model for a CO$_2$ absorber-desorber process using MEA is developed. The SAFT-VR thermodynamic model is used together with mass transfer correlations from Onda et al. (1968b). In the SAFT-VR thermodynamic model, the reactions are treated implicitly, with the products of the chemical reaction treated as aggregates of the reactant molecules, so that there is no need for explicit rates of reaction. It is also proposed not to use an enhancement factor as the reactions are implicitly treated within the thermodynamic model. The extent to which SAFT-VR can be integrated in a process model is assessed.
Chapter 3

Thermodynamic theory and molecular model

When absorbing or desorbing CO$_2$ in an amine solvent, the gas is experiencing both a change of phase and a chemical reaction. These two phenomena have to be precisely described with a molecular model in order to accurately predict the process behaviour. As discussed in chapter 2, different thermodynamic approaches have been proposed and used for the modelling of carbon capture in an absorber desorber process (Chen and Evans, 1986; Austgen et al., 1989, 1991; Kucka et al., 2002; Noeres et al., 2003; Kenig et al., 2003; Kucka et al., 2003a,b). A description of the process relies on the use of a thermodynamic model for the VLE and on reaction kinetics derived from experimental data specific to each reaction for the chemical reaction. In our current study, the SAFT-VR thermodynamic framework is used to represent both the phase and the chemical equilibrium. The theoretical background of the different thermodynamic models is described first; the discussion is the centred on the SAFT equation-of-state and its integration in the CO$_2$ capture process model.
3. Thermodynamic theory and molecular model

3.1 Thermodynamic theory

The treatment of the chemical-reaction equilibria relevant to the absorption process is a key aspect of the modelling strategy adopted in our work. The vast majority of models presented to date follow a chemical approach, in which each reaction product is modelled as an independent species. This requires a large amount of experimental data on speciation and its dependence on thermodynamic state (temperature, pressure, and composition) which limits the transferability of the model to other solvents. In the physical approach followed here, the chemical and physical interactions are treated on an equal footing, within the SAFT-VR equation of state. Before presenting the SAFT-VR equation of state, we review the different thermodynamic models.

There are three basic modelling approaches, historically categorised as chemical, quasichemical or physical. These three approaches are discussed briefly, followed by a more detail description of a specific physical approach: SAFT.

A critical assessment and comparison of chemical, quasichemical and physical approaches has been made by Economou and Donohue (1991): the associated-perturbed-anisotropic-chain theory (APACT) (Ikonomou and Donohue, 1986, 1988; Economou and Donohue, 1990; Elliott et al., 1990), a lattice physical approach based on the quasichemical theory, and SAFT, a continuum physical approach, were compared with traditional chemical approaches. They showed that the functional form of the expressions derived from APACT and SAFT are essentially identical, and very similar in form to those derived with chemical equilibrium theories, reinforcing the thermodynamic equivalence of the various approaches to associating fluids. The intermolecular potential parameters of the physical approach can be used to provide an explicit state dependence of the equilibrium constant.
3.1.1 Chemical approach

The chemical approach was developed by Dolezalek (1908), where association between two molecules can be treated as a chemical reaction. The n-mers resulting from the chemical reactions are considered as distinct ideal chemical species. The contribution to the free energy is thus completely entropic corresponding to $x_i \ln x_i$ for each chemical species $i$. The model developed is considered suitable for mixtures that are close to ideal (Acree, 1984; Prausnitz et al., 1999). This method should be applied with care as it could lead to an incorrect description. One could cite the example given by Dolezalek (1918), where the application of a chemical approach lead to the conclusion that argon was forming a polymer. Another disadvantage of this method is that if more than one associating component is handled, then a large number of parameters are required as association products are treated as distinct species and the use of temperature dependent equilibrium constants implies a significant amount a experimental data, which could be difficult to obtain or unavailable.

3.1.2 Quasi chemical approach

In the quasi-chemical approach, the non-idealities in the fluids are considered to arise from non-random mixing at the molecular level. The formation of distinct association compounds is no longer considered explicitly. As the strong interactions found in associating systems bias the random mixing expected in simple fluid mixtures, the quasi-chemical theories account for association by assigning large energetic contributions to the actual associating interactions. In a random mixture, the probability of pair of components $i$ and $j$ being in close proximity is taken to be proportional to the product of their mole fractions $x_i x_j$, while in a non-random treatment such as the so-called quasi-chemical approach developed by Guggenheim (1952), the probability is weighted by an appropriate Boltzmann factor: $x_i x_j \exp(-E_{ij}/kT)$, $E_{ij}$ being the energy characterising the interaction. This the-
theory is the basis for several well known treatments of liquid mixtures like the Non-Random Liquid Theory (NRTL) (Renon and Prausnitz, 1968), the UNIversal QUAsi-Chemical (UNIQUAC) (Abrams and Prausnitz, 1975), and the corresponding group contribution UNIversal Functional Activity Coefficient (UNIFAC) (Fredenslund et al., 1975) methods. These models have shown to successfully describe the thermodynamic properties of mixtures of non-polar, polar and associating liquids well below their critical points, but cannot be applied as successfully to gases as the approaches are generally cast as a lattice description of the fluid which is not appropriate for less dense fluids phases by not taking into account the changes in pressure. For example, the NRTL method does not account for compressibility of the fluid, hence an equation of state (typically a cubic equation) is used separately to describe the gas phase.

Brandani (1983) has developed a successful method to determine the association equilibrium constants for pure components to give a representation of enthalpy of hydrogen bonding. In a second paper Brandani and Evangelista (1984) used the UNIQUAC approach (an implementation of the quasichemical theory) to assess mixtures including alcohols and amines. They showed that UNIQUAC can be applied in a rigorous manner when one of the components in the mixture is associative and the other is not. When mixtures of two associative components are examined one has to determine a much larger set of interaction parameters (at least 7), limiting the practical applicability of the model.

### 3.1.3 Molecular perturbation approach, SAFT

One of the first continuum statistical-mechanical treatments of associating fluids were presented by Andersen (1973, 1974) and by Dahl and Andersen (1983). In this approach, association sites are located inside a repulsive core to mediate short-ranged and highly attractive forces. The major innovation of this theory is the introduction of the density of un-associated monomers as well as the usual total density. This multi-density formalism
is the key to the success of further developments of this method. It should be noted that in this original approach one could handle only one bond per association site. A major contribution was made shortly afterwards by Wertheim (1984a,b, 1986a,b), who used graphical summation techniques to derive an approximation for the degree of association and free energy of molecules with highly directional, strong, short-range attractive forces. The statistical associating fluid theory (SAFT) family of equations of state (Müller and Gubbins, 2001; Tan et al., 2008; McCabe and Galindo, 2010) stems from Wertheim’s first-order thermodynamic perturbation theory (TPT1) (Wertheim, 1984a,b, 1986a,b; Jackson et al., 1988; Chapman et al., 1988). In SAFT approaches molecules are modelled as chain of bonded spherical segments with embedded short-range association sites incorporated to mediate hydrogen bonding which lead to aggregate formation (speciation). The equation of state is developed using a perturbation approach, such that the free energy of a chain is obtained with respect to the properties (free energy and radial distribution function) of a reference monomeric (un-bonded) system. The original version of SAFT (Chapman et al., 1989, 1990) has been revised and modified by a number of researchers so that several versions are now available (Huang and Radosz, 1990, 1991; Blas and Vega, 1997; Gil-Villegas et al., 1997; Galindo et al., 1998; Gross and Sadowski, 2001, 2002; Lafitte et al., 2006, 2007). The intermolecular potential defining the interactions between spherical segments (monomers) varies from version to version. In the SAFT-VR equation of state for potentials of variable range (VR) first introduced by Gil-Villegas et al. (1997) and Galindo et al. (1998), a square-well (SW) potential is used to describe the monomer reference fluid. Fixed forms of the intermolecular potential were used in the development of earlier versions of SAFT; the SAFT-VR formulation allows for a generic description of the effect of the range of the interaction and has been implemented for the square-well (Gil-Villegas et al., 1997), Sutherland (Gil-Villegas et al., 1997), Lennard-Jones (Davies et al., 1998), Yukawa (Davies et al., 1999), and Mie (generalised Lennard-Jones) (Lafitte et al., 2006; Avendaño et al., 2013) potentials. Specific details of the SAFT-VR equation of state employed in our current work are discussed in the next section.
Figure 3.1: The square-well potentials for a monomer, $\Phi^{\text{mono}}$, and association between the sites, $\Phi^{\text{assoc}}$, employed in the SAFT-VR approach. (a) $\Phi^{\text{mono}}$ is defined by a hard-core of diameter $\sigma$, range of attraction $\lambda \sigma$ and depth $-\varepsilon$. (b) $\Phi^{\text{assoc}}$ is defined by an off-centre potential of depth $-\varepsilon_{ab}$ and of range $r_{cab}$. (c) The centre of the site is at a distance $r_d$ from the centre of the segment.

3.1.4 SAFT-VR

In the SAFT-VR SW approach, a molecule $i$ is modelled as a homonuclear chain of $m_i$ bonded spherical segments of diameter $\sigma_{ii}$. The interactions between two identical segments are described by a square-well potential of range $\lambda_{ii}$ and depth $\varepsilon_{ii}$ (cf. Figure 3.1). For each molecule $i$, the number of site types $N_{s,i}$ must be defined, as well as the number of sites of each type $a$, $N_{s,ia}$. The sites are characterised by site-site energetic $\varepsilon_{ab,ij}^{HB}$ and range $r_{cab,ij}$ parameters (cf. Figure 3.1).

In the SAFT framework, the Helmholtz free energy $A$ of a model mixture of associating chain molecules can be written as:

$$
\frac{A}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{mono}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{assoc}}}{NkT}
$$

(3.1)

where $N$ is the number of molecules, $k$ the Boltzmann constant, and $T$ the absolute temperature. The superscript $\text{ideal}$, $\text{mono}$, $\text{chain}$ and $\text{assoc}$ denote the contribution to
the Helmholtz free energy due to the ideal, the monomer, the chain, and the association contributions, respectively. The first two terms are obtained from an augmented van der Waals equation of state for a fluid of attracting hard-sphere molecules obtained with a Barker and Henderson high-temperature perturbation theory (Barker and Henderson, 1967). The third term represents the effect on the free energy of irreversibly fusing hard spheres into chains of $m$ segments. The final term represents the contribution due to the formation of bonds between association sites.

In order to model mixtures, combining rules based on the Lorentz-Berthelot approach (cf. Haslam et al. (2008)) are used to describe the cross interaction between segments on two different molecules $i$ and $j$:

\[
\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (3.2)
\]

\[
\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (3.3)
\]

\[
\lambda_{ij} = \frac{\sigma_{ii}\lambda_{ii} + \sigma_{jj}\lambda_{jj}}{\sigma_{ij}} \quad (3.4)
\]

where $k_{ij}$ is an adjustable parameter that characterises the unlike dispersion attractive interaction.

In recent work (Mac Dowell et al., 2010c; Rodríguez et al., 2012) the reactions involved in aqueous amine solutions of CO$_2$ have been treated implicitly within the SAFT-VR framework, with the products of the chemical reaction represented as aggregates of the reactant molecules. To do so, the overall set of reactions is reduced to (Blauwhoff et al., 1984):

\[
\text{CO}_2 + \text{HOC}_2\text{H}_4\text{N}^+\text{H}_2\text{O}^- \rightleftharpoons \text{HOC}_2\text{H}_4\text{N}^+\text{H}_2\text{O}^- + \text{HOC}_2\text{H}_4\text{N}^+\text{H}_2\text{O}^- + \text{HOC}_2\text{H}_4\text{NHCO}_2^-
\]

Association sites that allow the complexation of CO$_2$ and MEA are introduced in our SAFT-VR molecular models. The reaction products can thus be modelled as neutral aggregates of CO$_2$ and MEA, bonded at association sites as shown in Figure 3.2. An accurate representation of the vapour-liquid phase equilibria of MEA + CO$_2$ + H$_2$O can
Figure 3.2: Schematic representation of the association scheme between MEA and CO$_2$ showing two reaction products.

be obtained in this manner by estimating the molecular parameters from experimental fluid phase equilibria data, for the pure components and mixtures. One important implication of the physical treatment of chemical equilibrium is that there is no need to explicitly specify a reaction scheme or reaction products. The types of products formed (e.g., carbamates or bicarbonates) are dictated by the association scheme chosen (number of sites and strength of their interactions), and the relative extent of formation of the different products depends on the temperature-independent parameters that describe the association energies. The fraction of molecules associated or un-associated at a given site is an output of the SAFT-VR model (and others based on the Wertheim formalism) and the distribution of reaction products can be determined from a statistical analysis of the molecules not-bonded at given sites at the thermodynamic state of interest (Economou and Donohue, 1991). Thus, although no speciation data are used in deriving the SAFT-VR parameters, the speciation equilibria can nonetheless be described successfully (Rodríguez et al., 2012).

A SAFT approach greatly reduces the number of parameters needed to describe the mixture compared to explicit approaches such as eNRTL, in which every species must be described as a separate entity and temperature-dependent equilibrium constants must be derived for all the relevant reactions. The SAFT-VR approach has been shown to
be applicable to the absorption of CO\textsubscript{2} for a number of aqueous alkanolamine solutions (Rodríguez et al., 2012). In many cases, it is possible to transfer parameters from one alkanolamine to another based on molecular similarity, further reducing the need for experimental data.

One key assumption in adopting this type of physical approach is that all reactions are assumed to be at equilibrium, which is only applicable for processes in the physical regime, i.e., where mass transfer is the rate limiting process. In the case where a specific treatment of the charged electrolytic species is required, the SAFT-VRE equation approach (Galindo et al., 1999; Gil-Villegas et al., 2001; Patel et al., 2003; Behzadi et al., 2005; Paricaud et al., 2010) can be adopted following a chemical approach as appropriate. It is also possible to represent some or all species explicitly so that any chemical reaction that is not at equilibrium can then be modelled via a separate kinetic model. We do not follow such an approach here, but instead test the validity of the chemical equilibrium assumption.

### 3.2 Molecular model

The molecules considered in this study are MEA, H\textsubscript{2}O, CO\textsubscript{2}, and N\textsubscript{2}. A schematic of the molecular models used with the SAFT-VR equation is presented in figure 3.3.

The values of all parameters are listed tables 3.1, 3.2, 3.3 and 3.4.
Figure 3.3: A schematic of the molecular model used in the SAFT-VR method. (a) H$_2$O, (b) MEA, (c) CO$_2$ and (d) N$_2$. The sites $e$ represent the electron lone pairs on the oxygen atom, the sites $e^*$ correspond to a lone pair on the nitrogen atom, the sites $H$ correspond to the hydroxyls, the sites $H^*$ correspond to the amines hydrogens, and the sites $\alpha_1$ and $\alpha_2$ are acceptor sites.
Table 3.1: The SAFT-VR parameters characterising the pure component models studied in our current work: the number of segments $m_i$, the diameter of the spherical core $\sigma_{ii}$, the depth $\varepsilon_{ii}$ and range $\lambda_{ii}$ of the dispersive square well potential, the type and the number of hydrogen–bonding sites.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$m_i$</th>
<th>$\sigma_{ii}$ (Å)</th>
<th>$\varepsilon_{ii}/k$ (K)</th>
<th>$\lambda_{ii}$</th>
<th>e-sites</th>
<th>H-sites</th>
<th>$e^*$-sites</th>
<th>$H^*$-sites</th>
<th>$\alpha_1$-sites</th>
<th>$\alpha_2$-sites</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>1.0</td>
<td>3.03420</td>
<td>250.00</td>
<td>1.78890</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Clark et al. (2006)</td>
</tr>
<tr>
<td>MEA</td>
<td>2.0</td>
<td>3.57229</td>
<td>305.00</td>
<td>1.58280</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>Mac Dowell et al. (2010c)</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2.0</td>
<td>2.78640</td>
<td>179.27</td>
<td>1.51573</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>Rodríguez et al. (2012)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.4</td>
<td>3.07357</td>
<td>74.587</td>
<td>1.58795</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Mac Dowell (2010)</td>
</tr>
</tbody>
</table>
Table 3.2: Binary interaction parameters for the mixtures relevant to our current work. \( k_{ij} \) characterises the strength of the dispersion interaction between molecules of types \( i \) and \( j \), see equation 3.3.

<table>
<thead>
<tr>
<th>( i ) + ( j )</th>
<th>( k_{ij} )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA + CO(_2)</td>
<td>0.47878</td>
<td>Rodríguez et al. (2012)</td>
</tr>
<tr>
<td>MEA + H(_2)O</td>
<td>0.01000</td>
<td>Mac Dowell et al. (2010c)</td>
</tr>
<tr>
<td>MEA + N(_2)</td>
<td>0.03000</td>
<td>Mac Dowell (2010)</td>
</tr>
<tr>
<td>CO(_2) + H(_2)O</td>
<td>-0.06000</td>
<td>Mac Dowell et al. (2010c)</td>
</tr>
<tr>
<td>CO(_2) + N(_2)</td>
<td>-0.0599</td>
<td>Mac Dowell (2010)</td>
</tr>
<tr>
<td>H(_2)O + N(_2)</td>
<td>-0.3635</td>
<td>Mac Dowell (2010)</td>
</tr>
</tbody>
</table>

Table 3.3: The \( a - b \) site-site association energies \( \varepsilon_{ab,ij}^{HB} \) for MEA, H\(_2\)O and CO\(_2\) (Figure 3.3). The interaction matrix is symmetric, i.e., \( \varepsilon_{ab,ij}^{HB} = \varepsilon_{bc,ji}^{HB} \); the lower diagonal part has been left blank and is implied. The unlike association between sites of the same type is assumed to be symmetric, i.e., \( \varepsilon_{ab,ij}^{HB} = \varepsilon_{bc,ji}^{HB} = \varepsilon_{ac,ic}^{HB} = \varepsilon_{bc,ci}^{HB} \) (Mac Dowell et al., 2010c; Rodríguez et al., 2012).

<table>
<thead>
<tr>
<th></th>
<th>MEA</th>
<th>H(_2)O</th>
<th>CO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b \setminus a )</td>
<td>( e )</td>
<td>( H )</td>
<td>( e^* )</td>
</tr>
<tr>
<td>MEA</td>
<td>0</td>
<td>2357.79</td>
<td>0</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>-</td>
<td>0</td>
<td>550.00</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( e^* )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( H^* )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( e )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( H )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \alpha_1 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3.4: The $a-b$ site-site range parameters $r_{cab,ij}$ for mixtures containing MEA, H$_2$O and CO$_2$ (Figure 3.3). The interaction matrix is symmetric, i.e., $r_{c\sigma H,i\sigma} = r_{c\sigma He,i\sigma}$ and so the lower diagonal part has been left blank. The unlike association between sites of the same type is assumed to be symmetric, i.e., $r_{c\sigma e,ij} = r_{c\sigma He,ij} = r_{c\sigma e,ji} = r_{c\sigma He,ji}$ (Mac Dowell et al., 2010c; Rodríguez et al., 2012).

<table>
<thead>
<tr>
<th>b (a)</th>
<th>$e$</th>
<th>$H$</th>
<th>$e^*$</th>
<th>$H^*$</th>
<th>$e$</th>
<th>$H$</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e$</td>
<td>2.08979 0</td>
<td>2.65064 0</td>
<td>0 2.10763 0</td>
<td>0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H$</td>
<td>0 2.65064 0</td>
<td>0 2.10763 0</td>
<td>0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e^*$</td>
<td>- - 2.32894 0</td>
<td>0 2.22626 1.97978 1.96999</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H^*$</td>
<td>- - - 0 2.22626 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e$</td>
<td>- - - - 0 2.10822 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H$</td>
<td>- - - - - - 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$\alpha_1$</td>
<td>$\alpha_1$</td>
<td>$\alpha_2$</td>
<td>$\alpha_2$</td>
<td>$\alpha_1$</td>
<td>$\alpha_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>- - - - - - 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>- - - - - - 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The MEA molecule is represented with 2 tangent spherical segments and has 2 sites of type $e$ (electron lone pairs on the oxygen atom), 1 site of type $e^*$ (corresponding to the lone pair on the nitrogen atom), 1 site of type $H$ (hydroxyl), and two sites of type $H^*$ (amine hydrogens) (Mac Dowell et al., 2010c). The H$_2$O is represented with 1 spherical segment and has 2 $e$ sites and 2 $H$ sites (Clark et al., 2006). The CO$_2$ model comprises 2 segments and has 1 $\alpha_1$ site and 1 $\alpha_2$ site (acceptor sites) that interact only with the $e^*$ sites of MEA (Rodríguez et al., 2012). The N$_2$ model is non-spherical, with an aspect ratio of $m = 1.4$, and does not have association sites as it is chemically inert and does not have strong directional interactions (Paricaud et al., 2004; Mac Dowell, 2010). A site of type $e/e^*$ can bond with a site $H/H^*$ and vice versa. For example, when an $e$ site from MEA and an $H$ site from water come within the cut-off range $r_{c\sigma H,MEA-H_2O}$ of each other, there is a site-site hydrogen-bonding associative interaction of energy $-\varepsilon_{c\sigma H,MEA-H_2O}$. In the standard Wertheim TPT1 treatment commonly used in SAFT, association into linear-chain, branched-chain, and network aggregates are considered. Association into ring-like structures (Sear and Jackson, 1994a; Ghonasgi et al., 1994; Sear and Jackson, 1996a; Galindo et al., 2002) (and even double bonding (Sear and Jackson, 1994b) and bond co-
3. Thermodynamic theory and molecular model

Operativity (Sear and Jackson, 1996b) can be taken into account but this is not found to be necessary for the systems described in our current work. The values of the parameters are listed in tables 3.1-3.4, and the file used in the gPROMS software containing these parameters is in the appendix.

The SAFT-VR thermodynamic model is implemented as a foreign object in the gPROMS software (Process Systems Enterprise Ltd.; Kakalis et al., 2004). The thermodynamic properties needed to determine the fluid phase (and implicit chemical) equilibrium, namely the pressure, the chemical potential and the enthalpy, are obtained in the usual manner as the corresponding derivatives of the Helmholtz free energy.

3.3 Validation of the thermodynamic model

The thermodynamic model is used to calculate the VLE for the ternary mixture MEA-CO$_2$-H$_2$O. Rodríguez et al. (2012) presented a comparison of the SAFT-VR description of the VLE and the experimental data for three isotherms (313, 353 and 393 K) as shown in Figure 3.4. A good description of the partial pressure of CO$_2$ as a function of the CO$_2$ loading, which is defined as the number of moles of CO$_2$ absorbed in the liquid phase per mole of MEA, is obtained for both low temperature (313 K) corresponding to the absorber temperature range and high temperature (393 K) corresponding to the desorber temperature range.

Another important aspect in the model validation is the description of the degree of speciation of the system. The main products of reactions in the model are the carbamate (MEACOO$^-$) and the bicarbonate (HCO$_3^-$) (cf. Equations 1.1-1.8). Rodríguez et al. (2012) explained that the concentration of these products can be deduced from the number of bonded and unbonded $\alpha$ sites on the CO$_2$. The analysis of the degree of speciation for MEA + H$_2$O + CO$_2$ at 313 K and 353 K is presented in Figure 3.5. SAFT-VR provides very good predictions of the composition in carbamate and bicarbonate at different
Figure 3.4: Solubility of CO$_2$ in a 30wt% solution of MEA. SAFT-VR model predictions (continuous curves) from Rodríguez et al. (2012) and experimental data (squares) from Jou et al. (1995)
Figure 3.5: Predicted mole fraction of carbamate and bicarbonate in the ternary mixture of MEA + H$_2$O + CO$_2$ with a concentration of MEA in the liquid phase of 30 wt%. (a) $T = 313$ K and (b) $T = 353$ K. The symbols (squares for carbamate and diamonds for bicarbonate) correspond to the experimental data (Böttin ger et al., 2008) and the curves (continuous for carbamate and dashed for bicarbonate) to the SAFT-VR calculations (Rodríguez et al., 2012).
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3.4 Enthalpy of absorption

In the context of carbon capture processes, another important aspect to consider is the enthalpy of absorption of CO$_2$, as the major source of heat in the system is the heat released when CO$_2$ is absorbed by MEA. In this section, the SAFT-VR model predictions of the enthalpy of absorption of CO$_2$ are compared to experimental data (Kim and Svendsen, 2007). It is shown that despite providing a very good description of the experimental VLE and speciation data, SAFT-VR leads to value of the heat of absorption of CO$_2$, $\Delta H_{\text{abs}}^{\text{CO}_2}$, that are too low compared to experimental values (Kim and Svendsen, 2007). Most equations of state do not provide an accurate description of the caloric properties of complex fluids, although more recent developments can lead to a marked improvement (Lafitte et al., 2006, 2013). A parameter is introduced in the model to correct the enthalpy of absorption of CO$_2$.

3.4.1 Methodology

The experimental setup described by Kim and Svendsen (2007) has been modelled using the gPROMS software (Process Systems Enterprise Ltd.). The setup consists of a 2 dm$^3$ fixed volume equilibrium cell. A given number of moles of MEA, CO$_2$, H$_2$O and N$_2$ is placed in the cell at a given temperature. At the appropriate conditions the mixture separates into a liquid phase and a gas phase. The total enthalpy of the cell is obtained as the sum of the enthalpies from each coexisting phase using SAFT-VR. The procedure is then repeated for a different concentration of CO$_2$ and the enthalpy is then obtained as a function of the loading of CO$_2$ in the liquid phase. The difference in enthalpies divided by the difference in the number of moles of CO$_2$ between the two simulations gives the enthalpy of absorption. In this model, the feed and equilibrium temperatures are not
Table 3.5: List of specified variables for the simulation of the enthalpy of absorption of CO$_2$.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{total}$</td>
<td>$6.5705164 \times 10^{-5}$</td>
<td>mole</td>
</tr>
<tr>
<td>MEA Loading</td>
<td>30</td>
<td>wt%</td>
</tr>
<tr>
<td>CO$_2$ loading</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>$T_{equ}$</td>
<td>313</td>
<td>K</td>
</tr>
<tr>
<td>Volume total</td>
<td>2</td>
<td>L</td>
</tr>
<tr>
<td>$x_{in}(N_2)$</td>
<td>$2.8687698 \times 10^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>

equal as is the case in the experimental setup. However, the enthalpy resulting from the heat capacity of the mixture and the temperature difference is negligible compared to the enthalpy of absorption of CO$_2$. The specified values in the system are listed in Table 3.5.

### 3.4.2 Results

The comparison between the SAFT-VR predictions and the experimental data of the enthalpy of absorption of CO$_2$ in MEA is depicted in Figure 3.6. At 313 K, which is a typical temperature for CO$_2$ absorbers, SAFT-VR underestimates the enthalpy of absorption of CO$_2$ by about 50 kJ mol$^{-1}$. This underestimation is 80 kJ mol$^{-1}$ at 393 K, a typical temperature for CO$_2$ desorbers. To mitigate for this underestimation, the same strategy as in other thermodynamic approaches is adopted and a correction of the enthalpy of absorption $\delta H_{CO_2}$ is implemented (Kucka et al., 2003a; Gabrielsen et al., 2007; Plaza et al., 2010a). When operating in the temperature range of the absorber, the value of this parameter is fixed to $\delta H_{CO_2} = 50$ kJ mol$^{-1}$. When operating in the temperature range of the desorber, the value of this parameter is fixed to $\delta H_{CO_2} = 80$ kJ mol$^{-1}$. The corrected enthalpies of absorption of CO$_2$ are presented in Figure 3.6.
Figure 3.6: Enthalpy of absorption of CO$_2$ in a 30 wt% solution of MEA: SAFT-VR model predictions with no correction at 313 K (dashed curve), SAFT-VR model with a correction of $\delta H_{CO_2} = 50$ kJ mol$^{-1}$ at 313 K (continuous curve), and experimental data at 313 K (squares) from Kim and Svendsen (2007); SAFT-VR model predictions with no correction at 393 K (dotted curve), SAFT-VR model with a correction of $\delta H_{CO_2} = 80$ kJ mol$^{-1}$ at 393 K (dot-dashed curve) and experimental data at 393 K (void squares) from Kim and Svendsen (2007).
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3.5 Concluding remarks

The different thermodynamic models have been introduced in this chapter based on their background theory: chemical, quasi-chemical and physical. From this last category, the SAFT equation of state, is described in more details, focusing on SAFT-VR SW, the thermodynamic model used in the carbon capture process model which is the topic of this dissertation. The molecular models of the mixture of MEA, CO$_2$, H$_2$O, and N$_2$ is then detailed. Both the vapour-liquid equilibrium and the chemical equilibrium are treated within the SAFT-VR thermodynamic framework, ensuring a consistent and accurate representation of the physical interactions in the system under the assumption that reaction kinetics are not rate determining. This physical approach lends itself to extension to other solvents, as a consequence of the transferable nature of the SAFT molecular models and the relatively small number of parameters and data required to develop them. A correction on the enthalpy of absorption of CO$_2$ is proposed to compensate for an underestimation with the theory.
Chapter 4

Development of an absorber model using SAFT

4.1 Introduction

The role of the absorber in a solvent based carbon capture process and the need for a transferable model of absorber have been explained in chapter 2. The existing models and their performance have also been discussed. It appears that there are some reliable models in the literature, some of them being entirely predictive at the process scale but they always require a lot of kinetic and equilibrium data. This is a problem for solvent selection, which is an important issue in CO$_2$ capture. The alternative strategy used to describe the VLE and the chemical reactions has been presented in chapter 3. The goal of this study is to assess the applicability of this alternative strategy in a process model to get good predictions and some insights into the process behaviour (e.g., the cause of the formation of a temperature bulge). This chapter describes the development of a rate-based model of a CO$_2$ absorber that uses the approach introduced in chapter 3. A single thermodynamic theory is used to describe the liquid and the gas phases, their VLE,
their chemical equilibrium, and their enthalpy. Another distinctive feature of the model developed here is the implicit treatment of the chemical reactions, taking into account only the reactants, hence limiting the compounds considered explicitly in this model to only MEA, CO$_2$, H$_2$O, and N$_2$. These aspects of the modelling represent a radically different approach to absorber modelling (Pandya, 1983; Tontiwachwuthikul et al., 1992; Pintola et al., 1993; Kucka et al., 2003a; Tobiesen et al., 2007; Lawal et al., 2009, 2010; Faramarzi et al., 2010; Mores et al., 2011, 2012; Gáspár and Cormo, 2011). The use of the SAFT-VR thermodynamic theory for the development of a rate-based process model of a CO$_2$ absorber is presented in this chapter.

4.2 Non-equilibrium absorber model

The absorber is a counter-current vapour-liquid multistage separation column, with a liquid feed at the top stage and a vapour feed at the bottom stage. The vapour product comes off the top stage and the liquid product off the bottom stage. The inside of the column is filled with an inert packing material designed for a maximum mass transfer between the vapour and the liquid and for a low pressure drop. The vapour and liquid compositions vary continuously with packing height rather than discretely as in a tray column.

The modelling of such a column can be either discrete or continuous in the vertical direction. In a discrete model, the column is divided in hypothetical stages, each of which represents a section of packing in the packed column. The larger the number of stages the better the description (Taylor and Krishna, 1993). Taken to the limit, using an infinite number of stages is equivalent to modelling the column continuously. Although both models could be used, we chose the discrete approach for our study.

The modelling of the stages can be equilibrium or rate-based. In an equilibrium model, it is assumed that vapour-liquid equilibrium is achieved at each stage, everywhere on the stage. The rate-based model accounts for limitations due to transport phenomena.
Due to the complexity of the process modelled in this case, a rate-based approach is chosen over an equilibrium one in order to capture some of the key physical phenomena (Krishnamurthy and Taylor, 1985a,b).

For this model, the assumption is made that the two phases are distinct, and each phase is perfectly mixed at each stage. A diagram of a non-equilibrium stage is presented in Figure 4.1.

Vapour from the stage below is brought into contact with liquid from the stage above and the two phases exchange mass and energy through their common interface represented in the diagram by the wavy line. In a rate-based model, separate mass balances are written for each phase. The two phases are in contact through their interface where material lost by the vapour phase is gained by the liquid phase. The heat transfer is treated in a similar way. There is one energy balance in each phase, and the phases are linked via the rate of energy transferred across the phase interface. The compositions of the two phases at the interface are determined assuming equilibrium conditions at the interface.

The behaviour at the phase interface in the rate-based stages is described with a two-film theory (Krishnamurthy and Taylor, 1985a). Each phase is split into two parts: the bulk phase; and the film in which the reaction and heat and mass transfer occur. In the bulk
4. Development of an absorber model using SAFT

Figure 4.2: A schematic of the two-film model of a column stage. $\delta^V$ and $\delta^L$ represent the thickness of the gas and liquid films, respectively, $P^V$, $P^I$, and $P^L$ are the pressure in the bulk vapour phase, at the gas-liquid interface and in the bulk liquid, respectively. As can be seen an isobaric profile is assumed. The temperatures of the bulk vapour phase, at the gas-liquid interface and of the bulk liquid are denoted by $T^V$, $T^I$, and $T^L$, respectively. Finally, $y_i$ and $x_i$ are the mole fractions of component $i$ in the bulk vapour and liquid phases, respectively, and $y^I_i$ and $x^I_i$ are the mole fractions of component $i$ at the vapour-liquid interface in the vapour and the liquid phases, respectively.

As can be seen an isobaric profile is assumed. The temperatures of the bulk vapour phase, at the gas-liquid interface and of the bulk liquid are denoted by $T^V$, $T^I$, and $T^L$, respectively. Finally, $y_i$ and $x_i$ are the mole fractions of component $i$ in the bulk vapour and liquid phases, respectively, and $y^I_i$ and $x^I_i$ are the mole fractions of component $i$ at the vapour-liquid interface in the vapour and the liquid phases, respectively.

The following assumptions are made:

- The model is steady state.

- The bulk phases and films are at chemical equilibrium everywhere (i.e., the reac-
tion rates are faster than the mass transfer rates) (Laddha and Danckwerts, 1981; Blauwhoff et al., 1984).

- The interface is at phase and chemical equilibrium (Economo and Donohue, 1991).
- The interfacial surface area is the same for both heat and mass transfer.
- The effective area is equal to the wetted area.
- The absorption column is considered to be adiabatic.
- There is no pressure drop along the column.

4.3 Model equations

In this subsection, we present the equations used to model a packed column subsection (stage). The equations are grouped into different categories: energy and mass balances, rate equations, equilibrium equations, mass-transfer correlations, heat-transfer correlations, and diffusion correlation. We chose to list explicitly all of the equation of the model due to the radically different approach followed here. One important model parameter, \( \tau \), is introduced in this section to account for the scaling of the CO\(_2\) diffusivity. This parameter will be estimated from experimental data. In the following equations, the subscript \( i \) refers to the \( i^{th} \) component and \( j \) to the \( j^{th} \) stage. \( c \) is the total number of components and \( N_s \) is the number of stages in the column. It is fixed to 50 which is amply sufficient to assure numerical convergence without significantly impacting the computational time.

**Heat and mass balances**

The liquid and vapour phase mole balances for component \( i \) of stage \( j \) are given by

\[
L_{j-1}x_{i,j-1} + N_{i,j}^L = L_jx_{i,j} \quad i = 1, 2, ..., c; \ j = 1, 2, ..., N_s
\]  

(4.1)
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\[ V_{j+1} y_{i,j+1} - N_{i,j}^V = V_j y_{i,j} \quad i = 1, 2, \ldots, c; \ j = 1, 2, \ldots, N_s \]  
(4.2)

where \( L_j \) and \( V_j \) are the total liquid and vapour molar flowrate leaving stage \( j \) respectively (mol s\(^{-1}\)), \( x_{i,j} \) and \( y_{i,j} \) are the bulk liquid and vapour mole fractions of component \( i \) of stage \( j \) (-), \( N_{i,j}^L \) is the net gain of species \( i \) in the liquid phase due to interphase transport for stage \( j \) (mol s\(^{-1}\)), and \( N_{i,j}^V \) is the net loss of species \( i \) in the vapour phase due to interphase transport for stage \( j \) (mol s\(^{-1}\)).

The mole fractions in the streams leaving each stage must sum to unity:

\[ \sum_{i=1}^{c} x_{i,j} = 1 \quad \text{and} \quad \sum_{i=1}^{c} y_{i,j} = 1 \quad j = 1, 2, \ldots, N_s \]  
(4.3)

The energy balances for the liquid and vapour phases respectively are

\[ L_{j-1} H_{j-1}^L + N_{CO_2,j}^L \delta H_{CO_2} + E_j^L = L_j H_j^L \quad j = 1, 2, \ldots, N_s \]  
(4.4)

\[ V_{j+1} H_{j+1}^V - E_j^V = V_j H_j^V \quad j = 1, 2, \ldots, N_s \]  
(4.5)

where \( H_j^L \) and \( H_j^V \) are the enthalpies of the liquid and gas phase respectively of stage \( j \) (J mol\(^{-1}\)), \( \delta H_{CO_2} \) is the term correcting the enthalpy of absorption of CO\(_2\) (J mol\(^{-1}\)) as introduced in section 3.1. \( E_j^L \) is the net gain of energy of the liquid phase through the interface at stage \( j \) (W), and \( E_j^V \) is the net loss of energy from the vapour phase through the interface at stage \( j \) (W). \( H_j^L \) and \( H_j^V \) are determined from SAFT-VR as functions of the temperature of the bulk phases, \( T_j^L \) and \( T_j^V \) (K), the molar volumes of the phases, \( V_j^L \) and \( V_j^V \) (cm\(^3\) mol\(^{-1}\)), and the composition of the phases, \( \vec{x}_j \) and \( \vec{y}_j \).

There is no accumulation of mass or energy at the vapour–liquid interface:

\[ N_{i,j}^L = N_{i,j}^V \quad i = 1, 2, \ldots, c; \ j = 1, 2, \ldots, N_s \]  
(4.6)

\[ E_j^L = E_j^V \quad i = 1, 2, \ldots, c; \ j = 1, 2, \ldots, N_s \]  
(4.7)
Rate equations: mass transfer

According to the film model for mass transfer, we define the mass transfer rates as follows:

\[
N_{i,j}^L = k_{i,j}^L a_{T,j} (C_{i,j}^L - C_{i,j}^L) \quad i = 1, 2, ..., c; j = 1, 2, ..., N_s \tag{4.8}
\]

\[
N_{i,j}^V = k_{i,j}^V a_{T,j} (C_{i,j}^V - C_{i,j}^V) \quad i = 1, 2, ..., c; j = 1, 2, ..., N_s \tag{4.9}
\]

where \(a_{T,j}\) is the total interfacial area on stage \(j\) available for heat or mass transfer (m\(^2\)), \(k_{i,j}^L\) is the liquid-phase mass-transfer coefficient of stage \(j\) for component \(i\) (m s\(^{-1}\)), \(k_{i,j}^V\) is the vapour-phase mass-transfer coefficient of stage \(j\) for component \(i\) (m s\(^{-1}\)), \(C_{i,j}^L\) and \(C_{i,j}^V\) are the concentrations of component \(i\) in the bulk liquid and vapour phases of stage \(j\) (mol m\(^{-3}\)), and \(C_{i,j}^{IL}\) and \(C_{i,j}^{IV}\) are the concentrations of component \(i\) at the vapour-liquid interface in the liquid and vapour phases of stage \(j\) (mol m\(^{-3}\)).

The total area for heat and mass transfer is given by the product of the effective specific area and the stage volume:

\[
a_{T,j} = a'_j A_{section} D_z \quad j = 1, 2, ..., N_s \tag{4.10}
\]

where \(a'_j\) is the interfacial area density of stage \(j\) (m\(^2\) m\(^{-3}\)), \(A_{section}\) is the cross sectional area of the column (m\(^2\)), and \(D_z\) is the stage height (m) given by \(h_{packing}/N_s\), with \(h_{packing}\) as the total packing height (m).

Rate equations: heat transfer

The energy fluxes in the liquid and gas phases at stage \(j\) are given by the sum of the conductive and diffusive heat fluxes:

\[
E_{j}^L = Q_{cond,j}^L + Q_{diff,j}^L \quad j = 1, 2, ..., N_s \tag{4.11}
\]
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\[ E_j^V = Q_{\text{cond},j}^V + Q_{\text{diff},j}^V \quad j = 1, 2, ..., N_s \] (4.12)

where \( Q_{\text{cond},j}^L \) and \( Q_{\text{diff},j}^L \) are the conductive and diffusive heat fluxes at the interface into the liquid phase of stage \( j \) (W), and \( Q_{\text{cond},j}^V \) and \( Q_{\text{diff},j}^V \) are the conductive and diffusive heat fluxes at the interface out of the vapour phase of stage \( j \) (W).

The conductive heat transfer rate into the liquid phase and out of the gas phase of stage \( j \) are driven by temperature gradients between the bulk phases and the interface and given by

\[ Q_{\text{cond},j}^L = h_{T,j}^L \alpha_{T,j} (T_j^L - T_{j}^L) \quad j = 1, 2, ..., N_s \] (4.13)

\[ Q_{\text{cond},j}^V = h_{T,j}^V \alpha_{T,j} (T_j^V - T_{j}^V) \quad j = 1, 2, ..., N_s \] (4.14)

where \( h_{T,j}^L \) and \( h_{T,j}^V \) are the heat transfer coefficients in the liquid and gas phases of stage \( j \), respectively (W m\(^{-2}\) K\(^{-1}\)), and \( T_j^L \) is the temperature at the vapour-liquid interface of stage \( j \) (K).

The diffusive heat fluxes account for the variation in enthalpy in the liquid and gas streams associated with the transfer of mass from one phase to another. This is obtained based on the individual component fluxes and the corresponding enthalpies of the pure components:

\[ Q_{\text{diff},j}^L = \sum_{i=1}^{c} N_{i,j}^L H(T_j^L, V_{i,j}^L, \vec{z}_i) \quad j = 1, 2, ..., N_s \] (4.15)

\[ Q_{\text{diff},j}^V = \sum_{i=1}^{c} N_{i,j}^V H(T_j^V, V_{i,j}^V, \vec{z}_i) \quad j = 1, 2, ..., N_s \] (4.16)

where \( H(T_j^L, V_{i,j}^L, \vec{z}_i) \) and \( H(T_j^V, V_{i,j}^V, \vec{z}_i) \) are the enthalpies of a pure component in the bulk liquid and gas phase, respectively (J mol\(^{-1}\)). Strictly speaking, one needs to use partial molar enthalpies instead of a pure component enthalpies however, to keep the model simple this assumption has been deemed acceptable. \( \vec{z}_i \) denotes the molar composition of a stream consisting of pure component \( i \) defined by \( z_{k,i} = 1 \) if \( i = k \) and \( z_{k,i} = 0 \) otherwise. \( V_{i,j}^L \) and \( V_{i,j}^V \) are the molar volumes of pure component \( i \) in stage \( j \) in the bulk liquid and
gas phases respectively \((\text{cm}^3 \text{ mol}^{-1})\) given by

\[
P^L_j = P(T^L_j, V^L_{i,j}, z^L_i) \quad i = 1, 2, \ldots, c; \quad j = 1, 2, \ldots, N_s \quad (4.17)
\]

\[
P^V_j = P(T^V_j, V^V_{i,j}, z^V_i) \quad i = 1, 2, \ldots, c; \quad j = 1, 2, \ldots, N_s \quad (4.18)
\]

where \(P^L_j\) and \(P^V_j\) are the pressure of the bulk liquid and gas phases of stage \(j\) respectively (MPa).

When equating the vapour and liquid fluxes, one obtains an expression which includes the difference between the enthalpies in the vapour phase and in the liquid phase for a pure component \(i\); this is the enthalpy of vaporisation of this component. As we will see, the enthalpy of vaporisation of water plays a significant role in the process. We assume that the mass transfer of \(N_2\) between the two phases is small and that the enthalpy of vaporisation of \(CO_2\) is negligible as the operating conditions are close or above the critical point. In the case where only one phase is stable for a pure component at the conditions of interest, as is typically the case for \(CO_2\), one can access the hypothetical phase information by providing an adequate initial guess for the molar volume to the SAFT-VR equation of state.

**Equilibrium relations**

Both chemical and phase equilibrium are assumed to prevail at the interface so that the conditions of equality of pressure, temperature, and chemical potential must be satisfied:

\[
\mu(T^I_j, V^I_{j,V}, y^I_j) = \mu(T^I_j, V^I_{j,L}, x^I_j) = \mu^L_j = \mu^V_j \quad j = 1, 2, \ldots, N_s \quad (4.19)
\]

\[
P(T^I_j, V^I_{j,V}, y^I_j) = P(T^I_j, V^I_{j,L}, x^I_j) = P^I_j \quad j = 1, 2, \ldots, N_s \quad (4.20)
\]

where \(\mu^L_j\) and \(\mu^V_j\) are the vector of chemical potential on stage \(j\) in the liquid and gas phases respectively \((\text{J mol}^{-1})\), \(V^L_{j,L}\) and \(V^V_{j,V}\) are the molar volumes of the liquid phase and the gas phases at the vapour-liquid interface of stage \(j\) \((\text{cm}^3 \text{ mol}^{-1})\), and \(P^I_j\) is the
pressure at the liquid-vapour interface of stage $j$ (MPa). The chemical potentials and the molar volume are determined using the SAFT-VR foreign object.

The mole fractions at the interface must sum to unity:

$$\sum_{i=1}^{c} x_{i,j} = 1 \quad \text{and} \quad \sum_{i=1}^{c} y_{i,j} = 1 \quad j = 1, 2, ..., N_s \tag{4.21}$$

Each stage is assumed to be at mechanical equilibrium, so that

$$P_j^V = P_j^L = P_j^I \quad j = 1, 2, ..., N_s \tag{4.22}$$

where

$$P_j^V = P(T_j^V, V_j^V, \bar{y}_j) \quad j = 1, 2, ..., N_s \tag{4.23}$$

$$P_j^L = P(T_j^L, V_j^L, \bar{x}_j) \quad j = 1, 2, ..., N_s \tag{4.24}$$

Finally, the column pressure drop is assumed to be negligible

$$P_{j-1}^V = P_j^V \quad j = 2, ..., N_s \tag{4.25}$$

This assumption can easily be removed at a later stage of the model development. Preliminary results have indicated that the pressure drop has a negligible effect on the process used for the validation of our model.

The equations presented in the remainder of this section apply to each stage. The subscript $j$ has been omitted for the purpose of clarity.

**Mass transfer correlations**

The interfacial area, the liquid phase mass-transfer coefficient and the gas phase mass-transfer coefficient are obtained using the correlations from Onda et al. (1968a,b). Other
correlations exist, the most commonly used being the ones developed by Rocha et al. (1996) and Billet and Schultes (1999). Faramarzi et al. (2010) compared performances of the correlations and found that all three correlations provide a good description. They expressed a slight preference for the correlations of Rocha et al. (1996) but could not draw a general conclusion which is applicable to all operating conditions. The correlations of Rocha et al. (1996) apply to structured packing and have to be adapted for use in random packing, whereas those developed by Onda et al. (1968a,b) have been developed specifically using random Berl saddle packing, the same as the one employed in the pilot plant by Tontiwachwuthikul et al. (1992). This last set of correlations is sometimes reparametrised when used in commercial software like Aspen or ProTreat. The correlations developed by Onda et al. (1968a,b), as reported by Treybal (1981), are implemented in our model of the absorber column. The liquid phase mass transfer coefficient for component \( i \) is given by (Treybal, 1981)

\[
k_i^L = 0.0051 \left( \frac{\eta_L g}{\rho_L} \right)^{1/3} \left( \frac{Re_L'}{Sc_i^L} \right)^{2/3} \left( \frac{a_p L_p}{L_i} \right)^{0.4} \quad i = 1, 2, ..., c
\]  

(4.26)

where \( \rho_L \) is the density of the liquid phase (kg m\(^{-3}\)), \( \eta_L \) is the dynamic viscosity of the liquid phase (kg m\(^{-1}\) s\(^{-1}\)), \( g \) is the gravitational acceleration (m s\(^{-2}\)), \( Re_L' \) is the liquid-phase Reynolds number based on the interfacial area, \( Sc_i^L \) is the Schmidt number of component \( i \) in the liquid phase, \( a_p \) is the specific surface area of the packing (m\(^2\) m\(^{-3}\)), and \( L_p \) is the nominal packing size (m).

The Reynolds and the Schmidt numbers for component \( i \) in the liquid phase are

\[
Re_L' = \frac{\rho_L u_L}{\alpha_i \eta_L}
\]

(4.27)

\[
Sc_i^L = \left( \frac{\eta_L}{\rho_L D_i^L} \right) \quad i = 1, 2, ..., c
\]

(4.28)

where \( D_i^L \) is the diffusion coefficient of component \( i \) in the liquid phase (m\(^2\) s\(^{-1}\)), \( u_L \) is
the liquid velocity ($m \, s^{-1}$), and $a'$ is the interfacial area density defined in equation (4.32).

The vapour-phase mass-transfer coefficient is obtained from

$$k_i^V = 2a_p D_i^V Re_i^V 0.7 Sc_i^V 1/3 (a_p L_p)^{-2} \quad i = 1, 2, \ldots, c$$

(4.29)

where $D_i^V$ is the diffusivity of component $i$ in the vapour-phase ($m^2 \, s^{-1}$), $Re_i^V$ is the vapour-phase Reynolds number, and $Sc_i^V$ is the Schmidt number of component $i$ in the vapour phase.

The Reynolds and the Schmidt numbers for the vapour phase are

$$Re_i^V = \frac{\rho_i^V u_i^V}{\eta_i^V}$$

(4.30)

$$Sc_i^V = \left( \frac{\eta_i^V}{\rho_i^V D_i^V} \right) \quad i = 1, 2, \ldots, c$$

(4.31)

where $\rho_i^V$ is the density of the vapour phase ($kg \, m^{-3}$), $\eta_i^V$ is the dynamic viscosity of the vapour phase ($kg \, m^{-1} \, s^{-1}$), and $u_i^V$ is the vapour velocity ($m \, s^{-1}$).

The interfacial area density $a'$ is obtained from (Onda et al., 1968a,b)

$$\frac{a'}{a_p} = 1 - \exp(-1.45(\frac{\sigma_c}{\sigma})^{0.75}(Re_L^{1.0})(Fr_L)^{-0.05}(We_L)^{0.2})$$

(4.32)

where $\sigma_c$ is the critical surface tension of the packing material ($N \, m^{-1}$), $\sigma$ is the vapour-liquid surface tension ($N \, m^{-1}$), $Re_L$ is the liquid-phase Reynolds number based on the specific surface area, $Fr_L$ is the liquid-phase Froude number, and $We_L$ is the liquid-phase Weber number. The interfacial area density, together with the three dimensionless numbers used in equation 4.32, are properties of the mixture, not properties of individual
components.

The expressions of the dimensionless numbers are

\[
Rc^L = \frac{\rho^L u^L}{\eta^L a_p} \tag{4.33}
\]

\[
Fr^L = \frac{a_p u^L}{g} \tag{4.34}
\]

\[
We^L = \frac{\rho^L u^L}{a_p \sigma} \tag{4.35}
\]

The velocities of each phase are

\[
u^L = \frac{\dot{v}^L}{A_{section}} \tag{4.36}
\]

\[
u^V = \frac{\dot{v}^V}{A_{section}} \tag{4.37}
\]

where \(\dot{v}^L\) and \(\dot{v}^V\) are the volumetric flowrate of the liquid and gas phase respectively (m\(^3\) s\(^{-1}\)).

**Heat transfer correlations**

For the gas and liquid heat-transfer coefficients the correlations presented in Treybal’s *Mass Transfer Operations* (Treybal, 1981) are used. Once again these expressions apply to each stage. The expression for the liquid-phase heat-transfer coefficient is

\[
\frac{h^L_f d_s}{\lambda^L_f} = 25.1 \left( \frac{d_s L_{spec}}{\eta^L} \right)^{0.45} (Pr^L)^{0.45} \tag{4.38}
\]

where \(h^L_f\) is the liquid-phase heat-transfer coefficient (W m\(^{-2}\) K\(^{-1}\)), \(d_s\) is the diameter of a sphere of the same surface area as a single packing particle (not the same as \(a_p\)) (m), \(\lambda^L_f\) is the liquid thermal conductivity (W m\(^{-1}\) K\(^{-1}\)), \(L_{spec}\) is the specific liquid flowrate...
(kg s\(^{-1}\)), and \(P_{RL}\) is the liquid phase Prandtl number. Its expression is given by

\[
P_{RL} = \frac{C_{LP} \eta^L}{\lambda^L} \tag{4.39}
\]

where \(C_{LP}\) is the specific heat capacity of the liquid phase (J kg\(^{-1}\) K\(^{-1}\)). The vapour-phase heat-transfer coefficient is given by

\[
\frac{h_V}{C_p V_{spec}} P_{RV}^{2/3} = 1.195 \left( \frac{d_s V_{spec}}{\eta^V (1 - \epsilon_{L0})} \right)^{-0.36} \tag{4.40}
\]

where \(h_V\) is the vapour-phase heat transfer coefficient (W m\(^{-2}\) K\(^{-1}\)), \(C_p^V\) is the specific heat capacity of the vapour phase (J kg\(^{-1}\) K\(^{-1}\)), \(P_{RV}\) is the Prandtl number for the gas phase, \(V_{spec}\) is the specific vapour flowrate (kg s\(^{-1}\)), and \(\epsilon_{L0}\) is the operating void space in the packing. It is assumed to be equal to the void fraction \(\epsilon\). The Prandtl number for the gas phase is

\[
P_{RV} = \frac{C_{PV} \eta^V}{\lambda^V} \tag{4.41}
\]

where \(\lambda^V\) is the vapour thermal conductivity (W m\(^{-1}\) K\(^{-1}\)).

**Vapour-phase diffusion coefficient**

The vapour-phase diffusion coefficient used in equation (6.5) is obtained from the Fuller expression reported by Poling et al. (2001). It is assumed that the components are diffusing through air (Poling et al., 2001).

\[
D_i^V = 10^{-4} \frac{0.00143 T^{1.75}}{10 P^V M_{i-\text{air}}^{1/2} \left[ \Sigma_v^{1/3} + \Sigma_{v\text{air}}^{1/3} \right]} \quad i = 1, 2, ..., c \tag{4.42}
\]

where \(\Sigma_v\) is the atomic diffusion volume (Å), and \(M_{i-\text{air}}\) is given by

\[
M_{i-\text{air}} = 2 \left[ (1/M_{\text{air}}) + (1/M_i) \right]^{-1} \quad i = 1, 2, ..., c \tag{4.43}
\]
where $M_i$ is the molecular weight of component $i$ (g mol$^{-1}$).

**Liquid-phase diffusion coefficient**

The liquid-phase binary diffusion coefficients are obtained through different correlations. The mutual diffusion coefficients (cm$^2$ s$^{-1}$) of CO$_2$ at very low concentration in pure MEA and pure H$_2$O are derived from the Wilke-Chang correlation (Poling et al., 2001):

$$D_{CO_2,k}^o = \frac{7.4 \times 10^{-8}(\phi_k M_k)^{1/2} T^L}{\eta_k^L (V_{CO_2}^m)^0.6} \quad k = H_2O, MEA \quad (4.44)$$

where $\phi_k$ is the "association factor" of solvent $k$ (-), and $V_i^m$ is the molar volume of component $i$ at its normal boiling temperature (cm$^3$ mol$^{-1}$).

These mutual diffusion coefficients are used in the Takahashi correlation (Takahashi et al., 1982) to determine the diffusivity of CO$_2$ in a liquid mixture of H$_2$O and MEA:

$$D_{CO_2}^L = \tau 10^{-4} \left( \frac{V^L}{\eta^L} \right)^{1/3} \sum_{k=H_2O,MEA} x_k D_{CO_2,k}^o \left( \frac{\eta_k^L}{V_k^L} \right)^{1/3} \quad (4.45)$$

where we have introduced the scaling factor $\tau$ to the correlation. The factor $10^{-4}$ is converting the diffusion coefficient from cm$^2$ s$^{-1}$ to m$^2$ s$^{-1}$. Its value is discussed in section 5. A graph depicting the variation of the diffusion coefficient of CO$_2$ in the liquid phase with regard to the temperature is presented in Figure 4.3.

Finally, the Perkins and Geankoplis method (Perkins and Geankoplis, 1969) is used to calculate the diffusivity of H$_2$O, MEA and N$_2$ in the liquid phase:

$$D_i^L = 10^{-4} \frac{7.4 \times 10^{-8}(\phi M)^{1/2} T}{1000 \eta^L (V_i^m)^0.6} \quad i = H_2O, MEA, N_2 \quad (4.46)$$

where the term $(\phi M)_i$ represents the “association factor” of component $i$ in the liquid
Figure 4.3: Variation of the diffusion coefficient of CO$_2$ in the liquid phase with regard to the temperature. (a) Results obtained without scaling the diffusivity ($\tau = 1$), and (b) results obtained by scaling diffusivity to 3.7% of its original value ($\tau = 0.037$).
Table 4.1: Correlations used in the model.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Component</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid phase viscosity</td>
<td>H$_2$O</td>
<td>Westmeier (1977)</td>
</tr>
<tr>
<td></td>
<td>MEA</td>
<td>Leibush and Shorina (1947)</td>
</tr>
<tr>
<td></td>
<td>Mixture</td>
<td>Maham et al. (2002)</td>
</tr>
<tr>
<td>Vapour phase viscosity</td>
<td></td>
<td>Kestin et al. (1966)</td>
</tr>
<tr>
<td>Surface tension</td>
<td></td>
<td>Vazquez et al. (1997)</td>
</tr>
<tr>
<td>Heat conductivity</td>
<td></td>
<td>Haynes (2011)</td>
</tr>
<tr>
<td>Liquid heat capacity</td>
<td>H$_2$O</td>
<td>Laliberte (2009)</td>
</tr>
<tr>
<td></td>
<td>MEA</td>
<td>Mundhwa and Henni (2007)</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>Riddick et al. (1986)</td>
</tr>
<tr>
<td>Vapour heat capacity</td>
<td>N$_2$</td>
<td>Vargaftik (1972)</td>
</tr>
<tr>
<td></td>
<td>CO$_2$</td>
<td>Bender et al. (1981)</td>
</tr>
</tbody>
</table>

mixture (g mol$^{-1}$) and is derived from

$$(\phi M)_i = \sum_{j=1}^{n} x_j \phi_j M_j \quad i = \text{H}_2\text{O}, \text{MEA}, \text{N}_2 \quad (4.47)$$

The other correlations of experimental data used in our model are listed table 4.1.

In contrast with other CO$_2$-MEA absorber models, this model does not uses enhancement factor, defined as the ratio of the amount of gas absorbed in a reacting liquid to the amount which would be absorbed if there were no reaction (Danckwerts, 1970; DeCoursey, 1982; van Swaaij and Versteeg, 1992) It is generally accepted that for absorption within the fast pseudo first-order reaction regime, as is the case for CO$_2$ absorption with MEA (Laddha and Danckwerts, 1981; Blauwhoff et al., 1984) the enhancement factor could be approximated by the Hatta number (Danckwerts, 1970; Kucka et al., 2003b; Tobiesen et al., 2007) and is much greater than one. This means that the enhancement factor is increasing the value of the mass transfer coefficient and by doing so, favouring the mass transfer. It should be noted that the enhancement factor is not the same as the CO$_2$ diffusivity scaling parameter $\tau$ introduced in this chapter. They do not relate to the same physical properties as they stem from fundamentally differential approach towards the
modelling of the chemical reactions. The enhancement factor is introduced in a modelling approach using an explicit treatment of the chemical reactions whereas $\tau$ is introduced in an implicit reaction modelling approach.

4.4 Concluding remarks

A rate-based CO$_2$ absorber model incorporating a SAFT-VR thermodynamic treatment has been developed. The model combines physical and chemical interactions within the consistent thermodynamic framework (SAFT-VR) introduced in chapter 3, under the assumption that the chemical reactions are at equilibrium. The chemical reactions are treated implicitly in this formalism. Thus there is no need to incorporate an enhancement factor or to use experimental data on the rate of reaction. This greatly simplifies the description and provides a considerably more transferable model. At this point, it is more transferable in principle. Chapter 5 explores whether it is valid. Its transferability to other solvents is left for future work. A simple scaling of the CO$_2$ diffusivity in the liquid phase is proposed to account for the formation of carbamate. The correction of the enthalpy of absorption of CO$_2$ introduced in chapter 3 has been integrated in the energy balance. In the next chapter, this model is validated against pilot plant data and the model parameter $\tau$, accounting for the scaling of the CO$_2$ diffusivity in the liquid phase, is adjusted using pilot plant data.
Chapter 5

Absorber model results

5.1 Validation of the model

The absorber model developed in this study is validated by adjusting the model parameter $\tau$, as it appears in equation (4.45), to a small subset of the pilot plant experimental data obtained by Tontiwachwuthikul et al. (1992). These include measurements from one run at different points along the column of the temperature in the liquid phase, the mole fraction of CO$_2$ in the vapour phase, and the CO$_2$ loading in the liquid phase, defined as $\theta_{CO_2} = x_{CO_2}/x_{MEA}$, which have been successfully modelled by other authors (Kucka et al., 2003a; Gabrielsen et al., 2006; Faramarzi et al., 2010; Mac Dowell, 2010; Mac Dowell et al., 2013). The absorption column has an internal diameter of 0.1 m and a total packed height of 6.6 m; care has to be taken not to mistake the total column height of 7.2 m with the packed height, which is the relevant dimension in modelling the absorber. The absorption column internals are randomly packed 12.7 mm ceramic Berl saddles. The gas inlet stream is assumed to be free of MEA and the liquid solvent inlet stream free of N$_2$. The input values used are listed in Table 5.1 and the characteristics of the column and the packing are listed in Table 5.2.
Table 5.1: Inputs to absorber column model for runs T13 to T22 (Tontiwachwuthikul et al., 1992).

<table>
<thead>
<tr>
<th>Input variable</th>
<th>T13</th>
<th>T14</th>
<th>T15</th>
<th>T16</th>
<th>T17</th>
<th>T18</th>
<th>T19</th>
<th>T20</th>
<th>T21</th>
<th>T22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet gas flow (mol.m^{-2}.s^{-1})</td>
<td>17.54</td>
<td>17.54</td>
<td>18.4</td>
<td>17.51</td>
<td>17.54</td>
<td>18.29</td>
<td>16.72</td>
<td>18.32</td>
<td>13.72</td>
<td>18.3</td>
</tr>
<tr>
<td>Inlet gas pressure (MPa)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Inlet gas temperature (K)</td>
<td>292.15</td>
<td>292.15</td>
<td>292.15</td>
<td>292.15</td>
<td>293.15</td>
<td>293.15</td>
<td>292.15</td>
<td>292.15</td>
<td>292.15</td>
<td>292.15</td>
</tr>
<tr>
<td>Inlet gas CO₂ mole fraction</td>
<td>0.153</td>
<td>0.156</td>
<td>0.195</td>
<td>0.155</td>
<td>0.156</td>
<td>0.191</td>
<td>0.115</td>
<td>0.192</td>
<td>0.191</td>
<td>0.191</td>
</tr>
<tr>
<td>Inlet gas H₂O mass fraction</td>
<td>0.0058</td>
<td>0.0058</td>
<td>0.0058</td>
<td>0.0058</td>
<td>0.0058</td>
<td>0.0058</td>
<td>0.0058</td>
<td>0.0058</td>
<td>0.0058</td>
<td>0.0058</td>
</tr>
<tr>
<td>Inlet liquid flow (m³.m⁻².h⁻¹)</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>9.5</td>
<td>13.5</td>
<td>9.5</td>
<td>13.5</td>
<td>9.5</td>
<td>9.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Inlet liquid temperature (K)</td>
<td>292.15</td>
<td>292.15</td>
<td>292.15</td>
<td>292.15</td>
<td>293.15</td>
<td>293.15</td>
<td>292.15</td>
<td>292.15</td>
<td>292.15</td>
<td>292.15</td>
</tr>
<tr>
<td>Inlet MEA concentration (kmol.m⁻³)</td>
<td>2.00</td>
<td>2.00</td>
<td>2.03</td>
<td>2.08</td>
<td>3.08</td>
<td>2.00</td>
<td>2.00</td>
<td>2.55</td>
<td>2.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Lean loading, $\theta_{CO_2}$</td>
<td>$10^{-4}$</td>
<td>0.118</td>
<td>$10^{-4}$</td>
<td>0.237</td>
<td>$10^{-4}$</td>
<td>$10^{-4}$</td>
<td>$10^{-4}$</td>
<td>$10^{-4}$</td>
<td>$10^{-4}$</td>
<td>$10^{-4}$</td>
</tr>
</tbody>
</table>
Table 5.2: Characteristics of the column and the packing

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{\text{section}} ) (m(^2))</td>
<td>0.00785</td>
<td>Tontiwachwuthikul et al. (1992)</td>
</tr>
<tr>
<td>( a_p ) (m(^2).m(^{-3}))</td>
<td>466</td>
<td>Treybal (1981)</td>
</tr>
<tr>
<td>( \sigma_c ) (N m(^{-1}))</td>
<td>61</td>
<td>Perry and Green, 2008, pg. 18-34, table 18-11</td>
</tr>
<tr>
<td>( L_p ) (m)</td>
<td>0.0127</td>
<td>Tontiwachwuthikul et al. (1992)</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>0.63</td>
<td>Treybal, 1981, pg. 198, table 6.3</td>
</tr>
<tr>
<td>( D_z ) (m)</td>
<td>0.132</td>
<td>Tontiwachwuthikul et al. (1992)</td>
</tr>
<tr>
<td>( N_s )</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>( d_s ) (m)</td>
<td>0.31622</td>
<td>Treybal, 1981, pg. 206, table 6.5</td>
</tr>
</tbody>
</table>

Some of the data needed for the simulation of the process were not explicitly reported by Tontiwachwuthikul et al. (1992): in particular, the temperature of the flue gas; and the quantity of water in the flue gas. Close inspection of an earlier paper (Tontiwachwuthikul et al., 1989) detailing the experimental apparatus reveals that the temperature of the flue gas is controlled to be that of the lean solvent with a thermostatic bath. The inlet vapour stream is composed of ambient air and bottled CO\(_2\). Typical values of relative humidity of air lie between 20% to 70%, which, at 20°C and 1 bar, corresponds to an amount of H\(_2\)O in the flue gas between \( \omega_{\text{H}_2\text{O}} \) \( \simeq \) 0.0025 and \( \omega_{\text{H}_2\text{O}} \) \( \simeq \) 0.01, where \( \omega_{\text{H}_2\text{O}} \) is the mass fraction of component \( i \) in the vapour phase.

A sensitivity analysis of the extent of humidity indicates that the variation of \( \omega_{\text{H}_2\text{O}} \) between 0.0025 and 0.01 has a negligible impact on the temperature and composition profiles. The effect of the amount of water in the flue gas is discussed in more detail in the next section. For our working model, the amount of water in the inlet flue gas is fixed to \( \omega_{\text{H}_2\text{O}} \) \( = \) 0.0058, corresponding to 50% humidity at 20°C and 1 bar.

The validation is performed using the operating conditions of Run T22 (Tontiwachwuthikul et al., 1992). In preliminary calculations with unadjusted model parameters (i.e., \( \tau=1 \)), the rate of absorption of CO\(_2\) along the column was found to be over-predicted. In order to investigate the nature of the over-prediction of the rate of absorption, a sensitivity analysis is performed and the most influential parameter for the description of the composition profile is found to be the diffusivity of CO\(_2\) in the liquid phase. In our
reaction-implicit model, the amount of CO$_2$ in any phase represents a combination of free CO$_2$, bicarbonate and carbamate. The relative amount of each component can be extracted from the SAFT-VR treatment of the association aggregates (Rodríguez et al., 2012), although this information is not used explicitly in the process model. In practice, the CO$_2$ in the liquid phase is mostly carbamate, a much larger molecular species than CO$_2$, which is expected to have a reduced diffusion in the medium compared to free CO$_2$. The CO$_2$ diffusivity in the liquid phase is therefore scaled down to account for the high proportion of carbamate; a good estimate of the rate of absorption of CO$_2$ is thereby obtained. The extent of rescaling can be estimated from the experimental data obtained from Run T22 (Tontiwachwuthikul et al., 1992) for the gas and liquid composition profiles. On this basis, the value of the liquid-phase CO$_2$ diffusivity in our model that results in the minimum deviation with the pilot plant data corresponds to a scaling to 3.7% of its original value (i.e., $\tau = 0.037$). The scaling parameter $\tau$ is related to mass transfer effects so it was deemed appropriate to favour the composition profile over the temperature for the determination of its value. Han et al. (2013) recently presented a molecular dynamics study of diffusion of CO$_2$ in pure MEA, where CO$_2$ is treated as a combination of free CO$_2$ and CO$_2$-containing aggregates. They suggested a reduction of the liquid CO$_2$ diffusion coefficient by a factor of 0.025. Although no water was included in this theoretical investigation, leading to a comparatively high liquid viscosity, it is interesting to note that the relative change in diffusivity was found to be commensurate with that proposed here. The liquid-phase temperature, gas-phase CO$_2$ concentration, and liquid-phase CO$_2$ concentration profiles for Run T22, determined with and without a scaling of the diffusivity, are presented in Figure 5.1.

Because the parameter $\tau$ is estimated from pilot plant data the value found for $\tau$ may be correcting any potential errors in the chosen mass transfer correlation rather than the diffusivity only. To the best of our knowledge, there is no published experimental data for the diffusion of carbamate in MEA and H$_2$O mixtures. In order to assess the validity of the proposed scaling and the impact of choice of the mass-transfer correlation on its value, we implemented the mass-transfer correlations of Rocha et al. (1993, 1996) in our
Figure 5.1: Comparison of the pilot plant data (squares) (Tontiwachwuthikul et al., 1992) and the result of our model (curves) for Run T22 for the absorption of CO$_2$ in an 18wt% solution of MEA. The dashed curves represent the results obtained without scaling the diffusivity ($\tau = 1$) and the continuous curves the results obtained by scaling the CO$_2$ diffusivity in the liquid phase to 3.7% of its original value ($\tau = 0.037$). a) Temperature profile for the liquid phase, b) gas-phase CO$_2$ concentration profile, and c) liquid-phase CO$_2$ loading. Stage 50 corresponds to the bottom of the column.
5. Absorber model results

current model of the absorber with the same scaling of the diffusivity \((\tau = 0.037)\). The results for the liquid-phase temperature, gas-phase CO\(_2\) concentration, and liquid-phase CO\(_2\) concentration profiles for Run T22 with the two different mass transfer correlations are compared in Figure 5.2. It can be seen that the profiles obtained are very similar: with the correlation of Rocha et al. (1993, 1996) there is a slight underestimation of the composition of CO\(_2\) in the liquid and gas phases, but the temperature profile obtained with the correlation of Rocha et al. (1993, 1996) is more faithful to the pilot plant data than that of Onda et al. (1968a,b). In conclusion, the value of \(\tau\) is essentially found to be independent of the choice of the mass-transfer correlation, confirming our hypothesis that a scaling of the diffusivity is required.
Figure 5.2: Sensitivity analysis of the mass transfer correlation on the profiles predicted with our model compared with the experimental pilot plant data of Run T22 (Tontiwachwuthikul et al., 1992): Mass-transfer correlations from Onda et al. (1968a,b) (continuous curve), mass-transfer correlations from Rocha et al. (1993, 1996). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile, and (c) liquid phase CO$_2$ loading.
5.2 Model predictions

All the runs using MEA from the pilot plant absorber are simulated using the diffusivity parameter ($\tau=0.037$) obtained during the validation step (previous section). The predictions for the temperature profile in the liquid phase, gas phase CO$_2$ concentration, and liquid phase CO$_2$ concentration for the different Runs T13 to T21 (Tontiwachwuthikul et al., 1992) are presented in Figures 5.3 to 5.11. These runs represent a wide range of operating conditions in terms of amine concentration, inlet liquid phase CO$_2$ loading, inlet gas phase CO$_2$ concentration, and gas-to-liquid flow-rate ratio (see Table 5.1).
Figure 5.3: Comparison of the pilot plant data (squares) and the predictions with our model (continuous curves) for run T13 taken from the work of Tontiwachwuthikul et al. (1992). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile, and (c) liquid phase CO$_2$ loading.
Figure 5.4: Comparison between pilot plant data (squares) and models predictions (continuous curves) for run T14 taken from the work of (Tontiwachwuthikul et al., 1992). (a) Temperature profile for the liquid phase, (b) gas phase CO₂ concentration profile and, (c) liquid phase CO₂ loading.
Figure 5.5: Comparison between pilot plant data (squares) and models predictions (continuous curves) for run T15 taken from the work of (Tontiwachwuthikul et al., 1992). (a) Temperature profile for the liquid phase, (b) gas phase CO\textsubscript{2} concentration profile and, (c) liquid phase CO\textsubscript{2} loading.
Figure 5.6: Comparison between pilot plant data (squares) and models predictions (continuous curves) for run T16 taken from the work of Tontiwachwuthikul et al. (1992). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile and, (c) liquid phase CO$_2$ loading.
Figure 5.7: Comparison between pilot plant data (squares) and models predictions (continuous curves) for run T17 taken from the work of Tontiwachwuthikul et al. (1992). (a) Temperature profile for the liquid phase, (b) gas phase CO₂ concentration profile and, (c) liquid phase CO₂ loading.
Figure 5.8: Comparison between pilot plant data (squares) and models predictions (continuous curves) for run T18 taken from the work of Tontiwachwuthikul et al. (1992). (a) Temperature profile for the liquid phase, (b) gas phase CO\textsubscript{2} concentration profile and, (c) liquid phase CO\textsubscript{2} loading.
Figure 5.9: Comparison between pilot plant data (squares) and models predictions (continuous curves) for run T19 taken from the work of Tontiwachwuthikul et al. (1992). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile and, (c) liquid phase CO$_2$ loading.
Figure 5.10: Comparison between pilot plant data (squares) and models predictions (continuous curves) for run T20 taken from the work of Tontiwachwuthikul et al. (1992). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile and, (c) liquid phase CO$_2$ loading.
Good agreement is found between the model predictions and the pilot plant data for Runs T13, T14, T16, T17, T19, and T20 in relation to the liquid-phase temperature and the liquid- and gas-phase composition profiles along the entire length of the column. This demonstrates that the scaling procedure can be applied in a transferable manner to different operating conditions. There is a slight over-prediction of the temperature and the composition profile for runs T15 and T21, though the compositions at the top and the bottom of the column are accurately described. The outlet liquid temperature in run T18 is overestimated by about 12K. There is a good match between the model predictions and the experimental values for the composition profiles. Although there is a slight over-prediction in Run T16, a good representation of the temperature bulges in Runs T16 and T20 can be seen in terms of location along the column, and the amplitude is accurately predicted in run T20. To the best of our knowledge, no other published models provide a description of the temperature bulge to this level of accuracy (Kucka et al., 2003a; Gabrielsen et al., 2006; Faramarzi et al., 2010; Mac Dowell et al., 2013). In keeping with our objective to develop a predictive model to support solvent design activities, the CO$_2$ diffusivity scaling parameter $\tau$ is not readjusted for each of the pilot plant runs. This is in stark contrast with models based on an enhancement factor (van Swaaij and Versteeg, 1992), where the model has to be adjusted for the different operating conditions. The behaviour of runs T15, T18 and T21 could be represented more accurately if we undertook such a refinement.

In all runs but T18, flat profiles are found toward the top of the column. This plateau means that a maximum in the absorption is reached, meaning that equilibrium is achieved not only at the liquid-phase interface but also between the bulk liquid and the bulk vapour phases. As a result, the profiles would not be affected by making the column any higher. This plateau is depicted in Figure 5.12 for run T22. It can be seen that the temperature of the liquid, the vapour phase, and the vapour-liquid interface are all equal between stages 1 and 15 (i.e., the top of the column). Similarly, the CO$_2$ gas phase composition in the bulk vapour phase and at the vapour interface are equal, as are the CO$_2$ loadings in the liquid phase and at the interface between stages 1 and 15. Additionally, the profiles
Figure 5.11: Comparison between pilot plant data (squares) and models predictions (continuous curves) for run T21 taken from the work of Tontiwachwuthikul et al. (1992). (a) Temperature profile for the liquid phase, (b) gas phase CO\textsubscript{2} concentration profile and, (c) liquid phase CO\textsubscript{2} loading.
for the temperature of the liquid phase and the temperature at the interface are almost identical, suggesting that all the heat-transfer resistance is in the vapour film.

In this set of runs, T18 stands out as it does not exhibit a plateau in the profiles as found for the other operating conditions, meaning that the whole length of the column is used for absorption. This is illustrated in Figure 5.13. The conditions for equilibrium are briefly met at the bottom of the column (large values of the stages) for the compositions profiles but there is no clear levelling off of the profiles. From Table 5.1, it appears that Run T18 has the lowest amount of MEA in the lean solvent and the highest amount of CO$_2$ in the flue gas compared to the other runs. This explains why the whole column is used for absorption. In the other runs, the totality of CO$_2$ is absorbed as the gas travels upwards between stages 50 and 15. So the lean solvent flowing at the top of the absorber (stages 1 to 15) has nothing to absorb. Run T18 is the only run where there is still CO$_2$ in the gas stream leaving the absorber, so the lean solvent starts absorbing CO$_2$ as soon as it enters the column at the top.

Overall the model exhibits very good prediction capabilities over a very wide range of operating conditions.
Figure 5.12: Run T22 of the pilot plant data from Tontiwachwuthikul et al. (1992). Comparison of the predictions of our model for: (a) temperature of the bulk liquid phase (continuous curve), the temperature at the vapour-liquid interface (dashed curve) and the temperature for the bulk vapour phase (dot-dashed curve); (b) the gas phase CO\textsubscript{2} concentration in the bulk vapour phase (continuous curve) and at the interface (dashed curve); (c) the liquid phase CO\textsubscript{2} loading in the bulk liquid phase (continuous curve) and at the interface (dashed curve).
Figure 5.13: Run T18 of the pilot plant data from Tontiwachwuthikul et al. (1992). Comparison of the predictions of our model for: (a) temperature of the bulk liquid phase (continuous curve), the temperature at the vapour-liquid interface (dashed curve) and the temperature for the bulk vapour phase (dot-dashed curve); (b) the gas phase CO$_2$ concentration in the bulk vapour phase (continuous curve) and at the interface (dashed curve); (c) the liquid phase CO$_2$ loading in the bulk liquid phase (continuous curve) and at the interface (dashed curve).
5.3 Sensitivity analysis

The relative importance of several mass- and heat-transfer parameter is now assessed using a sensitivity analysis. Different key parameters in the model are altered to observe their impact on the predicted profiles. The values tested are listed in Table 5.3.

5.3.1 Mass transfer

The mass transfer in the model is mediated via mass-transfer coefficients (Onda et al., 1968a,b). These coefficients are highly dependent on the viscosity, the diffusivity, and the surface tension of the fluid considered; these three properties are thus considered as key parameters in the model and their influence on the temperature and composition profiles are assessed. The value of each parameter in each phase is doubled and halved in order to determine the effect on the temperature and composition profiles. Varying the diffusivity or viscosity in the gas phase has no visible effect on the liquid temperature profile or the composition profiles. However, varying these parameters in the liquid phase results in a significant variation in the profiles. The effect on the profiles due to the variation of the liquid viscosity and the diffusivity in the liquid phase is represented in Figures 5.14 and 5.15. Varying the surface tension also produces a significant variation in the profiles as can be seen in Figure 5.16. The data that were originally considered for the surface tension correlation in our model is for a mixture of only H$_2$O and MEA (Vazquez et al., 1997). Jayarathna et al. (2013) published very recently experimental data of the surface tension of liquid mixtures of H$_2$O, MEA and CO$_2$, finding an increase in the vapour-liquid interfacial tension on absorption of CO$_2$. A new correlation from these data is also implemented in our process model. The comparisons of the temperature and composition profiles obtained with the two different correlations is shown in Figure 5.16. The difference in the profiles is negligible so changing the surface tension correlation is not considered necessary.
Table 5.3: Sensitivity analysis of key parameters in the model

<table>
<thead>
<tr>
<th>Parameter description</th>
<th>Variation</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour diffusivity</td>
<td>doubled</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td></td>
</tr>
<tr>
<td>Liquid diffusivity</td>
<td>doubled</td>
<td>significant effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td>see figure 5.14</td>
</tr>
<tr>
<td>Vapour viscosity</td>
<td>doubled</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td></td>
</tr>
<tr>
<td>Liquid viscosity</td>
<td>doubled</td>
<td>significant effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td>see figure 5.15</td>
</tr>
<tr>
<td>Surface tension</td>
<td>doubled</td>
<td>significant effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td>see figure 5.16</td>
</tr>
<tr>
<td>Heat transfer liquid</td>
<td>× 10</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>÷10</td>
<td></td>
</tr>
<tr>
<td>Heat transfer vapour</td>
<td>× 10</td>
<td>limited effect</td>
</tr>
<tr>
<td></td>
<td>÷10</td>
<td>see figure 5.18</td>
</tr>
<tr>
<td>Enthalpy of absorption</td>
<td>doubled</td>
<td>significant effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td>see figure 5.17</td>
</tr>
<tr>
<td>Heat of vaporisation of water</td>
<td>doubled</td>
<td>significant effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td>see figure 5.19</td>
</tr>
</tbody>
</table>
It should be noted that the values of the profiles at the outlets are not affected by the variations of the surface tension or the viscosity and diffusivity in the liquid phase. It would be safe to assume that under these operating conditions, where the residence time is large enough for the system to reach equilibrium, the outlet values are determined solely by thermodynamic quantities while the composition profiles are mostly dependent on mass transfer.

### 5.3.2 Heat transfer

The major source of heat in the absorption process is a consequence of the exothermic reaction between MEA and CO$_2$, which occurs in the liquid phase. This heat can then be transferred to the vapour phase. Another major element in the energy balance is the heat associated with the transfer of water from one phase to the other. In the model, the heat transfer is mediated via the heat-transfer coefficients (Treybal, 1981). Four key thermal parameters can be identified in the model: the heat of absorption of CO$_2$, the heat-transfer coefficient for the liquid phase, the heat-transfer coefficient for the gas phase, and the heat of vaporisation of H$_2$O. Kvamsdal and Rochelle (2008) and Faramarzi et al. (2010) identified the heat capacities as sensitive parameters for the temperature profiles, this is due to the fact that in their model, the heat capacities are included in the energy balance as they are used explicitly to determine the enthalpies. This is not the case in our model as the enthalpies are derived from the SAFT-VR equation of state. Although the heat capacities are used inside SAFT-VR to determine the ideal contribution toward the enthalpies, they appear explicitly in the gPROMS model only in the heat-transfer coefficient correlations, hence the choice of these coefficients as key parameters. The values of the four parameters (the heat of absorption of CO$_2$, the heat transfer coefficient for the liquid phase, the heat transfer coefficient for the gas phase and the heat of vaporisation of H$_2$O) are hence varied to observe the impact on the liquid phase temperature profile and
Figure 5.14: Sensitivity analysis of the CO₂ diffusivity in the liquid phase on the profiles predicted with our model in terms of the scaling parameter \( \tau \) compared with the experimental pilot plant data of Run T22 (Tontiwachwuthikul et al., 1992). \( \tau = 0.037 \) (continuous curve), \( \tau = 0.074 \) (dashed curve), \( \tau = 0.0185 \) (dot-dashed curve). (a) Temperature profile for the liquid phase, (b) gas phase CO₂ concentration profile, and (c) liquid phase CO₂ loading.
Figure 5.15: Sensitivity analysis of the liquid viscosity on the profiles predicted with our model compared with the experimental pilot plant data of Run T22 (Tontiwachwuthikul et al., 1992): Nominal value (continuous curve), viscosity doubled (dashed curve), viscosity halved (dot-dashed curve). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile, and (c) liquid phase CO$_2$ loading.
Figure 5.16: Sensitivity analysis of the vapour-liquid surface tension on the profiles predicted with our model compared with the experimental pilot plant data of Run T22 (Tontiwachwuthikul et al., 1992): Nominal value (continuous curve) (Vazquez et al., 1997), surface tension doubled (dashed curve), surface tension halved (dot-dashed curve), surface tension correlation from data from Jayarathna et al. (2013) (dotted curve). (a) Temperature profile for the liquid phase, (b) gas phase CO₂ concentration profile, and (c) liquid phase CO₂ loading.
the composition profiles. For our particular model, the sensitivity of the heat of absorption of CO$_2$ can be assessed by varying the value of the correction factor $\delta H_{CO_2}$. Although the heat of absorption of CO$_2$ and the heat of vaporisation of water are known thermodynamic quantities, their variation provides insights into the behaviour of the column. Their values were doubled and halved, and the values of the heat transfer coefficients were multiplied by 10 and divided by 10 (Table 5.3). The variation of the liquid heat-transfer coefficient had no visible effect on the liquid-phase temperature and composition profile. The effects on the profiles resulting from varying the correction factor of the heat of absorption, the vapour heat-transfer coefficient, and the heat of vaporisation of water are presented in Figures 5.17, 5.18 and 5.19, respectively.

The first observation that can be made from these graphs is that varying the thermal parameters does not have a significant impact on the composition profiles. The effect is visible only on the liquid-phase temperature profile. The heat of absorption of CO$_2$ does have a significant effect on the outlet temperature value. However, its variation has a negligible impact on the amplitude of the temperature bulge, as can be seen in Figure 5.17. The effect of the variation of the vapour-phase heat-transfer coefficient is illustrated in Figure 5.18. Despite a variation of one order of magnitude in the parameter value, the effect on the temperature profile is very limited. Furthermore, the effect due to the variation of the liquid-phase heat-transfer coefficient is equally negligible. It can be concluded that for the operating conditions under consideration, the model is insensitive to the heat-transfer coefficients. This is why we have not refined the heat-transfer correlations in our current study.

The value of heat of vaporisation of H$_2$O is known experimentally but the sensitivity analysis allows to investigate the importance of water phase changes. Its variation is found to have a significant impact on the liquid phase temperature profile and a lesser impact on the composition profiles; it has virtually no effect on the end-point values. The effect on the temperature profile is concentrated on the temperature bulge. An increase in the
Figure 5.17: Sensitivity analysis of the heat of absorption of CO$_2$ on the profiles predicted with our model in terms of the correction factor $\delta H_{CO_2}$ compared with the experimental pilot plant data of Run T22 (Tontiwachwuthikul et al., 1992). $\delta H_{CO_2} = 50$ kJ mol$^{-1}$ (continuous curve), $\delta H_{CO_2} = 100$ kJ mol$^{-1}$ (dashed curve), $\delta H_{CO_2} = 25$ kJ mol$^{-1}$ (dot-dashed curve). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile, and (c) liquid phase CO$_2$ loading.
Figure 5.18: Sensitivity analysis of the vapour-phase heat-transfer coefficient on the profiles predicted with our model compared with the experimental pilot plant data of Run T22 (Tontiwachwuthikul et al., 1992). Nominal value (continuous curve), coefficient value increased ten times (dashed curve), coefficient value reduced ten times (dot-dashed curve). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile, and (c) liquid phase CO$_2$ loading.
Figure 5.19: Sensitivity analysis of the enthalpy of vaporisation of water on the profiles predicted with our model compared with the experimental pilot plant data of Run T22 (Tontiwachwuthikul et al., 1992). Nominal value (continuous curve), enthalpy doubled (dashed curve), enthalpy halved (dot-dashed curve). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile, and (c) liquid phase CO$_2$ loading.
heat of vaporisation magnifies the amplitude of the bulge, whereas a reduction eliminates the bulge. This suggests that the heat of vaporisation of H$_2$O is responsible for the rate at which the liquid heats up and cools down. The key elements to predict the temperature bulge accurately are therefore the enthalpy of absorption of CO$_2$ and the enthalpy of vaporisation of water. The absorption of CO$_2$ releases energy that heats both phases. As the gas temperature increases upon entering the column, water is transferred from the liquid phase to the gas phase through evaporation to maintain saturation; this results in an absorption of energy, and a consequent decrease in temperature.

In conclusion, the competition between those two thermal effects (absorption of CO$_2$, increases temperature and vaporisation of water, decreases temperature) are responsible for the observed and predicted temperature bulge. This interpretation is consistent with that reported in Mac Dowell et al. (2013).

5.3.3 Extent of water in the flue gas

The amount of water in the flue gas is considered as important in determining the position of the temperature bulge in the absorber (Kvamsdal and Rochelle, 2008; Kvamsdal et al., 2010). In the pilot plants of Tontiwachwuthikul et al. (1992) and Dugas (2006), the inlet flue gas is not saturated in water, while the flue gas is saturated in the pilot plants of Tobiesen et al. (2007) and Gabrielsen et al. (2007). In order to assess the impact of humidity in our model of the absorber, we have varied the amount of water in the inlet flue gas from $y_{H_2O} = 0$ to $y_{H_2O} = 0.08$ (above saturation). The effect on the profiles is represented in Figure 5.20. It is clear from the figure that varying the amount of water in the flue gas does not have a significant impact on the composition profiles. The effect is visible only for the liquid-phase temperature profile, where the outlet temperature value is higher by approximately 5 K for the saturated gas $y_{H_2O} = 0.08$ than for the dry gas $y_{H_2O} = 0$. This is in contrast to the work of Mac Dowell et al. (2013) who found a large
Figure 5.20: Sensitivity analysis of the amount of water in the inlet flue gas on the profiles predicted with our model compared with the experimental pilot plant data of Run T22 (Tontiwachwuthikul et al., 1992). Nominal value (continuous curve), $y_{H_2O} = 0.08$ (dashed curve), $y_{H_2O} = 0$ (dot-dashed curve). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile, and (c) liquid phase CO$_2$ loading.
effect of the humidity of the inlet gas on the profiles in the mass transfer zone.
5.4 Concluding remarks

The performances of the absorber model developed in chapter 3 and 4 have been assessed. Model validation has been carried out by comparison with published experimental pilot plant data (Tontiwachwuthikul et al., 1992). A central finding of our current study is that diffusivity of CO$_2$ in the liquid phase required adjustment in order to provide an accurate representation of the column profiles; this was done based on one pilot plant run, and used transferably to successfully model all other runs for different operating conditions. Very good predictions are obtained for the liquid-phase temperature profiles and liquid- and gas-phase compositions along the column. This highlights the importance of capturing the physical and chemical equilibria reliably; in addition the assumption that the process is not limited by reaction kinetics appears to be valid.

With a careful sensitivity analysis we show that the liquid viscosity and diffusivity, and vapour-liquid surface tension, are key properties for the prediction of the composition profiles. The heat generated by the absorption of CO$_2$ affects the magnitude of the temperature variation in the absorber and the vaporisation of water affects the presence and amplitude of the temperature bulge.

The transferability of this model to other operating conditions, more specifically its applicability to the desorption process is discussed in the next two chapters.
Chapter 6

Model of the regeneration module

6.1 Introduction

The solvent based carbon capture processes consist of two main parts: an absorber where the CO$_2$ is transferred from the gas phase to the liquid phase and reacts with the solvent (here MEA) to form a carbamate, and a solvent regeneration part where the rich solvent is heated up to break this carbamate and transfer the CO$_2$ to the gas phase. The lean solvent is then recycled back to the absorber. This second part is composed of a desorber column, similar to the absorber column, a reboiler at the bottom of the desorber to provide the heat required for the separation of the CO$_2$ from the solvent, and a condenser at the top of the desorber to condense the water back to the process and ensure a quasi-pure gas stream of CO$_2$. The heat requirement of the reboiler is the source of the high energy penalty in solvent-based carbon capture processes. The decarbonisation of a flue gas produced by a coal-fired power plant can represent an extra consumption of fuel of 20% (Parson and Keith, 1998). The energy penalty can be reduced in a number of ways, either by modifying the topology of the process to allow heat integration (Mimura et al., 1997; Desideri and Paolucci, 1999; Romeo et al., 2008; Jassim and Rochelle, 2006; Harkin et al., 2010; Ahn et al., 2013) or by changing the solvent (Mangalapally et al., 2009; Salkuyeh
and Mofarahi, 2012; Barzagli et al., 2012). Although some of these changes can reduce the energy penalty by up to 50%, there is still a need to reduce it further.

A number of models have been proposed for the amine-based CO₂ desorption. Most models are similar to those developed for the absorber: the heat- and mass-transfer models are identical, the thermodynamic model is similar but requires different parameter values based on experimental data for the temperature-dependent ones. These aspects have been covered in chapter 2. One important aspect of a desorber modelling is the treatment of the chemical reactions. In a desorber, the relevant temperature range is larger and there are limited data available for the rates of the reactions of interest at these temperatures so in some models, the chemical reactions are assumed to be instantaneous, i.e. chemical equilibrium prevails everywhere in the liquid phase, where the reactions are assumed to take place (Tobiesen et al., 2008; Lawal et al., 2010). If one wants to take into account the reaction kinetics then new rates of reactions are needed; this is the route followed by Greer et al. (2010); Plaza et al. (2010b); Gáspár and Cormo (2011) based on Aboudheir et al. (2003) experimental data. In all these models, the reboiler and condenser are modelled as equilibrium stages.

Tobiesen et al. (2008) validated their model against the CO₂ loading at the bottom of the desorber of their own pilot plant (Tobiesen et al., 2007, 2008). Their predictions exhibit an over prediction at higher loading. Although they reported experimental data for temperatures and flowrates in the flowsheet, they did not report any simulation results of these values.

Greer et al. (2010) did not validate their process model on pilot plant data.

Plaza et al. (2010b) validated their model using only one run from the pilot plant of Dugas (2006). Their model shows a good agreement for the temperature profile along the desorber column. However, due to the unreliability in some of the experimental data, they had to adjust some of them in order to close mass and energy balances and match CO₂ removal. An interfacial area factor was also introduced as an adjustable parameter in this model to correct the calculated interfacial area. Due to all these adjustments and the single run used for the validation, the predictive capabilities of their model is not
Lawal et al. (2010) also validated their results on the pilot plant from Dugas (2006). They presented two temperature profiles for two different runs with acceptable agreement of the trend between the model predictions and the experimental data. However, actual temperature values have a maximum error of about 5 K. There are no results on the CO\textsubscript{2} loading.

Gáspár and Cormo (2011) validated their model against pilot plant data from Tobiesen et al. (2007, 2008). They obtained a good agreement between the simulated values and the experimental values of the flowrate of the stream of CO\textsubscript{2} leaving the system. However, they simulated only 13 of the 19 runs performed by Tobiesen et al. (2008) and they did not validate the thermal predictions from their model.

Although it is fair to say that desorber validation is especially challenging because of the data uncertainties (Dugas, 2006; Tobiesen et al., 2008), no study to date has presented a comprehensive validation of an amine-based CO\textsubscript{2} desorber including compositions, temperatures and flowrates. This is the ambition of the model presented in this chapter and validated in the next chapter, using pilot plant data from Tobiesen et al. (2008).

The regeneration module is composed of three units: a desorber, a condenser and a reboiler. The models developed in this chapter are adapted from the absorber model presented earlier. These models can be divided in two parts: a thermodynamic model, in which the SAFT-VR equation of state is used, and a mass transfer model. The thermodynamic model used is identical to the one used for the absorber. The desorber column is described via rate-based stages with a different mass transfer correlation to model the different type of packing. The condenser and the reboiler are modelled as equilibrium stages.
6.2 Model of the desorber column

The model developed for the absorber is used for the desorber. However, in relation to specific pilot plant data, this model should be modified to be applicable to structured packing. The only change required are in the correlations for the mass transfer. They are presented in this section. A schematic of the desorber is presented in Figure 6.1.

The interfacial area, the liquid phase mass transfer coefficient and the gas phase mass transfer coefficient are obtained using the correlations from Rocha et al. (1996). These correlations have been developed specifically for structured packing, as used in the pilot plant by Tobiesen et al. (2008). The liquid phase mass transfer coefficient for component $i$ is given by

$$k_i^L = 2\left(\frac{C_e D_i^L u_c^L}{\pi S}\right)^{1/2} \quad i = 1, 2, ..., c$$  \hspace{1cm} (6.1)

where $C_e$ is a factor slightly less than unity to account for those parts of the packed bed that do not encourage rapid surface renewal (-), $D_i^L$ is the diffusion coefficient of
component $i$ in the liquid phase (m$^2$ s$^{-1}$), $u_e^L$ is the effective liquid-phase velocity (m s$^{-1}$), $S$ is the side dimension of corrugation (m).

The effective liquid-phase velocity is defined by

$$u_e^L = \frac{u^L}{\varepsilon h_t \sin \theta} \quad (6.2)$$

where $u^L$ is the superficial liquid velocity (m s$^{-1}$), $\varepsilon$ is the packing void fraction (-), $h_t$ is the liquid holdup (-), and $\theta$ is the angle with respect to the horizontal for falling film or corrugation channel.

The vapour phase mass transfer coefficient is obtained from

$$k_i^V = 0.054 \frac{D_i^V}{S} \left( \frac{\rho_i^V}{\eta_i^V} \frac{|u_e^L + u_e^V|}{1 - h_t} \right)^{0.8} \left( Sc_i^V \right)^{0.33} \quad i = 1, 2, ..., c \quad (6.3)$$

where $D_i^V$ is the diffusion coefficient of component $i$ in the vapour phase (m$^2$ s$^{-1}$), $\rho_i^V$ is the density of the vapour phase (kg m$^{-3}$), $u_e^V$ is the effective vapour-phase velocity (m s$^{-1}$), $\eta_i^V$ is the dynamic viscosity of the vapour phase (kg m$^{-1}$ s$^{-1}$), $Sc_i^V$ is the Schmidt number of component $i$ in the vapour phase.

The effective vapour-phase velocity is defined by

$$u_e^V = \frac{u^V}{\varepsilon (1 - h_t) \sin \theta} \quad (6.4)$$

where $u^V$ is the superficial vapour velocity (m s$^{-1}$). The Schmidt number for the vapour phase is

$$Sc_i^V = \left( \frac{\eta_i^V}{\rho_i^V D_i^V} \right) \quad i = 1, 2, ..., c \quad (6.5)$$

The interfacial area density $a'$ is obtained from the third part of the correlations from Rocha et al. (1996)

$$\frac{a'}{a_p} = F_{SE} \frac{29.12 (W e^L F r^L)^{0.15} S^{0.359}}{Re_e^{0.2} \varepsilon^{0.6} (1 - 0.93 \cos \gamma) (\sin \theta)^{0.3}} \quad (6.6)$$
where the factor $F_{SE}$ accounts for the variations in surface enhancements (lancing, fluting, etc.) and the contact angle $\gamma$ accounts for surface wettability. $Re^L$ is the liquid-phase Reynolds number based on the specific surface area, $Fr^L$ is the liquid-phase Froude number, and $We^L$ is the liquid-phase Weber number. The interfacial area density, together with the three dimensionless numbers used in this expression, are not component dependent.

The equations for the dimensionless numbers are:

\[
Re^L = \frac{\rho^L u^L}{\eta^L a_p} \quad (6.7)
\]
\[
Fr^L = \frac{a_p u^L}{g} \quad (6.8)
\]
\[
We^L = \frac{\rho^L u^L}{a_p \sigma} \quad (6.9)
\]

where $u^L$ is the liquid superficial velocity (m s$^{-1}$), $\rho^L$ is the density of the liquid phase (kg m$^{-3}$) and $\eta^L$ is the dynamic viscosity of the liquid phase (kg m$^{-1}$ s$^{-1}$).

The superficial velocities of each phase are

\[
u^L = \frac{\dot{v}^L}{A_{section}} \quad (6.10)
\]
\[
u^V = \frac{\dot{v}^V}{A_{section}} \quad (6.11)
\]

where $\dot{v}^L$ and $\dot{v}^V$ are the volumetric flowrates of the liquid and gas phase respectively (m$^3$ s$^{-1}$), and $A_{section}$ is the sectional area of the column (m$^2$).

The holdup expression is:

\[
h_t = \left( \frac{4F_t}{S} \right)^{2/3} \left( \frac{3\mu^L u^L}{\rho^L \varepsilon g_{eff} \sin \theta} \right)^{1/3} \quad (6.12)
\]
where $F_t$ stands for:

$$F_t = \frac{a'}{a_p F_{SE}}$$  \hspace{1cm} (6.13)$$

and $g_{eff}$ is the effective gravity defined by:

$$g_{eff} = g \frac{\rho_L - \rho_V}{\rho_L}$$  \hspace{1cm} (6.14)$$

where $g$ is the gravitational acceleration (m s$^{-2}$).

6.3 Reboiler

The role of the reboiler is to heat up the incoming liquid solvent and vaporise the CO$_2$ and H$_2$O to obtain a lean stream of solvent. The prevailing effect is the phase separation and not the mass transfer as is the case in the desorber, hence a rate-based description is not necessary. The reboiler is modelled as an equilibrium stage with a liquid inlet, a liquid outlet and a vapour outlet (cf. Figure 6.2).

The component mass balance is:

$$L_{r_i}^{in} x_{r_i}^{in} = L_{r_i}^{out} x_{r_i}^{out} + V_{r_i}^{out} y_{r_i}^{out} \hspace{1cm} i = 1, 2..., c$$  \hspace{1cm} (6.15)$$

where $L_{r_i}^{in}$ is the liquid molar flowrate entering the reboiler (mol s$^{-1}$), $L_{r_i}^{out}$ and $V_{r_i}^{out}$ are the liquid and vapour molar flowrates leaving the reboiler respectively (mol s$^{-1}$), $x_{r_i}^{in}$ is
the molar fraction of component $i$ in the liquid stream entering the reboiler and $x_{r,i}^{out}$ and $y_{r,i}^{out}$ are the molar fractions of component $i$ in the liquid and the vapour streams leaving the reboiler, respectively.

The mole fractions in the streams leaving the reboiler must sum to unity:

$$\sum_{i=1}^{c} x_{r,i}^{out} = 1 \quad \text{and} \quad \sum_{i=1}^{c} y_{r,i}^{out} = 1 \quad (6.16)$$

The net gain of species $i$ in the liquid phase due to interphase transport in the reboiler $N_{r,i}^L$ (mol s$^{-1}$) is given by:

$$N_{r,i}^L = -V_r y_{r,i}^{out} \quad i = 1, 2, \ldots, c \quad (6.17)$$

The enthalpy balance for the reboiler is given by:

$$L_r^{in} H_r^{L,in} + Q_r + N_{r,CO_2}^L \delta H_{CO_2}(T_r) = L_r^{out} H_r^{L,out} + V_r^{out} H_r^{V,out} \quad (6.18)$$

where $H_r^{L,in}$ is the enthalpy of the liquid phase entering the reboiler (J mol$^{-1}$), $H_r^{L,out}$ and $H_r^{V,out}$ are the enthalpies of the liquid and vapour phase leaving the reboiler respectively (J mol$^{-1}$), and $Q_r$ is the reboiler heat duty (W). The reboiler operates at high temperature (around 393 K), so the enthalpy of absorption of CO$_2$ as defined in chapter 3 takes the value of $\delta H_{CO_2}(T_r) = 80$ kJ mol$^{-1}$.

Both chemical and phase equilibrium are assumed to prevail in the reboiler. Thus, the conditions of equality of pressure, temperature and chemical potential must be satisfied:

$$\mu_{r,i}^L = \mu_{r,i}^V \quad i = 1, 2, \ldots, c \quad (6.19)$$

and only one temperature, $T_r^{out}$ and one pressure, $P_r^{out}$ are defined in the reboiler. $\mu_{r,i}^L$ and $\mu_{r,i}^V$ are the chemical potential of component $i$ in the reboiler in the liquid and gas
Figure 6.3: Diagram of the condenser

phases respectively (J mol\(^{-1}\)), obtained using the SAFT-VR foreign object:

\[ \vec{\mu}_L = \vec{\mu}(T_{\text{out}}^{L}, V_{\text{out}}^{L}, x_{\text{out}}^{L}) \]  
(6.20)

\[ \vec{\mu}_V = \vec{\mu}(T_{\text{out}}^{V}, V_{\text{out}}^{V}, y_{\text{out}}^{V}) \]  
(6.21)

where \( V_{\text{out}}^{L} \) and \( V_{\text{out}}^{V} \) are the molar volumes of the liquid phase and the gas phases, respectively in the reboiler (m\(^3\) kmol\(^{-1}\)), also obtained via SAFT-VR:

\[ P_{\text{out}}^{L} = P(T_{\text{out}}^{L}, V_{\text{out}}^{L}, x_{\text{out}}^{L}) \]  
(6.22)

\[ P_{\text{out}}^{V} = P(T_{\text{out}}^{V}, V_{\text{out}}^{V}, y_{\text{out}}^{V}) \]  
(6.23)

6.4 Condenser

The condenser is modelled as an equilibrium stage with only a vapour inlet, a vapour outlet and a liquid outlet (cf. Figure 6.3).

The component mole balance is:

\[ V^{\text{in}}_{c,i} x^{\text{in}}_{c,i} = L^{\text{out}}_{c} x^{\text{out}}_{c,i} + V^{\text{out}}_{c} y^{\text{out}}_{c,i} \quad i = 1, 2, ..., c \]  
(6.24)

where \( V^{\text{in}}_{c} \) is the vapour molar flowrate entering the condenser (mol s\(^{-1}\)), \( L^{\text{out}}_{c} \) and \( V^{\text{out}}_{c} \) are the liquid and vapour molar flowrates leaving the condenser respectively (mol s\(^{-1}\)), \( x^{\text{in}}_{c,i} \) is the molar fraction of component \( i \) in the liquid stream entering the condenser and
\( x_{c,i}^{\text{out}} \) and \( y_{c,i}^{\text{out}} \) are the molar fractions of component \( i \) of the liquid and the vapour streams leaving the condenser, respectively.

The mole fractions in the streams leaving the condenser must sum to unity:

\[
\sum_{i=1}^{c} x_{c,i}^{\text{out}} = 1 \quad \text{and} \quad \sum_{i=1}^{c} y_{c,i}^{\text{out}} = 1 \quad (6.25)
\]

The net gain of species \( i \) in the liquid phase due to interphase transport in the condenser \( N_{c,i}^{L} \) (mol s\(^{-1}\)) is given by:

\[
N_{c,i}^{L} = L_{c} x_{c,i}^{\text{out}} \quad i = 1, 2,..., c \quad (6.26)
\]

The enthalpy balance for the condenser is given by:

\[
V_{c}^{\text{in}} H_{c}^{V,\text{in}} + Q_{c} + N_{c,\text{CO}_2}^{L} \delta H_{\text{CO}_2}(T_{r}) = L_{c}^{\text{out}} H_{c}^{L,\text{out}} + V_{c}^{\text{out}} H_{c}^{V,\text{out}} \quad (6.27)
\]

where \( H_{c}^{V,\text{in}} \) is the enthalpy of the vapour phase entering the condenser (J mol\(^{-1}\)), \( H_{c}^{L,\text{out}} \) and \( H_{c}^{V,\text{out}} \) are the enthalpies of the liquid and vapour phase leaving the condenser respectively (J mol\(^{-1}\)) and \( Q_{c} \) is the condenser heat duty (W). The condenser operates at both high and low temperature (around 393 K and 313 K), so assigning the value the enthalpy of absorption of \( \text{CO}_2 \) as defined in chapter 3 based on the temperature does not make sense here. However, there is almost no MEA in the condenser so the enthalpy of absorption of \( \text{CO}_2 \) is not a sensitive parameter here. We chose to assign it the value of \( \delta H_{\text{CO}_2}(T_{r}) = 80 \) kJ mol\(^{-1}\), corresponding to the higher temperature (393 K).

Both chemical and phase equilibrium are assumed to prevail in the condenser. Thus, the conditions of equality of pressure, temperature and chemical potential must be satisfied:

\[
\mu_{c,i}^{L} = \mu_{c,i}^{V} \quad i = 1, 2,..., c \quad (6.28)
\]

and only one temperature, \( T_{c}^{\text{out}} \) and one pressure, \( P_{c}^{\text{out}} \) are defined in the condenser. \( \mu_{c,i}^{L} \) and \( \mu_{c,i}^{V} \) are the chemical potentials of component \( i \) in the condenser in the liquid and gas
phases respectively \((\text{J mol}^{-1})\), obtained using the SAFT-VR foreign object:

\[
\vec{\mu}_L^c = \mu(T_{c,\text{out}}, V_{c,\text{out}}, \vec{x}_{c,\text{out}}) \tag{6.29}
\]

\[
\vec{\mu}_V^c = \mu(T_{c,\text{out}}, V_{c,\text{out}}, \vec{y}_{c,\text{out}}) \tag{6.30}
\]

where \(V_{c,\text{out}}^{L}\) and \(V_{c,\text{out}}^{V}\) are the molar volumes of the liquid phase and the gas phases, respectively, in the condenser \((\text{m}^3 \text{ kmol}^{-1})\), also obtained via SAFT-VR:

\[
P_{c,\text{out}}^{L} = P(T_{c,\text{out}}^{L}, V_{c,\text{out}}^{L}, \vec{x}_{c,\text{out}}) \tag{6.31}
\]

\[
P_{c,\text{out}}^{V} = P(T_{c,\text{out}}^{V}, V_{c,\text{out}}^{V}, \vec{y}_{c,\text{out}}) \tag{6.32}
\]

### 6.5 Concluding remarks

The model for the solvent regeneration unit presented in this chapter is developed with transferability as the key requirement. The desorber column model is transferred directly from the absorber. It uses the same thermodynamic model and the same approach towards heat and mass transfer. The scaling in the diffusivity of \(\text{CO}_2\) introduced in chapter 4 is conserved intact. The condenser and reboiler are developed using the same thermodynamic model and the heat- and mass-transfer are simplified as these process units are considered to be equilibrium stages. The predictive capabilities of this model are presented in the next chapter.
Chapter 7

Regeneration module results

The scope of this chapter is to assess the transferability of the absorber model developed in chapter 3 and 4 and adapted to the desorption conditions in chapter 6. The predictive capabilities of this solvent regeneration model are assessed using extensive pilot plant data.

7.1 Model predictions

The desorber model developed in the current work is validated by comparing the model predictions with the pilot plant experimental data obtained by Tobiesen et al. (2008). These include measurements of the temperature and the CO$_2$ loading in the liquid phase at the bottom of the desorber and at the reboiler outlet, and flowrate of the liquid and gas streams leaving the condenser. The experimental results for the loading at the bottom of the desorber have been successfully reproduced by the model developed by Tobiesen et al. (2008). The experimental values of the flowrate of the gas stream of CO$_2$ leaving the condenser have been successfully reproduced by the model developed by Gáspár and Cormo (2011) for 13 out of 19 runs. New pilot plant data have been recently published by
Notz et al. (2012). They presented detailed experimental pilot plant data for a complete absorber-desorber process. However, only two runs are presented and the topology used is slightly more complex due to the addition of a washer section at the top of the desorber column. Moreover, the development and validation of the desorber model presented in our study was already well under way at the time of their publication. These are the reasons why the work from Notz et al. (2012) has not been chosen for the validation of the desorber model.

The topology of the regeneration system including the desorber, the reboiler and the condenser is represented in Figure 7.1. It should be noted that in this particular system, the liquid condensate is fed back directly to the reboiler. In most similar systems, the condensate is fed back to the top of the desorber (Dugas, 2006; Notz et al., 2012). The desorption column has an internal diameter of 0.1 m and a total packed height of 3.89 m. The desorption column internals are structured packing Mellapack 250Y. The input values used are listed in Table 5.1 and the characteristics of the column and the packing are listed in Table 5.2. The outputs of the simulation are the temperature and the CO₂ loading at the bottom of the desorber column, the temperature and the CO₂ loading at the reboiler outlet, the flowrate of condensed water leaving the condenser and the flowrate of the CO₂ gas stream leaving the condenser. This model is implemented and simulated using the gPROMS software (Process Systems Enterprise Ltd.).

All runs have been successfully simulated. The predictions for the temperature and liquid phase CO₂ loading at the bottom of the desorber and at the reboiler outlet, and the flowrates of the liquid and gas streams out of the condenser are compared with the experimental values from Tobiesen et al. (2008) in Figure 7.2. These runs represent a wide range of operating conditions in terms of flowrates, liquid compositions, heat duties, and temperatures (cf. Table 7.1). Good agreement is found between the model predictions and the pilot plant data in relation to the temperature and the loading of the desorber and the reboiler, and for the liquid flowrate out of the condenser. Although there is a slight over-prediction of the CO₂ loading and the temperature in both process units, these deviations may be explained on the basis of the experimental measurements error.
Table 7.1: Inputs for the simulated runs for the desorber model

<table>
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<th>Run</th>
<th>Rich solvent flowrate (m$^3$ h$^{-1}$)</th>
<th>Desorber pressure (MPa)</th>
<th>Rich solvent temperature (°C)</th>
<th>MEA concentration (kmol m$^{-3}$)</th>
<th>Rich solvent CO$_2$ loading</th>
<th>Reboiler duty (kW)</th>
<th>Reboiler pressure (MPa)</th>
<th>Condenser temperature (°C)</th>
<th>Condenser pressure (MPa)</th>
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<td>15</td>
<td>0.1992</td>
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<td>17</td>
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<td>0.2058</td>
<td>111</td>
<td>5.1</td>
<td>0.429</td>
<td>13.4</td>
<td>0.2058</td>
<td>31</td>
<td>0.2038</td>
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<tr>
<td>18</td>
<td>0.54</td>
<td>0.2047</td>
<td>113</td>
<td>5.2</td>
<td>0.407</td>
<td>11.7</td>
<td>0.2047</td>
<td>19</td>
<td>0.2027</td>
</tr>
<tr>
<td>19</td>
<td>0.54</td>
<td>0.2067</td>
<td>116</td>
<td>5.2</td>
<td>0.350</td>
<td>13.6</td>
<td>0.2067</td>
<td>22</td>
<td>0.2047</td>
</tr>
</tbody>
</table>
Figure 7.1: Topology of the solvent regeneration unit

Table 7.2: Desorber column properties

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{section}$ (m)</td>
<td>0.1</td>
<td>Tobiesen et al. (2008)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>$\pi/4$</td>
<td>Rocha et al. (1996)</td>
</tr>
<tr>
<td>$F_{se}$</td>
<td>350</td>
<td>Rocha et al. (1996)</td>
</tr>
<tr>
<td>$C_e$</td>
<td>0.9</td>
<td>Rocha et al. (1996)</td>
</tr>
<tr>
<td>$a_p$ (m$^2$ m$^{-3}$)</td>
<td>250</td>
<td>Rocha et al. (1996)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.95</td>
<td>Rocha et al. (1996)</td>
</tr>
</tbody>
</table>
described by Tobiesen et al. (2008). In relation to the CO\textsubscript{2} loading, they explained that it was extremely hard to obtain sufficient accuracy in the desorber outlet loading reading to justify a detailed comparison with simulated values. Errors in the loading have a very strong effect on the flowrate of CO\textsubscript{2} leaving the condenser. For example, in run 11, the measured loading varies from 0.392 at the top of the desorber to 0.291 at the reboiler outlet. However, the simulated value for the loading at the reboiler outlet is 0.335, which represent a 15% error. This error is directly repercuted on the CO\textsubscript{2} flowrate leaving the condenser which is simulated at 4.5 kg h\textsuperscript{-1} instead of 8.3 kg h\textsuperscript{-1} as measured. This explains the deviation between simulated results and experimental data observed in Figure 7.2. This error magnification was highlighted by Tobiesen et al. (2008) and they concluded that comparing simulated results of the flowrate of gaseous CO\textsubscript{2} leaving the condenser to experimental data was irrelevant. The same approach is followed here. Hence, these measurements are not used to assess the predictive capabilities of the model.

With regard to the temperature measurements, the exact position of the temperature probe at the bottom of the desorber or in the reboiler has a significant impact on the temperature reading and can lead to an error in the reboiler temperature reading of about 2-2.5 K and to an even higher error in the desorber temperature reading (Tobiesen et al., 2008). The error bars for the temperatures in figure 7.2 represent only a 2.5 K error. The desorber temperature probe is placed at the bottom of the column, lower than the bottom of the packing, this difference between the total height of the column (4.1 m) and the total packing height (3.89 m) is not taken into account in the model.

Despite the uncertainties, this demonstrates that the model developed in our current work is suitable for the operating conditions under which a CO\textsubscript{2} desorber operates, and that the scaling procedure devised under the absorber operating conditions can be applied in a transferable manner to different operating conditions.
Figure 7.2: Comparison between the model predictions and the experimental data from Tobiesen et al. (2008) (a) Loading at the bottom of the desorber, (b) loading at the reboiler outlet, (c) temperature at the bottom of the desorber, (d) temperature at the reboiler outlet, (e) condensate flowrate out of the condenser and, (f) CO$_2$ flowrate out of the condenser. This last value is not used to assess the validity of the model (see text).
7.2 Sensitivity analysis

The relative importance of several mass- and heat-transfer parameter is now assessed using a sensitivity analysis. Different key values in the model are altered to observe their impact on the predicted profiles along the column of the temperature in the liquid phase, the mole fraction of CO\textsubscript{2} in the vapour phase and the CO\textsubscript{2} loading in the liquid phase. The impact is also observed on the temperature and CO\textsubscript{2} loading at the bottom of the desorber column and in the reboiler, and the flowrates of the streams leaving the condenser. The values tested are listed in Table 7.3.

7.2.1 Mass transfer

As explained in the absorber model, the mass transfer in the desorber is mediated via mass transfer coefficients (Rocha et al., 1996). These coefficients are highly dependent on the viscosity, the diffusivity and the surface tension of the fluid considered; thus, these three properties are considered as key parameters in the model and their influence on the temperature and composition profiles are therefore assessed. The value of each parameter in each phase was doubled and halved in order to determine their effect on the temperature and composition profiles. As obtained in the absorber model, varying the diffusivity or viscosity in the gas phase has no visible effect on the liquid temperature profile or the composition profiles. However, neither does the variation of the diffusivity of CO\textsubscript{2}, the viscosity of the liquid phase or the surface tension of the liquid phase. We explain this result by fact that the differences in composition between the bulk phase and the film for the gas and the liquid phases are very low, as presented in Figure 7.3. Hence, this counteracts any variation in the mass transfer coefficients.

The mass transfer in the desorber is very limited. For example on run 12, the loading varies from 0.392 to 0.382. This is to be compared with the values in the absorber, where the loading varies from 0 to 0.5.
Table 7.3: Sensitivity analysis of key parameters in the model

<table>
<thead>
<tr>
<th>Parameter description</th>
<th>Variation</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour diffusivity</td>
<td>doubled</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td></td>
</tr>
<tr>
<td>Liquid diffusivity</td>
<td>doubled</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td></td>
</tr>
<tr>
<td>Vapour viscosity</td>
<td>doubled</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td></td>
</tr>
<tr>
<td>Liquid viscosity</td>
<td>doubled</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td></td>
</tr>
<tr>
<td>Surface tension</td>
<td>doubled</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td></td>
</tr>
<tr>
<td>Heat transfer liquid</td>
<td>$\times 10$</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>$\div 10$</td>
<td></td>
</tr>
<tr>
<td>Heat transfer vapour</td>
<td>$\times 10$</td>
<td>negligible effect</td>
</tr>
<tr>
<td></td>
<td>$\div 10$</td>
<td></td>
</tr>
<tr>
<td>Enthalpy of absorption of CO$_2$</td>
<td>doubled</td>
<td>limited effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td>see Figures 7.4 and 7.5</td>
</tr>
<tr>
<td>Heat of vaporisation of water</td>
<td>doubled</td>
<td>limited effect</td>
</tr>
<tr>
<td></td>
<td>halved</td>
<td>see Figures 7.6 and 7.7</td>
</tr>
</tbody>
</table>
Figure 7.3: Run 12 of the pilot plant data from Tobiesen et al. (2008). Comparison of the predictions of our model for: (a) temperature of the bulk liquid phase (continuous curve), the temperature at the vapour-liquid interface (dashed curve) and the temperature for the bulk vapour phase (dot-dashed curve); (b) the gas phase CO$_2$ concentration in the bulk vapour phase (continuous curve) and at the interface (dashed curve); (c) the liquid phase CO$_2$ loading in the bulk liquid phase (continuous curve) and at the interface (dashed curve).
The loading is further reduced in the reboiler from 0.382 to 0.335, indicating that the majority of the mass transfer between phases takes place in the reboiler, where the mass transfer coefficients do not have any impact as the reboiler is modelled as an equilibrium stage.

In accordance with the results on the profiles, the variation of the three mass transfer properties (viscosity, diffusivity and surface tension) has no noticeable effect on the temperature and CO$_2$ loading at the bottom of the desorber column and in the reboiler, and the flowrates of the streams leaving the condenser.

### 7.2.2 Heat transfer

The major heat consumption in the system is the reverse endothermic reaction to separate MEA and CO$_2$, which occurs in the liquid phase. This separation needs a high temperature to take place, hence the need for a reboiler. There can be heat transfer between the liquid phase and the gas phase. In the model, the heat transfer is mediated via the heat transfer coefficients (Treybal, 1981). Four key parameters can be identified in the model: the heat of absorption of CO$_2$, the heat of vaporisation of water, the heat transfer coefficient for the liquid phase and the heat transfer coefficient for the gas phase.

The values of these four parameters are varied to observe the impact on the liquid phase temperature profile and the composition profiles. For this particular model, the sensitivity of the heat of absorption of CO$_2$ was assessed by varying the value of the correction parameter $\delta H_{CO_2}$ of the enthalpy of absorption of CO$_2$. Although the heat of absorption of CO$_2$ and the heat of vaporisation of water are known thermodynamic quantities, their variation provides insights into the behaviour of the column. Their values were doubled and halved as before and the values of the heat transfer coefficients were multiplied by 10 and divided by 10 (Table 7.3).

The variation of the liquid and vapour heat transfer coefficients has no visible effect on
the liquid phase temperature and composition profiles.
The variation of the heat of absorption of CO$_2$ has no visible impact on the desorber profile but only on the liquid outlet temperature as can be seen in Figure 7.4. This contrasts with the absorber model where this parameter was a key factor in predicting the temperature profile of the column but its qualitative effect is similar, as its impact is mostly on the outlet liquid temperature at the bottom of the column. The effect of the variation of the heat of vaporisation on the temperature and liquid phase CO$_2$ loading at the bottom of the desorber and at the reboiler outlet, and the flowrates out of the condenser for selected runs is represented in Figure 7.5. These runs were selected based on the loading of the rich solvent fed to the desorber. Tobiesen et al. (2008) used three loading ranges during the pilot plant campaign: low CO$_2$ loading, $\theta_{CO_2} = 0.26-0.32$, medium CO$_2$ loading, $\theta_{CO_2} = 0.33-0.40$, and high CO$_2$ loading, $\theta_{CO_2} = 0.41-0.46$. Two runs of each loading range have been selected. The heat of absorption of CO$_2$ has a very limited effect on the temperature and loading at the bottom of the desorber and at the reboiler outlet. However, it has a noticeable impact on the flowrate of the streams leaving the condenser.

The variation of the heat of vaporisation of water has a very limited impact on the liquid phase temperature profile and the gas phase composition profile, and a negligible impact on the CO$_2$ liquid loading profile as represented in Figure 7.6. Halving the heat of vaporisation of water reduces the outlet temperature of the desorber by only about 2-3 K. The effect of the variation of the enthalpy of vaporisation of water on the temperature and the CO$_2$ loading at the bottom of the desorber and in the reboiler, and on the flowrates of water and CO$_2$ leaving the condenser for several selected runs is represented in Figure 7.7. While the limited impact on the CO$_2$ liquid loading is confirmed for the desorber, there is a significant impact on the loading in the reboiler for the lower loading runs. The negligible impact on the temperature is confirmed for the different runs. The impact is significant for the flowrate of water from the condenser, but it is almost negligible for the lower flowrate while doubling it or halving it at higher flowrates. The variation of the enthalpy of vaporisation of water has a consistent effect on the CO$_2$ leaving the condenser: the lower the heat of vaporisation, the higher the flowrate and the better the match be-
Figure 7.4: Sensitivity analysis of the heat of absorption of CO$_2$ on the profiles predicted with our model in terms of the correction factor $\delta H_{CO_2}$ compared with the experimental pilot plant data of Run 12 from Tobiesen et al. (2008). $\delta H_{CO_2} = 80$ kJ mol$^{-1}$ (continuous curve), $\delta H_{CO_2} = 160$ kJ mol$^{-1}$ (dashed curve), $\delta H_{CO_2} = 40$ kJ mol$^{-1}$ (dot-dashed curve).

(a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile and, (c) liquid phase CO$_2$ loading.
Figure 7.5: Sensitivity analysis of the heat of absorption of CO$_2$ on the predictions of our model in terms of the correction factor $\delta H_{CO_2}$ compared with the experimental pilot plant data of 6 selected runs from Tobiesen et al. (2008). $\delta H_{CO_2} = 80$ kJ mol$^{-1}$ (squares), $\delta H_{CO_2} = 160$ kJ mol$^{-1}$ (upward triangles), $\delta H_{CO_2} = 40$ kJ mol$^{-1}$ (downward triangles). (a) Loading at the bottom of the desorber, (b) loading at the reboiler outlet, (c) temperature at the bottom of the desorber, (d) temperature at the reboiler outlet, (e) condensate flowrate out of the condenser and, (f) CO$_2$ flowrate out of the condenser.
tween experimental data and model predictions. Essentially, the extra energy available in the reboiler due to lower heat of vaporisation of $\text{H}_2\text{O}$ is used to boil more water, hence the increase of water flowrate, and to desorb more CO$_2$, explaining the lower loading in the reboiler and the higher CO$_2$ flowrate leaving the condenser.

The composition of the streams leaving the condenser are not normally affected by the heat of vaporisation of water. Indeed, under the conditions of phase separation, the gas stream will be almost exclusively CO$_2$ and the liquid stream water; this holds whatever the temperature used in the condenser.
Figure 7.6: Sensitivity analysis of the enthalpy of vaporisation of water on the profiles predicted with our model compared with the experimental pilot plant data of Run 12 from Tobiesen et al. (2008). Nominal value (continuous curve), enthalpy doubled (dashed curve), enthalpy halved (mixed curve). (a) Temperature profile for the liquid phase, (b) gas phase CO$_2$ concentration profile and, (c) liquid phase CO$_2$ loading.
Figure 7.7: Sensitivity analysis of the enthalpy of vaporisation of water on the predictions of our model compared with the experimental pilot plant data of 6 selected runs from Tobiesen et al. (2008). Nominal value (squares), enthalpy doubled (upward triangles), enthalpy halved (downward triangles). (a) Loading at the bottom of the desorber, (b) loading at the reboiler outlet, (c) Temperature at the bottom of the desorber, (d) temperature at the reboiler outlet, (e) Condensate flowrate out of the condenser, (f) CO₂ flowrate out of the condenser.
7.3 Energy requirements in the reboiler

The reboiler is the major consumer of external energy in the process. This is due to three main physical phenomena taking place in this unit: the reverse carbamate formation when the CO$_2$-MEA bonds are broken and the CO$_2$ is desorbed, the vaporisation of water, and the increase in temperature of the liquid stream. The energy required by these phenomena is brought into the system via the reboiler; this is the heat duty of the reboiler. This section details the relative energy consumption of each of the three phenomena described above.

The energy balance on the reboiler can be written as follows:

$$Q_r + Q_{CO_2} + Q_{H_2O} + Q_{\Delta T} = 0 \quad (7.1)$$

Here we chose not to include the heat of mixing as it is negligible. where $Q_{CO_2}$ is the power for the desorption of CO$_2$ (W), $Q_{H_2O}$ is the power of the vaporisation of H$_2$O (W), and $Q_{\Delta T}$ is the power for the temperature increase of the liquid stream. The power for the desorption of CO$_2$ is given by:

$$Q_{CO_2} = N_{r,CO_2}L_{CO_2} \Delta H_{CO_2} \quad (7.2)$$

where $\Delta H_{CO_2}$ is the enthalpy of absorption of CO$_2$ (J mol$^{-1}$). The power for the vaporisation of H$_2$O is given by:

$$Q_{H_2O} = N_{r,H_2O}L_{\text{cap},H_2O} \quad (7.3)$$

Each of these contributions is expressed as a percentage of the total reboiler heat duty for a set of selected runs in Table 7.4. It is clear from this table that there is a correlation between the proportion of the heat consumed for the CO$_2$ desorption and the vaporisation and H$_2$O and the loading range of CO$_2$. The higher the loading, the more important the share of energy for the desorption of CO$_2$ and the lesser the share of energy for the
vaporisation of H$_2$O.

The heat duty of the reboiler was an input in the pilot plant experimental campaign and is also an input in the model so its value on each run should be fixed to the value reported by Tobiesen et al. (2008). However, for the sake of understanding further the process, its value has been doubled and halved and the effect of its variation on the temperature and liquid phase CO$_2$ loading at the bottom of the desorber and at the reboiler outlet, and the flowrates out of the condenser for selected runs is represented in Figure 7.8. Increasing the heat duty of the reboiler reduces the CO$_2$ loading at the bottom of the desorber and in the reboiler, hence resulting in a better match between the experimental data and the simulated results. A direct consequence of this better prediction of the CO$_2$ loading is the better prediction of the CO$_2$ flowrate leaving the condenser. However, an increase in the heat duty also results in an increase in the flowrate of H$_2$O leaving the condenser, leading to an important over estimation. The effect on the temperature is somewhat limited as it increases the predictions by about only 3 K. Doubling the reboiler heat duty gives better predictions for the CO$_2$ composition and flowrate across the whole process but degrades the quality of the predictions for the temperature and the flowrate of H$_2$O.

---

Table 7.4: Heat consumption

<table>
<thead>
<tr>
<th>Run</th>
<th>Loading range</th>
<th>CO$_2$ desorption %</th>
<th>H$_2$O vaporisation %</th>
<th>Liquid stream $\Delta T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.26-0.32</td>
<td>18</td>
<td>67</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>0.26-0.32</td>
<td>13</td>
<td>71</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>0.33-0.40</td>
<td>26</td>
<td>59</td>
<td>15</td>
</tr>
<tr>
<td>12</td>
<td>0.33-0.40</td>
<td>30</td>
<td>53</td>
<td>17</td>
</tr>
<tr>
<td>14</td>
<td>0.41-0.46</td>
<td>38</td>
<td>26</td>
<td>36</td>
</tr>
<tr>
<td>16</td>
<td>0.41-0.46</td>
<td>38</td>
<td>21</td>
<td>41</td>
</tr>
</tbody>
</table>
Figure 7.8: Sensitivity analysis of the reboiler heat duty on the predictions of our model compared with the experimental pilot plant data of 6 selected runs from Tobiesen et al. (2008). Nominal value (squares), heat duty doubled (upward triangles), heat duty halved (downward triangles). (a) Loading at the bottom of the desorber, (b) loading at the reboiler outlet, (c) Temperature at the bottom of the desorber, (d) temperature at the reboiler outlet, (e) Condensate flowrate out of the condenser and, (f) CO$_2$ flowrate out of the condenser.
7.4 Effect of the pressure in the reboiler

From the sections above, it appears that a large part of the desorption of CO$_2$ takes place in the reboiler. Being an equilibrium stage, the predictive capabilities of the model rely on the precision of the VLE obtained with the SAFT-VR approach. In Section 7.1, it was shown that the complete desorber process model slightly over predicted the CO$_2$ loading in the liquid phase at the bottom of the desorber and in the reboiler. This over prediction could be the result of uncertainties in the experimental data as explained in Section 7.1; it could also arise from the mass-transfer model but this is unlikely as the sensitivity analysis showed that the desorber model was almost insensitive to changes in key mass-transfer related model properties. This leaves the precision of the SAFT-VR approach as possible source of error.

In order to assess the precision of the thermodynamic approach in this process model, the reboiler is isolated and simulated as a stand alone unit. The operating conditions of Run 13 (Tobiesen et al., 2008) are chosen as the condensate rate is null, simplifying the determination of the composition of the stream entering the reboiler. The composition of the inlet liquid stream is deduced from the MEA concentration and the reported loading at the bottom of the desorber. The temperature and pressure of the stream and the heat duty of the reboiler are also known experimentally. The flowrate is estimated on the basis that it decreases only slightly along the desorber column. The simulated values of the CO$_2$ loading and the temperature in the reboiler are compared with the experimental values (cf. Table 7.5). It can be seen that the reboiler loading and temperature are too high. Varying the inlet flowrate has only a limited impact on the loading and temperature and

<table>
<thead>
<tr>
<th>Table 7.5: Standalone reboiler simulation for Run T13</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pressure (MPa)</strong></td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>CO$_2$ loading</td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
</tbody>
</table>
varying the heat duty would either increase the loading and decrease the temperature or vice versa. However, although the inlet pressure is a given experimental value, reducing it from 0.209 Mpa to 0.14 MPa leads to a significant improvement in the agreement between the simulated and the experimental values for both the loading and the temperature in the reboiler as presented in Table 7.5. This confirms the hypothesis that errors in the thermodynamic model lead to significant deviation between the process model predictions and pilot plant data at higher temperatures.

The influence of the pressure is assessed on the complete desorber model. It appears that reducing the pressure from about 0.2 MPa to 0.14 MPa in the desorber column or in the condenser has a negligible effect and as expected reducing the pressure in the reboiler has a major effect on the CO$_2$ loading and temperature at the bottom of the desorber and in the reboiler and on the flowrates of the streams leaving the condenser as presented in Figure 7.9. Albeit improving the prediction for the loading and the CO$_2$ gas stream flowrate, this pressure reduction impairs the quality of the predictions for the temperature of the desorber. In conclusion, the potential error in the thermodynamic model does have an impact on the predictive capability of the model but this is not the only significant factor.
7. Regeneration module results

Figure 7.9: Impact of the reduction of the pressure in the reboiler on the predictions of our model compared with the experimental pilot plant data of 6 selected runs from Tobiesen et al. (2008). Nominal value, $P \simeq 0.2$ Mpa (squares), reduced pressure $P = 0.14$ Mpa (downward triangles). (a) Loading at the bottom of the desorber, (b) loading at the reboiler outlet, (c) Temperature at the bottom of the desorber, (d) temperature at the reboiler outlet, (e) Condensate flowrate out of the condenser and, (f) CO$_2$ flowrate out of the condenser.
7.5 Concluding remarks

The performance of the rate-based CO$_2$ desorber model developed and extended from the absorber model (cf. Chapters 4 and 5) has been assessed. Model validation has been carried out by comparison with published experimental pilot plant data (Tobiesen et al., 2008). It is shown that good predictive capabilities can be obtained over a wide range of operating conditions without any need for modifying the modelling approach between the absorber and the desorber. The model parameter scaling the diffusivity of the CO$_2$ in the liquid phase and adjusted based on the absorber operating conditions appears to be transferable to the desorber conditions. The precision of the predictions were not as good as those obtained for the absorber model. This is due to the low desorption rate of the chosen pilot plant (Tobiesen et al., 2008) where a higher level of accuracy is needed. The model is expected to give better predictions for a pilot plant with a higher rate of desorption.

With a careful sensitivity analysis we show that the model was almost insensitive to variation in key mass-transfer related model properties. It was highlighted that the higher the CO$_2$ loading in the process, the more important the share of reboiler heat duty for the desorption of CO$_2$ and the lesser the share of reboiler heat duty for the vaporisation of H$_2$O. Finally, it was shown that the pressure in the reboiler has a significant impact on the amount of CO$_2$ being desorbed in the reboiler.

These two models can now be combined to provide a complete model of the absorber desorber CO$_2$ capture process. This is done in the next chapter.
Chapter 8

Application of the model

In this chapter, we combine the absorber model presented in chapters 4 and 5 with the desorber model presented in chapter 6 and 7 in order to represent a complete process of CO$_2$ capture.

8.1 Closed flowsheet

A schematic of the complete process model is presented in Figure 8.1. The configuration presented by Tobiesen et al. (2008) of desorber, reboiler and condenser is used. The outlet stream of rich solvent from the absorber is fed to the top of the desorber and the outlet stream of lean solvent from the desorber is fed to the top of the absorber. A pump and a heater are added on each of these two streams to adjust their pressure and temperature. The model of the pump is simple, corresponding to specifying a pressure (1 bar for the absorber and 2 bar for the desorber), while the heater changes the temperature via a specified heat duty. In Table 8.1 the model conditions that have to be specified for the simulated run are given. Due to numerical constraint on gPROMS and the SAFT-VR foreign object, there must be H$_2$O, MEA, CO$_2$ and N$_2$ in all the streams, liquid or gas. This
is why in the process model there is a trace of MEA in the flue gas \( (y_{MEA} = 1.4575647 \times 10^{-6}) \). The high precision of the numbers reflect the difficulties of obtaining a converged solution from gPROMS (Process Systems Enterprise Ltd.). The absorber column characteristics are similar to those used in Chapter 5, the desorber column characteristics are similar to those used in Chapter 7. The stream tables for this run are presented in Figure 8.2. The liquid-phase temperature, gas-phase CO\(_2\) concentration, and liquid-phase CO\(_2\) concentration profiles in the absorber and the desorber columns are presented in Figure 8.3. The temperature and compositions profiles for the absorber column are really similar to those obtained in Chapter 5 when reproducing the pilot plant results from Tontiwachwuthikul et al. (1992). The temperature profile of the desorber presents a sharp drop in stage 1. This suggests that there is a flash of the rich solvent stream upon entering the desorber. This rich solvent is at equilibrium when leaving the absorber. As it passes through the pump its pressure is increased, moving it away from equilibrium into the liquid phase. It then passes through a heater. The resulting increase in temperature could be enough to vaporise some of the liquid. This phenomenon is observed in this case. The difference in loading between the rich and the lean solvent is much more important in this simulation than in the experimental data from Tobiesen et al. (2008).
Figure 8.2: Stream tables for the reference run
Figure 8.3: Model predictions for a complete absorber-desorber flowsheet. (a) Absorber temperature profile for the liquid phase, (b) absorber gas phase CO$_2$ concentration profile, (c) absorber liquid phase CO$_2$ loading (d) desorber temperature profile for the liquid phase, (e) desorber gas phase CO$_2$ concentration profile, and (f) desorber liquid phase CO$_2$ loading.
Table 8.1: Inputs to the complete process model

<table>
<thead>
<tr>
<th>Input variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet gas flow (mol m(^{-2}) s(^{-1}))</td>
<td>30</td>
</tr>
<tr>
<td>Inlet gas pressure (MPa)</td>
<td>0.1</td>
</tr>
<tr>
<td>Inlet gas temperature (K)</td>
<td>292.15</td>
</tr>
<tr>
<td>Inlet gas CO(_2) mole fraction</td>
<td>0.1264</td>
</tr>
<tr>
<td>Inlet gas H(_2)O mole fraction</td>
<td>0.014</td>
</tr>
<tr>
<td>Inlet gas MEA mole fraction</td>
<td>1.457647(\times 10^{-6})</td>
</tr>
<tr>
<td>Cooler outlet temperature (K)</td>
<td>285.846</td>
</tr>
<tr>
<td>Heater outlet temperature (K)</td>
<td>394.949</td>
</tr>
<tr>
<td>Desorber pressure (MPa)</td>
<td>0.2067</td>
</tr>
<tr>
<td>Reboiler heat duty (kW)</td>
<td>14.95</td>
</tr>
<tr>
<td>Condenser temperature (K)</td>
<td>295.15</td>
</tr>
</tbody>
</table>

The CO\(_2\) removal rate \(\Psi\) (%) is defined as

\[
\Psi = \frac{V_{\text{in}CO_2}}{V_{\text{out}CO_2}}
\]

where \(V_{\text{in}CO_2}\) is the CO\(_2\) molar flowrate in the flue gas and \(V_{\text{out}CO_2}\) is the CO\(_2\) molar flowrate in the gas stream leaving the condenser (this is the captured CO\(_2\)). For the selected run \(\Psi = 99.98\) %. This rate is exceptionally high compared to pilot plant data. Cottrell et al. (2009) state that a typical removal rate is 85-95 % while Notz et al. (2012) reported removal rates of 75.9 % and 51.3 %. The liquid flowrate entering the absorber is equal to \(L = 1.07\) mol s\(^{-1}\) and the concentration in MEA of the stream entering the desorber is 16.9 wt.%.

The concentration in MEA in the liquid solvent and the liquid circulation rate are not specified but determined in the simulation. In order to gain control on these parameters, we added a solvent make-up in the liquid loop, just before the liquid inlet of the absorber to add more degrees of freedom in the system. It should be noted that having a solvent make-up is compulsory for real processes to compensate for the MEA and H\(_2\)O losses in the clean flue gas stream and the CO\(_2\) gas stream. In the model these losses are compensated by the H\(_2\)O and the trace of MEA present in the flue gas stream.

The flowrate of this solvent make-up has been varied and the effect of this variation on
Table 8.2: Liquid solvent flowrate, MEA concentration and, CO$_2$ recovery rate for different flowrates of MEA addition

<table>
<thead>
<tr>
<th>$L_{MEA}^{\text{make-up}}$ (mol s$^{-1}$)</th>
<th>0</th>
<th>$10^{-7}$</th>
<th>$10^{-6}$</th>
<th>$10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid flowrate (mol s$^{-1}$)</td>
<td>1.07</td>
<td>0.62</td>
<td>0.47</td>
<td>0.33</td>
</tr>
<tr>
<td>MEA concentration (wt%)</td>
<td>16.9</td>
<td>21.20</td>
<td>33.60</td>
<td>58.92</td>
</tr>
<tr>
<td>$\Psi$ (%)</td>
<td>99.98</td>
<td>99.95</td>
<td>99.98</td>
<td>99.95</td>
</tr>
</tbody>
</table>

the behaviour of the process is discussed in the remainder of this section.

8.1.1 Addition of MEA

The composition of the make-up solvent is nearly pure MEA (the mole fraction of H$_2$O, CO$_2$, and N$_2$ are set to $10^{-8}$). The flowrate is increased from $L_{MEA}^{\text{make-up}} = 0$ to $10^{-5}$ mol s$^{-1}$. The temperature and pressure are set to be equal to the one of the main liquid stream entering the absorber. The impact of this addition of MEA on the temperature and composition profiles along the absorber and desorber columns is presented in Figure 8.4. It appears that an ever so slight addition of MEA in the system leads to tremendous changes in the temperature profiles. The liquid flowrate, MEA concentration and, CO$_2$ recovery rate for different values of solvent make-up flowrates are listed in Table 8.2. Complete stream tables are presented in Figures 8.2 and 8.5 to 8.7.

It is observed that an addition of MEA in the process via the solvent make-up decreases the liquid flowrate and increases the MEA concentration. The case where $L_{MEA}^{\text{make-up}} = 10^{-6}$ mol s$^{-1}$ is not feasible in reality as the MEA concentration is too high and this would lead to severe corrosion of the columns. The CO$_2$ recovery rate is only slightly affected and stays consistently very high. Looking at both Figure 8.4 and Table 8.2, it can be seen that the lower the liquid flowrate, the higher and wider the temperature bulge. This is explained by the fact that there is less liquid to cool the column down, so there is an accumulation of energy in the absorber, leading to the build up of the temperature bulge. Although the behaviour of the temperature profile with changes in the flowrate of make-
Figure 8.4: Impact of addition of MEA in the system via the solvent make-up on the model predictions for a complete absorber-desorber flowsheet. $L_{\text{MEA}}^{\text{make-up}} = 0$ mol s$^{-1}$ (continuous line), $L_{\text{MEA}}^{\text{make-up}} = 10^{-7}$ mol s$^{-1}$ (dashed line), $L_{\text{MEA}}^{\text{make-up}} = 10^{-6}$ mol s$^{-1}$ (dot-dashed line) and, $L_{\text{MEA}}^{\text{make-up}} = 10^{-5}$ mol s$^{-1}$ (dotted line). (a) Absorber temperature profile for the liquid phase, (b) absorber gas phase CO$_2$ concentration profile, (c) absorber liquid phase CO$_2$ loading (d) desorber temperature profile for the liquid phase, (e) desorber gas phase CO$_2$ concentration profile and, (f) desorber liquid phase CO$_2$ loading.
Figure 8.5: Stream tables of the process model with $L_{\text{MEA}} = 10^{-7}$ and $\varepsilon = 1$. 

<table>
<thead>
<tr>
<th>Stream</th>
<th>Flowrate</th>
<th>Mole Fraction (H2O)</th>
<th>Mole Fraction (MEA)</th>
<th>Mole Fraction (CO2)</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>0.622421 mol/s</td>
<td>0.923487 -</td>
<td>0.0732872 -</td>
<td>0.00322558 -</td>
<td>2.32015E-12 K</td>
<td>0.10000 MPA</td>
</tr>
<tr>
<td>Outlet</td>
<td>1.00000E-07 mol/s</td>
<td>1.00000 -</td>
<td>0.0000000 -</td>
<td>1.0000000 -</td>
<td>285.846 K</td>
<td>0.10000 MPA</td>
</tr>
<tr>
<td>Outlet</td>
<td>0.641431 mol/s</td>
<td>0.985905 -</td>
<td>0.011151 -</td>
<td>0.0323659 -</td>
<td>1.37811E-05 K</td>
<td>0.206799 MPA</td>
</tr>
<tr>
<td>Temperature</td>
<td>-7407.02 J/s</td>
<td>396.819 K</td>
<td>285.846 K</td>
<td>394.949 K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Heat duty $= 5278.88$ J/s

Temperature in $= 321.415$ K

Temperature out $= 394.949$ K

Reboiler duty $= 14950.0$ J/s

Flowrate $= 0.241491$ mol/s

Mole fraction (H2O) $= 0.992451$

Mole fraction (MEA) $= 0.00344613$

Mole fraction (CO2) $= 0.00417017$

Mole fraction (N2) $= 1.12433E-08$

Temperature $= 295.159$ K

Pressure $= 0.204709$ MPA
### Figure 8.6: Stream tables of the process model with $L_{\text{MEA}} = 10^{-6}$ and $\varepsilon = 1$

#### Stream 1
- **Flowrate:** 0.470961 mol/s
- **Mole fraction ($H_2O$):** 0.861977
- **Mole fraction (MEA):** 0.128695
- **Mole fraction ($CO_2$):** 0.08032777
- **Mole fraction ($N_2$):** 4.87084E-12
- **Temperature:** 398.627 K
- **Pressure:** 0.206780 MPa

#### Heat Duty
- **Temperature in:** 398.627 K
- **Temperature out:** 394.949 K
- **Heat Duty:** 3866.70 J/s

#### Reboiler Duty
- **Heat Duty:** 14950.0 J/s

#### Stream 2
- **Flowrate:** 0.353839 mol/s
- **Mole fraction ($H_2O$):** 0.876422
- **Mole fraction (MEA):** 0.113736
- **Mole fraction ($CO_2$):** 0.060282
- **Mole fraction ($N_2$):** 4.38714E-11
- **Temperature:** 397.761 K

#### Stream 3
- **Flowrate:** 0.386439 mol/s
- **Mole fraction ($H_2O$):** 0.950362
- **Mole fraction (MEA):** 0.0973018
- **Mole fraction ($CO_2$):** 0.0082365
- **Mole fraction ($N_2$):** 396.698 K
- **Temperature:** 398.627 K

#### Stream 4
- **Flowrate:** 0.109017 mol/s
- **Mole fraction ($H_2O$):** 0.0130168
- **Mole fraction (MEA):** 1.36533E-06
- **Mole fraction ($CO_2$):** 0.086553
- **Mole fraction ($N_2$):** 0.00042909
- **Temperature:** 295.159 K
- **Pressure:** 0.204709 MPa

#### Stream 5
- **Flowrate:** 0.129425 kmol/s
- **Mole fraction ($H_2O$):** 0.0141443
- **Mole fraction (MEA):** 9.19756E-06
- **Mole fraction ($CO_2$):** 2.21236E-05
- **Mole fraction ($N_2$):** 0.985824
- **Temperature:** 286.887 K
- **Pressure:** 0.108880 kPa

### Heat Duty
- **Temperature in:** 398.627 K
- **Temperature out:** 285.846 K
- **Heat Duty:** -6139.08 J/s

### Reboiler Duty
- **Heat Duty:** 14950.0 J/s
### Application of the model

#### Figure 8.7: Stream tables of the process model with $L_{\text{MEA}^-} = 10^{-5}$ and $\Delta = 1$

<table>
<thead>
<tr>
<th>Flowrate</th>
<th>Mole Fraction</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.330786$ mol/s</td>
<td>($H_2O$)</td>
<td>0.630794</td>
<td>295.846 K</td>
</tr>
<tr>
<td></td>
<td>($MEA^-$)</td>
<td>0.288340</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>($CO_2$)</td>
<td>0.0308458</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>($N_2$)</td>
<td>7.7111E-12</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$1.0000E-05$ mol/s</td>
<td>($H_2O$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($MEA^-$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($CO_2$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($N_2$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>$0.34972$ mol/s</td>
<td>($H_2O$)</td>
<td>0.644516</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($MEA^-$)</td>
<td>0.272672</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($CO_2$)</td>
<td>0.0827552</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($N_2$)</td>
<td>2.673831E-05</td>
</tr>
<tr>
<td></td>
<td>$0.206799$ MPa</td>
<td>($H_2O$)</td>
<td>0.000005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($MEA^-$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($CO_2$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($N_2$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>$394.949$ K</td>
<td>($H_2O$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($MEA^-$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($CO_2$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($N_2$)</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>$0.129443$ kmol/s</td>
<td>($H_2O$)</td>
<td>0.0141776</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($MEA^-$)</td>
<td>7.82905E-05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($CO_2$)</td>
<td>6.60407E-05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($N_2$)</td>
<td>0.985678</td>
</tr>
<tr>
<td></td>
<td>$0.148440$ mol/s</td>
<td>($H_2O$)</td>
<td>0.0140886</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($MEA^-$)</td>
<td>1.45756E-06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($CO_2$)</td>
<td>0.126440</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($N_2$)</td>
<td>0.859599</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.180000$ MPa</td>
<td>($H_2O$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($MEA^-$)</td>
<td>0.723939</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($CO_2$)</td>
<td>0.245292</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($N_2$)</td>
<td>0.0307152</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($H_2O$)</td>
<td>7.39597E-08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($MEA^-$)</td>
<td>7.39597E-08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($CO_2$)</td>
<td>7.39597E-08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($N_2$)</td>
<td>1.31346E-07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$486.247$ K</td>
<td>($H_2O$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($MEA^-$)</td>
<td>0.949933</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($CO_2$)</td>
<td>0.0825252</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($N_2$)</td>
<td>0.0825252</td>
</tr>
</tbody>
</table>

### Heat duty
- Inlet: 2971.43 J/s
- Outlet: 305.161 K
- Temperature: 394.949 K

### Reboiler duty
- 14950.0 J/s
up MEA is monotonic (the higher the flowrate, the higher the temperature), this is not the case for the loading in both columns and for the CO$_2$ composition in the gas phase in the desorber. For example in the desorber, as the flowrate of make-up MEA is increased, the mole fraction of CO$_2$ in the gas phase and the CO$_2$ liquid loading first reduce but then increase again, highlighting the highly non-linear behaviour of the process.

### 8.2 Application to an other pilot plant

The newest detailed pilot plant data available in the literature are presented by Notz et al. (2012). As explained in Chapter 7, these data have not been used for the validation of the model for two reasons: firstly, they were published after the development of the absorber model and during the development of the desorber model, and secondly, only two runs are presented, which in our opinion is not sufficient to fully validate a process model. However, their study presents extensive experimental data for a complete absorber-desorber MEA-based CO$_2$ capture process. The topology is modified by the addition of a water washer at the top of each column. We chose to confirm the transferability of the model developed in our study by applying it to the pilot plant data from Notz et al. (2012). The results presented in this section are not yet final as this is part of a work in progress study.

#### 8.2.1 Absorber

The absorber column used in the work of Notz et al. (2012) is 4.20 m high and is filled with the Sulzer Mellapack 250.Y$^{\text{TM}}$ structured packing. Its diameter is 0.125 m. The flue gas stream and the liquid lean solvent stream characteristics for the two simulated runs are listed in Table 8.3. The comparisons between the simulated and experimental values for the liquid phase temperature and the mass fraction of CO$_2$ in the liquid phase profiles are presented in Figure 8.8 and 8.9.
Table 8.3: Inputs to the absorber model

<table>
<thead>
<tr>
<th>Input variable</th>
<th>Run 1</th>
<th>Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet gas flow (kg h(^{-1}))</td>
<td>72</td>
<td>72.4</td>
</tr>
<tr>
<td>Inlet gas pressure (MPa)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Inlet gas temperature (K)</td>
<td>321.16</td>
<td>321.3</td>
</tr>
<tr>
<td>Inlet gas CO(_2) mass fraction</td>
<td>0.085</td>
<td>0.165</td>
</tr>
<tr>
<td>Inlet gas H(_2)O mass fraction</td>
<td>0.071</td>
<td>0.069</td>
</tr>
<tr>
<td>Inlet gas MEA mass fraction</td>
<td>4.5 \times 10^{-6}</td>
<td>4.5 \times 10^{-6}</td>
</tr>
<tr>
<td>Liquid solvent flow (kg h(^{-1}))</td>
<td>200.1</td>
<td>200.0</td>
</tr>
<tr>
<td>Liquid solvent temperature (K)</td>
<td>313.18</td>
<td>313.33</td>
</tr>
<tr>
<td>Liquid solvent CO(_2) mass fraction</td>
<td>0.052</td>
<td>0.063</td>
</tr>
<tr>
<td>Liquid solvent H(_2)O mass fraction</td>
<td>0.673</td>
<td>0.653</td>
</tr>
<tr>
<td>Liquid solvent MEA mass fraction</td>
<td>0.275</td>
<td>0.284</td>
</tr>
</tbody>
</table>

Figure 8.8: Comparison between pilot plant data (squares) and models predictions (continuous curves) for Run 1 taken from the work of Notz et al. (2012). (a) Temperature profile for the liquid phase and, (b) mass fraction of CO\(_2\) in the liquid phase.
Very good agreement is found between the model predictions and the pilot plant data for Runs 1 and 2 in relation to the profile for the mass fraction of CO$_2$ in the liquid phase along the entire length of the column. This is a good confirmation of the transferability of the absorber model. In relation to the temperature profile in the liquid phase, the model prediction of the outlet temperature value is in acceptable agreement with the experimental data. However, the model predictions are underestimating the temperature profile for the liquid phase. This underprediction should be investigated via a sensitivity analysis in order to assess the relative importance of the process model parameters. In particular, the heat-transfer related parameters might have a significant effect under these operating conditions as the flue gas flowrate ratio to the liquid solvent flowrate is higher in this pilot plant (Notz et al., 2012) than in the pilot plant used for the absorber model validation (Tontiwachwuthikul et al., 1992).

### 8.3 Concluding remarks

This chapter first presented the application of the model developed in this study to a complete MEA based absorber-desorber CO$_2$ capture process. The high sensitivity of
the process to the flowrate of MEA in the solvent make-up was highlighted. The carbon capture model has also been employed to reproduce experimental results from a recently published pilot plant study (Notz et al., 2012). Very good agreement was found between the model predictions and the pilot plant data for different runs of absorber in relation to the mass fraction of CO$_2$ in the liquid phase along the entire length of the column. The predictions for the liquid temperature profile were not as good and additional work on the model is required to assess the cause for the temperature deviation.
Chapter 9

Concluding remarks

9.1 Summary of thesis

The focus of this thesis has been the integration of the SAFT-VR thermodynamic approach in the development of an absorber-desorber process model for carbon capture. The aim of the model is to be as predictive as possible, limiting the reliance on experimental data and bearing in mind that it must ultimately be used for solvent design.

The development of the process model has been done in two steps: we first presented a model for an absorber column and secondly we transferred this model to a desorber column and added a condenser and a reboiler.

In both columns the heat- and mass-transfer is described with rate-based equations. Both the vapour-liquid equilibrium and the chemical equilibrium are treated within the SAFT-VR thermodynamic framework, ensuring a consistent and accurate representation of the physical interactions in the system under the assumption that reaction kinetics are not rate-determining. This approach lends itself to extension to other solvents, as a consequence of the transferable nature of the SAFT molecular models and the relatively small number of parameters and data required to develop them.

Model validation has been carried out for the absorber model by comparison with pub-
lished experimental pilot plant data (Tontiwachwuthikul et al., 1992). A central finding of our current study is that diffusivity of CO$_2$ in the liquid phase required adjustment in order to provide an accurate representation of the column profiles; this was done based on different operating conditions. Very good predictions are obtained for the liquid-phase temperature profiles and liquid- and gas-phase compositions along the column. This highlights the importance of capturing the physical and chemical equilibria reliably; in addition the assumption that the process is not limited by reaction kinetics appears to be valid.

With a careful sensitivity analysis we show that the liquid viscosity and diffusivity, and vapour-liquid surface tension, are key properties for the prediction of the composition profiles. The heat generated by the absorption of CO$_2$ affects the magnitude of the temperature variation in the absorber and the vaporisation of water affects the presence and amplitude of the temperature bulge.

The CO$_2$ desorber model has been developed and extended from the absorber model. Model validation has been carried out by comparison with published experimental pilot plant data (Tobiesen et al., 2008). It is shown that good predictive capabilities can be obtained over a wide range of operating conditions without any need for modifying the modelling approach between the absorber and the desorber. The model parameter scaling the diffusivity of the CO$_2$ in the liquid phase and adjusted based on the absorber operating conditions appears to be transferable to the desorber conditions.

With a careful sensitivity analysis we show that the model is almost insensitive to variations in key mass-transfer related model properties. It was highlighted that the higher the CO$_2$ loading in the process, the more important the share of reboiler heat duty for the desorption of CO$_2$ and the lesser the share of reboiler heat duty for the vaporisation of H$_2$O. Finally, it was shown that the pressure in the reboiler has a significant impact on the amount of CO$_2$ being desorbed in the reboiler.

Once both the absorber and the desorber model are developed and validated, an application of this model to simulate a complete MEA based absorber-desorber CO$_2$ capture process is presented. The carbon capture model is also employed to reproduce experi-
mental results from a recently published pilot plant study (Notz et al., 2012). Although additional work on the model is required to assess the cause for the temperature deviation between the model predictions and the pilot plant data, good agreement is found for the CO\textsubscript{2} composition profile confirming the transferable aspect of the carbon capture model developed in this study.

\section*{9.2 Key contributions}

The contributions of this thesis include:

- The development of a predictive and transferable rate-based model of absorber-desorber carbon capture process based on the SAFT-VR thermodynamic approach.

- An extensive validation of the model on different pilot plants and for a wide range of operating conditions.

- A demonstration that the concept of implicit reactions and the dominance of mass transfer limitations works.

- A detailed understanding of the impact of the mass- and heat-transfer phenomena in the process model.

- A complete model that can be used for process optimisation and solvent selection.

\section*{9.3 Directions for future work}

In this thesis, a complete model of amine based CO\textsubscript{2} capture process has been developed. The directions for future work arising from this study can be divided across several objectives: increase the accuracy of the model, validate it further and, use the model for process
design, and treatment of impurities. The last paragraph provides a wider perspective on the use of the model in the global effort to reduce global warming.

9.3.1 Increase the model accuracy

The first direction would be to reassess the accuracy of the SAFT-VR thermodynamic approach in the temperature range of the desorber. When developing the molecular model, the aim was to have one single model applicable to different temperatures. Due to the deviation of the model predictions compared to experimental data at higher temperatures, this would need to be reviewed and one should explore whether adding a dependence in temperature on the parameters describing the MEA+CO\(_2\) interaction is improving the accuracy of the results when used in the process model.

A second direction to improve the accuracy would be to assess the heat transfer correlation sensitivity under different operating conditions in order to gain better predictions of the temperature profiles.

9.3.2 Validate further

An experimental study of the diffusion of carbamate in MEA would be very useful to obtain a diffusion correlation and so suppressing the model parameter introduced in this study.

More advanced version of SAFT are available and integrating them in the process would be beneficial. For example, SAFT-VR Mie is thought to provide a better description of the heat related parameters, hence potentially suppressing the need for a correction of the heat of absorption of CO\(_2\). The SAFT-VR Mie molecular model of H\(_2\)O, MEA and CO\(_2\) and their cross interactions are still under development.
9. Concluding remarks

9.3.3 Process design

A potential application of this model is its use with different solvents. It would be relatively straight-forward to transfer from MEA to AMP for example. In this case one should reassess the assumption that the process is mass-transfer limited due to the slower kinetics of AMP. The model could also be applied to blends of solvents but this would require the determination of new SAFT-VR parameters to mediate the solvent-solvent interactions. Using a blend of solvents can improve the characteristics of the absorption process (e.g. reduce the energy penalty) while improving the behaviour of the solvent (less degradation).

SAFT-γ is a group contribution approach which can be used for molecular design to find new solvents. A process-wide optimisation of the carbon capture system including solvent design could be performed.

9.3.4 Extending the model to account for impurities

The model developed in this study does not account solvent degradation or impurities. As explained in chapter 2, an important limitation of amine-based carbon capture processes is the degradation of the solvent with oxygen. In order to take into account this phenomena in the model, future work should focus on developing a model for oxygen and its interaction with the amine solvent considered (for example MEA). A set of SAFT parameters should be derived from solubility data of O₂ in a mixture of H₂O and MEA.

The best strategy to address the impurities problem would be to use this model as a tool to explore different configurations and solvents for the carbon capture process. Once a promising solvent and topology have been selected, a more detailed model including the effect of impurities can be used to validate further the characteristics of a certain combination of solvent and configuration.
9.3.5 Potential use of this model

The major advantage of this model is that it can reduce the number of experimentation needed for the design and the optimisation of an amine based carbon capture process. This model is a tool to explore different process configurations and identify suitable solvents in a cheaper and faster way than a full-scale experimentation like pilot or demonstration plant. The importance of improving the solutions available to reduce the emissions of CO\textsubscript{2} in the atmosphere have been explained in the first chapter of this thesis. It is reconfirmed by the report recently published by the UN’s climate change panel (IPCC, 2013) highlighting the urgent need for “substantial and sustained reductions of greenhouse gas emissions”. By providing researchers a tool capable of understanding and improving carbon capture processes, the model developed in this study is playing a part in the common effort needed to stop global warming.

9.4 Publications and presentations

9.4.1 Publications


9. Concluding remarks

C. V. Brand, J. Rodríguez, A. Galindo, G. Jackson, C. S. Adjiman, Development and validation of an MEA carbon capture absorber process integrating advanced thermodynamics and process modelling, Submitted to Energy & Environmental Science.

9.4.2 Conference presentations and posters


C. V. Brand, J. Rodríguez, A. Galindo, G. Jackson, C. S. Adjiman, Application of the SAFT-VR framework to the development of a carbon dioxide absorber using aqueous amine solutions, (talk), UKCCSC Early Careers Winter School, January 2012, University of Cambridge, UK.

C. V. Brand, J. Rodríguez, A. Galindo, G. Jackson, C. S. Adjiman, Validation of an absorber model of carbon dioxide capture in an aqueous amine solvent developed based on the SAFT-VR framework, (poster), Centre for Process System Engineering PhD symposium, March 2012, Imperial College London, UK.


C. V. Brand, J. Rodríguez, A. Galindo, G. Jackson, C. S. Adjiman, CO₂ capture using mono solutions: Development and validation of a process model based on the SAFT-VR equation of state, (talk), IC4S Annual meeting, April 2013, Imperial College London, UK.
Nomenclature

$\delta H_{\text{CO}_2}$  Correction to the enthalpy of absorption of CO$_2$ (J mol$^{-1}$)

$\Delta H_{\text{CO}_2}^{\text{abs}}$  Enthalpy of absorption of CO$_2$ (J mol$^{-1}$)

$\dot{v}^L$  Volumetric flowrate of the liquid phase (m$^3$ s$^{-1}$)

$\dot{v}^V$  Volumetric flowrate of the vapour phase (m$^3$ s$^{-1}$)

$\epsilon$  Void fraction (-)

$\epsilon_{L_0}$  Operating void space in the packing (-)

$\eta^L$  Dynamic viscosity of the liquid phase (kg m$^{-1}$ s$^{-1}$)

$\eta^V$  Dynamic viscosity of the vapour phase (kg m$^{-1}$ s$^{-1}$)

$\gamma$  Contact angle (deg)

$\lambda_T^L$  Liquid thermal conductivity (W m$^{-1}$ K$^{-1}$)

$\lambda_T^V$  Vapour thermal conductivity (W m$^{-1}$ K$^{-1}$)
Nomenclature

$\lambda_{ij}$ Parameter of the attractive range of the intermolecular potential between two segments $i$ and $j$ (-)

$\mu^L_i$ Chemical potential of component $i$ in the liquid phase (J mol$^{-1}$)

$\mu^V_i$ Chemical potential of component $i$ in the gas phase (J mol$^{-1}$)

$\omega^V_i$ Mass fraction of component $i$ in the vapour phase

$\phi_M$ Association factor for the liquid mixture (-)

$\phi_j$ Association factor of solvent $j$ (-)

$\Psi$ CO$_2$ removal rate (%)  

$\rho^L$ Density of the liquid phase (kg m$^{-3}$)

$\rho^V$ Density of the vapour phase (kg m$^{-3}$)

$\sigma$ Vapour-liquid surface tension (N.m$^{-1}$)

$\sigma_c$ Critical surface tension of the packing material (N m$^{-1}$)

$\Sigma_v$ Atomic diffusion volume (Å)

$\sigma_{ii}$ Diameter of segments forming molecule $i$ (Å)

$\tau$ Scaling factor for the liquid diffusivity of CO$_2$ in the solvent (-)

$\theta$ Angle with horizontal for falling film or corrugation channel (deg)

$\theta_{\text{CO}_2}$ CO$_2$ loading in the liquid phase (-)
$\varepsilon_{ab,ij}$  Depth of the interaction potential between association site $a$ on molecule $i$ and site $b$ of molecule $j$ (J K$^{-1}$)

$\varepsilon_{ij}$  Depth of the intermolecular potential between two segments $i$ and $j$ (J K$^{-1}$)

$\bar{x}$  Liquid mole fraction (-)

$\bar{y}$  Vapour mole fraction (-)

$\bar{z}_i$  Molar composition of a stream consisting of pure component $i$ (-)

$a'$  Interfacial area density (m$^2$ m$^{-3}$)

$a_p$  Specific surface area of the packing (m$^2$ m$^{-3}$)

$A_{section}$  Cross sectional area of the column (m$^2$)

$a_T$  Total interfacial area available for heat or mass transfer (m$^2$)

$c$  Total number of components

$C^L$  Concentration in the liquid phase (mol m$^{-3}$)

$C^V$  Concentration in the vapour phase (mol m$^{-3}$)

$C^{I,L}$  Concentration at the liquid-vapour interface in the liquid phase (mol m$^{-3}$)

$C^{I,V}$  Concentration at the liquid-vapour interface in the vapour phase (mol m$^{-3}$)

$C_e$  Correaction factor for surface renewal (-)

$C_p^L$  Specific heat capacity of the liquid phase (J kg$^{-1}$ K$^{-1}$)

$C_p^V$  Specific heat capacity of the vapour phase (J kg$^{-1}$ K$^{-1}$)
\( D_i^L \)  \( \text{Diffusion coefficient of component } i \text{ in the liquid phase (m}^2 \text{s}^{-1}) \)

\( D_i^V \)  \( \text{Diffusion coefficient of component } i \text{ in the vapour phase (m}^2 \text{s}^{-1}) \)

\( D_{i,j}^0 \)  \( \text{Mutual diffusion coefficient of solute } i \text{ at very low concentrations in solvent } j \text{ (cm}^2 \text{s}^{-1}) \)

\( d_s \)  \( \text{Diameter of a sphere of the same surface as a single packing particle (m)} \)

\( D_z \)  \( \text{Stage height (m)} \)

\( E^L \)  \( \text{Net gain of energy of the liquid phase (W)} \)

\( E^V \)  \( \text{Net loss of energy from the vapour phase (W)} \)

\( F_{SE} \)  \( \text{Factor for surface enhancement (-)} \)

\( Fr_L \)  \( \text{Liquid-phase Froude number (-)} \)

\( g \)  \( \text{Gravitational acceleration (m s}^{-2}) \)

\( g_{\text{eff}} \)  \( \text{Effective gravitational acceleration (m s}^{-2}) \)

\( H^L \)  \( \text{Enthalpy of the liquid phase (J mol}^{-1}) \)

\( H^V \)  \( \text{Enthalpy of the vapour phase (J mol}^{-1}) \)

\( h_t \)  \( \text{Liquid holdup (-)} \)

\( h^L_T \)  \( \text{Liquid-phase heat-transfer coefficient (W m}^{-2} \text{K}^{-1}) \)

\( h^V_T \)  \( \text{Vapour-phase heat-transfer coefficient (W m}^{-2} \text{K}^{-1}) \)

\( h_{\text{packing}} \)  \( \text{Total packing height (m)} \)
\( k^L \) Liquid-phase mass-transfer coefficient (m s\(^{-1}\))
\( k^V \) Vapour-phase mass-transfer coefficient (m s\(^{-1}\))
\( k_{ij} \) Binary interaction parameter used to compute the strength of the interactions between segments \( i \) and \( j \) (-)
\( L_j \) Liquid molar flowrate leaving stage \( j \) (mol s\(^{-1}\))
\( L_p \) Nominal packing size (m)
\( L_{spec} \) Specific liquid flowrate (kg s\(^{-1}\))
\( M_i \) Molecular weight of component \( i \) (g mol\(^{-1}\))
\( m_i \) Number of segments in the molecule \( i \) (-)
\( N_i^L \) Net gain of species \( i \) in the liquid phase due to interphase transport (mol s\(^{-1}\))
\( N_i^V \) Net loss of species \( i \) in the vapour phase due to interphase transport (mol s\(^{-1}\))
\( N_s \) Number of stage in the column (-)
\( N_{s,ia} \) Number of sites of each type \( a \) on molecule \( i \)
\( N_{s,i} \) Number of site types for molecule \( i \)
\( P^I \) Pressure at the vapour-liquid interface (MPa)
\( P^L \) Pressure in the liquid phase (MPa)
\( P^V \) Pressure in the vapour phase (MPa)
\( Pr^L \) Prandtl number for the liquid phase (-)
Nomenclature

Pr\textsuperscript{V} Prandtl number for the vapour phase (-)

Q\textsubscript{cond}\textsuperscript{L} Conductive heat flux in the liquid phase (W)

Q\textsubscript{diff}\textsuperscript{L} Diffusive heat flux in the liquid phase (W)

Q\textsubscript{cond}\textsuperscript{V} Conductive heat flux in the vapour phase (W)

Q\textsubscript{diff}\textsuperscript{V} Diffusive heat flux in the vapour phase (W)

Q\textsubscript{r} Reboiler heat duty (W)

Q\textsubscript{ΔT} Power for the temperature increase of the liquid stream (W)

Q\textsubscript{CO\textsubscript{2}} Power for the desorption of CO\textsubscript{2} (W)

Q\textsubscript{H\textsubscript{2}O} Power for the vaporisation of H\textsubscript{2}O (W)

r\textsubscript{c,ab,ij} Attractive range of the interaction potential between association site a on molecule i and site b of molecule j (Å)

Re\textsuperscript{L} Liquid-phase Reynolds number based on the specific surface area (-)

Re\textsuperscript{V} Vapour-phase Reynolds number (-)

S Side dimension of corrugation (m)

Sc\textsubscript{i}\textsuperscript{L} Schmidt number of component i in the liquid phase (-)

Sc\textsubscript{i}\textsuperscript{V} Schmidt number of component i in the vapour phase (-)

T\textsubscript{I} Temperature at the vapour-liquid interface (K)

T\textsubscript{L} Temperature of the liquid phase (K)
Nomenclature

$T^V$ Temperature of the vapour phase (K)

$u^L$ Liquid velocity (m s$^{-1}$)

$u^L_e$ Effective liquid-phase velocity (m s$^{-1}$)

$u^V$ Vapour velocity (m s$^{-1}$)

$u^V_e$ Effective vapour-phase velocity (m s$^{-1}$)

$V^L$ Molar volume of the liquid phase (cm$^3$ mol$^{-1}$)

$V^V$ Molar volume of the vapour phase (cm$^3$ mol$^{-1}$)

$V_{i,L}^*$ Molar volume of the pure component $i$ in the bulk liquid phase (cm$^3$ mol$^{-1}$)

$V_{i,V}^*$ Molar volume of the pure component $i$ in the bulk vapour phase (cm$^3$ mol$^{-1}$)

$V_{I,L}$ Molar volume of the liquid phase at the vapour-liquid interface (cm$^3$ mol$^{-1}$)

$V_{I,V}$ Molar volume of the gas phase at the vapour-liquid interface (cm$^3$ mol$^{-1}$)

$V_{i,m}$ Molar volume of solute $i$ at its normal boiling temperature (cm$^3$ mol$^{-1}$)

$V_j$ Vapour molar flowrate leaving stage $j$ (mol s$^{-1}$)

$V_{spec}$ Specific vapour flowrate (kg s$^{-1}$)

$We^L$ Liquid-phase Weber number (-)

$Re^L$ Liquid-phase Reynolds number based on the interfacial area (-)
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Table 1: SPF file used for the SAFT-VR foreign object

| Component | SPF File Used | MW, Molecular Weight | IFLAG (Spectra Data Available) | 18.015d0 (MW, Molecular Weight) | 3.24255d4 (1.92835d3-1.055492d-5-.3.596461d-9) | 2 4 2 6 | 1 4 2 2 | 1 2 1440.06d0 2.10822d-10 | 0 0 0 0 | 61.083d0 | 0 9.31140 3.009d-1-1.818d-4 4.656d-8 | 2 4 0 | 3.57229d4-10 | 1 5.82860d0 | 30.24d0 | 4 1 2 1 2 3 4 2 1 1 2 1 0 0 0 | 28.014d0 | 3.115d1-1.357d-2 2.680d-5-1.168d-8 | 1.4d0 | 3.073578d4-10 | 1.587523d0 | 74.587238d0 | 0 0 0 0 | 1 2 2 0.01 | 1 2 3 1780.71d0 1 2 | 1 2 3 1780.71d0 2.1 | 1 2 3 1517.10d0 1 4 | 1 2 3 1517.10d0 2 3 | 1 2 4 2.1076d3-10 1 2 | 1 2 4 2.1076d3-10 2 1 | 1 2 4 2.226d6-10 1 4 | 1 2 4 2.226d6-10 2 3 | 1 3 2 -0.06d0 | 2 3 2 0.47d88 | 2 3 3 5290d0 3 1 | 2 3 4 1.97978d10 3 1 | 2 3 3 3982.66d0 3 2 | 2 3 4 1.96999d10 3 2 | 1 4 2 -0.36d15d | 2 4 2 0.05d80 | 3 4 2 -0.05990 | 0 0 0 |

| Component | SPF File Used | MW, Molecular Weight | IFLAG (Spectra Data Available) | 18.015d0 (MW, Molecular Weight) | 3.24255d4 (1.92835d3-1.055492d-5-.3.596461d-9) | 2 4 2 6 | 1 4 2 2 | 1 2 1440.06d0 2.10822d-10 | 0 0 0 0 | 61.083d0 | 0 9.31140 3.009d-1-1.818d-4 4.656d-8 | 2 4 0 | 3.57229d4-10 | 1 5.82860d0 | 30.24d0 | 4 1 2 1 2 3 4 2 1 1 2 1 0 0 0 | 28.014d0 | 3.115d1-1.357d-2 2.680d-5-1.168d-8 | 1.4d0 | 3.073578d4-10 | 1.587523d0 | 74.587238d0 | 0 0 0 0 | 1 2 2 0.01 | 1 2 3 1780.71d0 1 2 | 1 2 3 1780.71d0 2.1 | 1 2 3 1517.10d0 1 4 | 1 2 3 1517.10d0 2 3 | 1 2 4 2.1076d3-10 1 2 | 1 2 4 2.1076d3-10 2 1 | 1 2 4 2.226d6-10 1 4 | 1 2 4 2.226d6-10 2 3 | 1 3 2 -0.06d0 | 2 3 2 0.47d88 | 2 3 3 5290d0 3 1 | 2 3 4 1.97978d10 3 1 | 2 3 3 3982.66d0 3 2 | 2 3 4 1.96999d10 3 2 | 1 4 2 -0.36d15d | 2 4 2 0.05d80 | 3 4 2 -0.05990 | 0 0 0 |