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The Development of a Molecular Systems Engineering Approach to the Design of Carbon-capture Solvents

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1.1 Introduction

Carbon capture, utilization and storage (CCUS) is widely considered to be a comprehensive strategy to reduce the impact of the carbon dioxide (CO₂) that is produced through the use of fossil fuels across a range of human activities. Carbon capture is an important first step in the implementation of such an approach. Despite the significant effort devoted to the development of carbon-capture techniques, their implementation remains challenging due to the high energetic costs, large environmental impacts and rapid degradation of capture materials associated with some of the current processes. Of the many alternatives available for carbon capture, solvent-based absorption is a competitive and mature technology for carbon dioxide removal from gas streams [1, 2]. A solvent can absorb CO₂ through two broad mechanisms: chemical absorption and physical absorption. Chemical absorption entails the formation of chemical bonds between solvent molecules and CO₂, typically through the formation of ionic species. Physical absorption, on the other hand, is driven by weaker van der Waals forces that promote interactions between the solvent and CO₂.

Chemical absorption has some advantages over its physical counterpart: chemical solvents usually have a higher capacity for CO₂ [3], chemisorption processes can be applied to streams with relatively low CO₂ partial pressures, and mass transfer from the gas to the liquid phase may be enhanced due to the depletion of CO₂ from the liquid phase caused by the reactions. The thermal regeneration of chemical solvents can, however, be highly energy intensive [4], whereas physical solvents can be regenerated simply with a less costly pressure-swing process.

The carbon-capture potential of many aqueous solutions of alkanolamines, amino acids, ammonia and caustic soda has been investigated [5], yet monoethanolamine (MEA) aqueous solutions remain the most widely used class of chemisorption solvents. A number of physical absorption processes are in common use such as the Rectisol

process (with methanol as solvent), the Selexol process (with a blend of dimethyl ethers of polyethylene glycol), the Purisol process (with *N*-methyl-2-pyrrolidone), the Morphysorb process (with morpholine), and the Fluor solvent process (with propylene carbonate) [6]. Hybrid processes in which a blend of physical and chemical solvents are employed have also been investigated [1], as have switchable solvents. Switchable solvents are a new class of solvent blends that undergo both physical and chemical absorption and form ionic liquids in the presence of CO₂ [7].

The performance of absorption technologies is closely linked to the choice of solvent. Given the need to develop low-cost and sustainable CO₂ absorption processes, new solvents are being explored. In the quest for new solvents (and blends), it is highly unlikely that a universal 'best' solvent for CO₂ capture will be found. Instead, the optimal solvent for CO₂ capture is a function of a number of process specifications such as the conditions of the feed to be separated (pressure, temperature and chemical composition), output requirements (e.g. the purity and the pressure of the treated gas), and process constraints (e.g. available equipment, restrictions on size, temperature and pressure). Solvent selection and process design have, however, traditionally been tackled as separate or sequential activities [8], and this makes the task of finding improved solvents arduous. Experiments at the laboratory scale to find superior solvents are not only time consuming and expensive, but also can be extremely difficult to interpret in this multi-dimensional solvent and process design space. On the other hand, large combinatorial spaces can in principle be explored efficiently using computational methods. It is especially desirable to combine computational studies that can identify the optimal (and near optimal) solvent(s) based on appropriate models of the relevant properties and processes with a small number of targeted experiments [9].

Computer-aided molecular design (CAMD) methods have a useful role to play in this but are often focussed on finding molecules deemed optimal based on a few 'key' physicochemical properties [9–14]. There have been several studies to account for the impact of solvent properties on the overall performance of the process through process-based measures of varying levels of detail [15–18]. This makes it possible to take into account the dependence of physicochemical properties on process variables (such as operating pressure and temperature), the values of which are often unknown at the time of solvent selection. It has become clear that a design that takes into account both the solvent and the process can be deemed optimal only when the strong interactions between process and molecules are taken into account in arriving at the proposed design [18].

In recognition of this, several methodologies for the simultaneous design of both molecules (such as solvents) and processes have emerged. The molecular structure and process variables are optimized with respect to a process or plant-wide objectives. This class of design strategies, known as computer-aided molecular and process design (CAMPD), or integrated molecular and process design, presents many challenges. The CAMPD problem and possible solution approaches (not limited to carbon capture) have been discussed by a number of authors [8, 16, 17, 19–30].

Given the importance of intermolecular interactions to the performance of absorption processes, CO₂ capture studies are well suited to the application of a molecular systems engineering (MSE) approach in which a detailed molecular perspective is integrated with a description of the processes for the purpose of improved design [18, 31]. To apply an MSE approach to solvent design it is necessary to build tools for each of the

steps involved in the formulation and solution of CAMPD problems. First, the formulation of the CAMPD problem requires predictive models that relate the structure of the solvent to all relevant pure component and mixture properties, as well as predictive models of the process units and topology that are needed to evaluate the design objective(s) and constraints. Secondly, the design problem must be formalized by posing one or more optimization problems that make it possible to explore the trade-offs between the different design decisions. Finally, algorithms that can solve these highly challenging optimization problems are needed. We emphasize that data from experiments (e.g. physical property measurements and relevant process parameters) are also indispensable to the MSE approach; they are used to develop and improve property prediction and process models as well as to validate the results of the design. Thus, MSE entails multi-scale modelling and experimental studies of phenomena across various sub-system sizes, from molecules to processes [2, 18]. A balance must be struck between the accuracy of the models of the various sub-systems, their predictive power and their computational complexity, to ensure that the resulting CAMPD optimization problems are numerically tractable. To this end, it is sometimes advantageous to develop physical and chemical property models that offer a similar computational performance to widely used engineering correlations and other highly parameterized models, but that are applicable to a broader range of molecules and mixtures. This can be achieved through a judicious choice of assumptions and physical abstractions. The appropriate level of abstraction can only be determined by considering the different elements of an MSE approach (models, problem formulations and optimization algorithms) in an integrated manner.

In the specific context of the integrated design of solvents and carbon-capture absorption processes, the deployment of an MSE approach requires a wide range of physico-chemical properties: thermodynamic properties such as density, kinematic properties such as viscosity, and interfacial properties such as surface tension. These properties are required as a function of process-operating conditions. The property models used should preferably provide continuous and consistent descriptions of matter across the fluid region [26], avoiding the use of different models (e.g. equations of state or activity coefficient models) for the gas and liquid phases. This is particularly important in the vicinity of vapour–liquid critical points or in unit operations involving phase changes, such as heat-exchange equipment, to avoid having to identify the phase(s) of the mixture before selecting an appropriate model. Furthermore, it is desirable to use accurate models that provide predictions of properties related to phase equilibrium such as activity coefficients as well as calorific properties, to ensure thermodynamic consistency; it can be challenging to find such broadly applicable models [32–34]. Finally, an additional challenge in the modelling of absorption in reactive solvents is the need for predictive models of chemical equilibrium and/or kinetics, that provide a quantitative assessment of chemical changes within the process, as well as changes to physical properties.

In recent years, several groups have focussed on the development and application of CAMPD approaches to CO₂ capture. For instance, optimal solvents and process conditions for physical absorption of CO₂, while using the statistical associating fluid theory platform for property prediction, have been designed in [17], [25], [26], and [27]. Ng *et al.* [35] employed CAMD in the context of the use of ionic liquids for carbon capture. CAMD approaches have been applied to the design of alkanolamines and their blends in [36] and [37], respectively. CAMPD of novel chemisorption solvents has also been studied [29, 38, 39].

In this chapter, we provide a review of the recent work carried out in our research group on the application of MSE concepts to carbon capture, with a brief mention of other work based on similar thermodynamic models. In Section 1.2, thermodynamic models are discussed, with a special focus on the SAFT family of thermodynamic approaches (SAFT is statistical associating fluid theory). In Section 1.3, we show how one can take advantage of the physical association concept used with the equation of state (EoS) to describe the reaction equilibria relevant to chemical absorption. In Section 1.4, we discuss approaches to the solution of the integrated solvent and process design problem that embed these thermodynamic models.

1.2 Predictive Thermodynamic Models for the Integrated Molecular and Process Design of Physical Absorption Processes

The modelling of solvent-based carbon-capture processes that are driven by physisorption requires high-fidelity thermodynamic models that capture the highly non-ideal behaviour of the mixtures involved. This behaviour arises from the presence of species that can form hydrogen bonds (e.g. methanol, ethers, water), of apolar compounds such as hydrocarbons, and of CO₂ with its large quadrupole moment and critical point that falls within the range of operating conditions. Due to the wide range of temperatures and pressures that are typical of physical absorption processes, thermodynamic models that are predictive over a wide range of conditions are required. Additional complexity can arise when modelling solvent blends due to the complex interactions that need to be considered and the larger number of model parameters required.

Given the need for thermodynamic models that are predictive outside the domain of available experimental data, thermodynamic models rooted in molecular theories and statistical mechanics, for example SAFT-based approaches (for an overview, see [40], [41] and references therein), have been developed. These require fewer temperature-dependent parameters than traditional thermodynamic models. The impact of molecular shape and non-sphericity on thermodynamic properties can be described by representing molecules as chains of fused segments and the effect of strong directional interactions induced by hydrogen bonding or polarity can be captured by including appropriate association sites. SAFT EoSs are applicable across the entire fluid region so that consistent gas- and liquid-phase models can be used; this is highly advantageous for modelling processes for which vapour–liquid and vapour–liquid–liquid equilibria are important. As a result, the modelling of mixtures containing CO₂, water and/or hydrocarbons has long been a topic of interest in the development of SAFT-based equations (e.g. [42–45]). In this section, we present a brief overview of the SAFT family of thermodynamic approaches. We highlight in particular the development of group contribution versions of the EoSs, and we discuss the development of models applicable to the physical absorption of CO₂.

1.2.1 An Introduction to SAFT

In this section, we briefly describe the SAFT EoSs and highlight their relevance to the design of physical absorption processes.

SAFT-based approaches constitute a family of state-of-the-art equations of state with a firm theoretical grounding in statistical mechanics, a field which originates from the desire to describe thermodynamic systems in terms of statistical mechanical principles and which bridges the gap between the behaviour of individual molecules and bulk thermodynamics. The original version of SAFT [46, 47] was proposed to address the need for an equation of state for associating fluids that could not be described reliably by traditional cubic EoSs. The theory of association used within SAFT is based on Wertheim's thermodynamic perturbation theory (TPT) [48–51], which makes it possible to evaluate the contribution in free energy due to association in any fluid of monomers. The directional forces causing the monomers to associate are accounted for by specifying appropriate 'association sites' or 'sticky sites', which are defined by an inter-site potential function that is usually of the square-well (SW) form. Accurate thermodynamic properties of the fluid can thus be obtained starting from information on intermolecular forces.

Within SAFT, molecules are represented as chains of spherical segments that interact via intermolecular potentials that determine the forces present between segments and between association sites. In homonuclear (or more precisely homosegmented) versions of SAFT, a molecule i is formed from m_i identical segments that interact via a potential. The number of segments, m_i , can be treated as an adjustable parameter and for molecules with non-integer values of m_i , segments are sometimes referred to as fused. To model real pure fluids or mixtures of real compounds, parameters are required to specify the number of segments, the energy and the range of interaction between segments and between association sites. Homonuclear models are often used to represent whole molecules, i.e. one set of parameters is used to describe one specific compound.

Various versions of SAFT for homonuclear models exist for neutral molecules, with differences arising from the potential used to describe the repulsive and dispersive interactions between monomers, the types of interactions considered in the model (e.g. whether to include dipole interactions), and other choices made in the derivation of the equations such as the order of the perturbation expansion or the reference fluid employed in developing the theory. Well-known variants [41] include the original SAFT [46, 47], Chen and Kreglewski SAFT (CK-SAFT) [52], simplified SAFT [53], Lennard-Jones SAFT (LJ-SAFT) [42, 54], variable-range SAFT (SAFT-VR) [55, 56], SAFT-VR Mie [33], soft-SAFT [57], perturbed chain SAFT (PC-SAFT) [58], and simplified PC-SAFT [59]. Some examples of polar and quadrupolar variants of SAFT include a variant of SAFT-VR [60], a variant of CK-SAFT [61], and variants of PC-SAFT [62–72]. Extensions of the SAFT methodology that can be used to model charged compounds have also been developed [73–81].

The SW and Mie potentials are of most relevance to this chapter and are therefore discussed in more detail. The mathematical form of the SW potential used in SAFT-VR SW [55, 56] is given by

$$u_{12}^{\text{SW}}(r_{12}) = \begin{cases} \infty & r_{12} < \sigma_i, \\ -\varepsilon_i & \sigma_i \leq r_{12} < \lambda_i \sigma_i, \\ 0 & r_{12} \geq \lambda_i \sigma_i, \end{cases} \quad (1.1)$$

where the potential, u_{12}^{SW} , is a function of the distance, r_{12} , between the centres of two identical monomeric segments 1 and 2 of type i , and where σ_i is the diameter of the monomeric segments, ε_i the depth of the potential well, and λ_i characterizes the range of attraction. The SW potential is popular due to its simple form, leading to exact statistical mechanical calculations such as the algebraic evaluation of the second and third virial coefficients [82].

The Mie (generalized Lennard-Jones) potential, $u_{12}^{\text{Mie}}(r_{12})$, used in our recently developed SAFT-VR Mie EoS [33] as well as in an earlier version [83], is given by

$$u_{12}^{\text{Mie}}(r_{12}) = C_i \varepsilon_i \left[\left(\frac{\sigma_i}{r_{12}} \right)^{\lambda_i^r} - \left(\frac{\sigma_i}{r_{12}} \right)^{\lambda_i^a} \right], \quad (1.2)$$

$$C_i(\lambda_i^r, \lambda_i^a) = \frac{\lambda_i^r}{\lambda_i^r - \lambda_i^a} \left(\frac{\lambda_i^r}{\lambda_i^a} \right)^{\frac{\lambda_i^r}{\lambda_i^r - \lambda_i^a}}, \quad (1.3)$$

where λ_i^r and λ_i^a are the repulsive and attractive exponents respectively, which determine the softness or hardness of the repulsive interactions and the range of attraction and the constant C_i is defined such that the minimum of the potential corresponds to $-\varepsilon_i$. The Lennard-Jones (LJ) potential is equivalent to a Mie potential with $\lambda_i^r = 12$ and $\lambda_i^a = 6$. The characteristic form of the Mie potential is a steep curve at short separations, resulting in a large repulsive force, and a smooth shallow curve at greater separations, tapering off to zero as the distance increases. It is thus longer ranged and smoother than the SW potential, as can be seen in Figure 1.1 where a comparison between the SW potential and the Mie potential is shown.

Associating molecules are treated in SAFT by adding off-centre, spherically symmetrical SW bonding sites. The SW potential provides a good approximation for highly

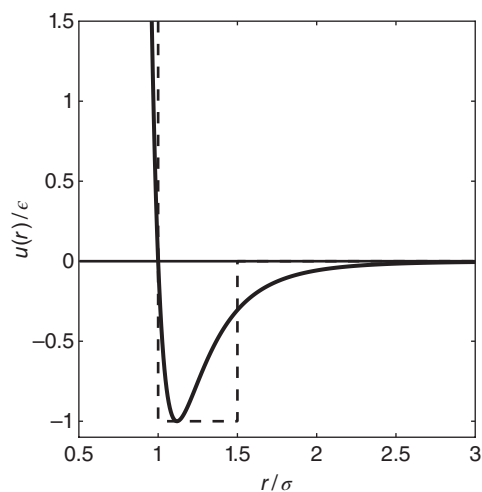


Figure 1.1 Examples of the Mie (continuous curve) and the SW (dotted lines) potentials between two monomeric segments as a function of the scaled segment-to-segment distance.

directional and short ranged interactions (e.g. hydrogen bonds) [84]. The interaction between two association sites 'a' and 'b' on two molecules of type i is characterized by an association energy $-\varepsilon_{abii}^{\text{HB}}$, and a bonding volume K_{abii} .

In SAFT, the Helmholtz free energy A of a system is written as the sum of different perturbative contributions that are added to a reference free energy. This concept is illustrated in Figure 1.2, where a fluid consisting of monomeric spherical segments is used as reference fluid, as is the case for example in the SAFT-VR EoSs. The corresponding general form of the equation of state is given in dimensionless form as

$$\frac{A}{NkT} = \frac{A^{\text{IDEAL}}}{NkT} + \frac{A^{\text{MONO.}}}{NkT} + \frac{A^{\text{CHAIN}}}{NkT} + \frac{A^{\text{ASSOC.}}}{NkT}, \quad (1.4)$$

where N is the total number of molecules, k is the Boltzmann constant, and T is the temperature. A^{IDEAL} is the free energy of an ideal gas (Figure 1.2a), $A^{\text{MONO.}}$ includes the free energy of a reference hard-sphere fluid (at this stage, the segments are assigned a volume) and the perturbative contributions arising from the chosen inter-segment potential (Figure 1.2b), A^{CHAIN} represents the free energy due to bonding the segments to form the molecular chains (Figure 1.2c), and $A^{\text{ASSOC.}}$ is the free energy due to

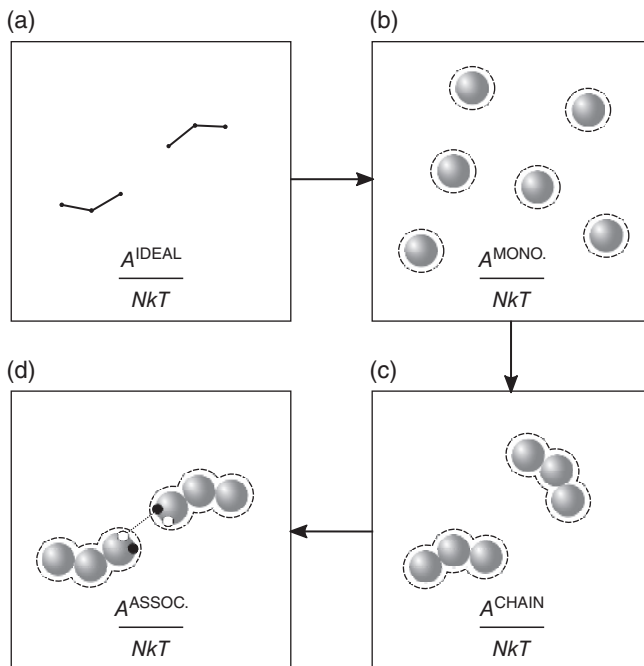


Figure 1.2 Procedure for forming a molecule in most versions of SAFT. (a) The fluid is represented as an ideal gas (no intermolecular interactions). (b) Monomeric spherical segments corresponding to the 'atomized' molecules are considered, with repulsion and dispersion interactions shown by the dotted circles (note that the potential between two particles is a function of the distance). (c) Chains are formed from tangentially bonded segments. (d) Association sites are added. This figure is based on Figure 1 in [53] and Figure 3.1 in [85].

association between sites (Figure 1.2d) – this term can account for hydrogen bonding, charge transfer and other types of complexation. After obtaining the Helmholtz free energy of the system, the thermodynamic properties can be derived from standard relations. For example, the pressure is related to the partial derivative of the free energy with respect to the volume, $P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$, and the chemical potential can be obtained from its partial derivative with respect to the number of molecules, $\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$.

A recent major advance in SAFT-VR has been the inclusion of the Mie potential (a generalized Lennard-Jones potential) to describe dispersion interactions between monomeric segments in a fluid, leading to the SAFT-VR Mie equation [33, 84, 86]. The use of the Mie potential is advantageous for the prediction of properties that are functions of the second derivatives of the Helmholtz free energy, such as heat capacities, isothermal compressibilities and speeds of sound, whilst simultaneously providing a good description of vapour–liquid equilibria (VLE) [33, 83, 84, 86]. These properties are sensitive to the slope of the potential between segments, particularly the nature of repulsive interactions. In addition, the higher-order perturbation expansion within the SAFT-VR Mie formulation leads to a much improved representation of the critical point compared to SAFT-VR SW [33, 84, 86].

These aspects are particularly important when considering thermodynamic models for carbon capture and storage: the critical point for CO₂ is well within the relevant operating ranges and the phase behaviour and other thermodynamic properties of CO₂-containing mixtures can be modelled more accurately with SAFT-VR Mie, reducing the number of empirical correlations required to estimate key properties. Importantly, the assumption of ideal mixing that often needs to be made to compute the heat capacity of mixtures can be lifted. Although the Mie potential requires the specification of one more parameter than the SW potential, it has been shown that a conformal description of the thermodynamics can be achieved with an interrelationship between λ_i^+ and λ_i^a [87], meaning that only λ_i^+ or λ_i^a needs to be determined during model development.

The implementation of several SAFT EoSs in commercial chemical process simulation packages is a strong indicator that their predictive nature makes them desirable in industrial applications. Implementations within process modelling environments also make these EoSs accessible to a wider community. For example, the process simulator ASPEN PLUS [88] has an implementation of PC-SAFT [58]. The DWSIM [89] open source simulator also comes with an implementation of this EoS, as does the Multiflash [90] thermodynamic modelling tool. The equation-oriented modelling environment gPROMS [91] has an implementation (gSAFT [92]) that includes the SAFT-VR SW [55, 56] and SAFT-VR Mie [33] equations, as well as the group contribution version, SAFT- γ Mie [34].

1.2.2 Group Contribution (GC) Versions of SAFT

Group contribution (GC) approaches [93] exploit the idea that although there are many possible chemical compounds of relevance to industry, the number of different chemical functional groups which form these compounds is significantly smaller. For example, the family of primary linear alkanolamines (monoethanolamine (MEA), C₂H₇ON; monopropanolamine (MPA), C₃H₉ON, etc.) can be represented with a small

number of functional groups, e.g. CH_2NH_2 , CH_2OH and CH_2 . This reduces the number of parameters required to describe fluids consisting of different molecules; once parameters describing the relevant functional groups have been obtained, new molecules can be quickly analysed by using the functional groups as building blocks. A key assumption in GC methods is that the thermodynamic properties of a fluid can be described for the contributions made by each functional group, regardless of its environment and connectivity [94]. For example, the CH_2OH group is assumed to behave in the same way in both monopropanolamine and monopentanolamine. The assumption of transferability of groups to other molecules is valid only if there is no significant difference in the polarization of the same functional groups present in different molecules. If proximity effects are important or differences between isomers [94] are of interest, 'second-order' groups can be used which specify the functional groups in close proximity (e.g. see [95–97]). To ensure the transferability of functional groups, parameters are estimated from experimental data for a wide range of different molecules that contain the functional groups rather than from data specific to a given molecule.

Several group contribution versions of SAFT equations of state have been proposed, each differing in the GC schemes (e.g. mixing rules) used. GC SAFT methods can be classified into two main approaches: homonuclear and heteronuclear. In homonuclear approaches, the monomeric segments used to represent a given molecule are considered identical. Some examples of homonuclear GC SAFT approaches include the work of Vijande *et al.* [98], who proposed a homonuclear GC scheme for the PC-SAFT EoS [58]; the work of Tobaly and co-workers [99, 100], who proposed GC approaches for the original SAFT [46, 47], SAFT-VR [55, 56] and PC-SAFT [58] relations; and the work of Tihic *et al.* [101], who applied the GC scheme proposed in [95] to a simplified version of PC-SAFT [59]. In the aforementioned approaches, parameters describing functional groups are averaged, using group contribution rules, to calculate the equation of state parameters (see e.g. Equations (11)–(14) in [99]).

Heteronuclear GC SAFT methods have been developed, in which the averaging step is no longer needed as segments used to model a given compound are not identical [102], giving additional flexibility in developing models. Versions that have been proposed include GC extensions to the SAFT-VR SW EoS, namely SAFT- γ SW [103, 104], GC-SAFT-VR [105], which builds on the hetero-SAFT-VR EoS [106], and SAFT- γ Mie [34], which is based on SAFT-VR Mie [33]. A GC version of perturbed-chain polar SAFT (PCP-SAFT) [69], the GPC-SAFT EoS [102], has also been proposed recently.

An example of a heteronuclear fused molecular model for 3-amino-1-propanol (MPA) is shown in Figure 1.3(a), following the model developed in [107] within the framework of SAFT- γ SW [103, 104]. A molecular (homonuclear) model for MPA (Figure 1.3(b)) is also shown for comparison, along with the skeletal formula for MPA (Figure 1.3(c)). As can be seen, in the molecular version, it is not possible to assign a specific functional group to a specific segment since all are identical. Group contribution versions of SAFT not only extend the predictive capabilities of the approach, but they also enable the broader use of the SAFT-type platform for the formulation and solution of CAMD/CAMPD problems, as will be discussed in Section 1.4.

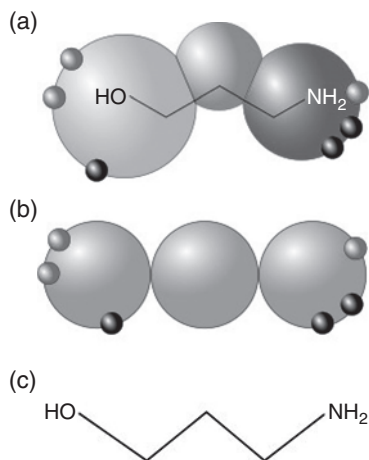


Figure 1.3 (a) The heteronuclear model for MPA developed in [107]. From left to right, the segments represent the CH₂OH, CH₂ and CH₂NH₂ functional groups, respectively. The association sites represent the lone pairs of electrons (green) and hydrogens (black) on the amino and hydroxyl functional groups. These sites mediate the directional short-ranged interactions between molecules. (b) A homonuclear model for MPA where the segments are identical, with the same association scheme as in (a). (c) The skeletal formula for MPA.

1.2.3 Model Development in SAFT

The development of a SAFT model consists in selecting the basic structure of the molecular model (number of segments, number and types of association sites) and in estimating the remaining unknown parameters, by minimizing the deviations between the values of some of the properties predicted by the model and corresponding experimental measurements. The parameters required to model the thermodynamic properties of a pure component are summarized in Table 1.1 for SAFT-VR SW and SAFT-VR Mie. The properties included in parameter estimation for homonuclear models of pure components are usually those that are readily accessible experimentally, and commonly include saturated liquid densities and vapour pressures taken at temperatures between the triple point and close to the critical temperature (e.g. temperatures up to 95% of the critical temperature). In some cases, other properties such as heats of vaporization, single-phase liquid densities or speed of sound can be used.

In the case of heteronuclear models, the parameters needed to model a molecule and a given functional group k are listed in Table 1.2 for SAFT- γ SW and SAFT- γ Mie. Unlike group–group interactions can often be obtained from pure component data alone, although more reliable values of the parameters can be estimated by including mixture data such as enthalpies of mixing or binary mixture phase-equilibrium data. The main unlike group–group interaction to be estimated is ε_{kl} , the dispersive interaction energy between groups of type k and l . Where relevant, the association energy between sites of type a on group k and sites of type b on group l , ε_{abkl}^{HB} , is also estimated. Finally, the corresponding exponents characterizing the interaction ranges are sometimes estimated. All unlike interaction parameters that are not regressed to experimental data are derived from combining rules as presented in [103] for SAFT- γ SW, in [34] for SAFT- γ Mie, and in [84] for SAFT-VR Mie.

Table 1.1 Parameters required to model pure components in SAFT-VR Mie and SAFT-VR SW homonuclear approaches.

Parameter	Definition	Potential
m_i	Number of segments in molecule i	Mie, SW
σ_i	Diameter of monomeric segments in molecule i	Mie, SW
ε_i	Depth of potential well between segments in molecule i	Mie, SW
λ_i	Width of potential well for segments in molecule i	SW
λ_i^a	Attractive exponent of the Mie potential for segments in molecule i (usually set to 6)	Mie
λ_i^r	Repulsive exponent of the Mie potential for segments in molecule i	Mie
NST_i	Number of site types on molecule i	Mie, SW
$n_{a,i}$	Number of sites of type a on molecule i , $a = 1, \dots, NST_i$	Mie, SW
ε_{abii}^{HB}	Association energy between sites of types a and b on two molecules of type i , $a = 1, \dots, NST_i$, $b = 1, \dots, NST_i$	Mie, SW
r_{abii}^c or K_{abii}	Range of association or bonding volume between sites of types a and b on two molecules of type i , $a = 1, \dots, NST_i$, $b = 1, \dots, NST_i$	Mie, SW

Table 1.2 Parameters needed to model group self-interactions in SAFT- γ Mie and SAFT- γ SW heteronuclear group-contribution approaches.

Parameter	Definition	Potential
$\nu_{i,k}$	Number of groups of type k in molecule i	Mie, SW
ν_k^*	Number of identical segments in group k	Mie, SW
S_k	Shape factor of segments in group k	Mie, SW
σ_k	Diameter of segments in group k	Mie, SW
ε_k	Depth of potential well for segments in group k	Mie, SW
λ_k	Width of potential well for segments in group k	SW
λ_k^a	Attractive exponent of the Mie potential for segments in group k (usually set to 6)	Mie
λ_k^r	Repulsive exponent of the Mie potential for segments in group k	Mie
NST_k	Number of site types on group k	Mie, SW
$n_{a,k}$	Number of sites of type a on group k , $a = 1, \dots, NST_k$	Mie, SW
ε_{abkk}^{HB}	Association energy between sites of types a and b on two groups of type k , $a = 1, \dots, NST_k$, $b = 1, \dots, NST_k$	Mie, SW
r_{abkk}^c or K_{abkk}	Range of association or bonding volume between sites of types a and b on two groups of type k , $a = 1, \dots, NST_k$, $b = 1, \dots, NST_k$	Mie, SW

The parameter estimation problem that must be solved to estimate the molecular parameters is non-convex, which leads to the possibility of converging to parameter values that correspond to a local minimum rather than the global minimum. In addition, a variety of parameter sets (models) can provide equivalent performance due to

the degenerate nature of the parameter space and the high degree of correlation between some parameters such as the dispersion energy and the range of dispersion interactions, or the dispersion and association energies. This becomes an issue when the number of model parameters increases, e.g. for complex associating compounds, or when experimental data are scarce. As a result, the best model is not always the one that corresponds to the global optimum [86, 108, 109]. The issue of model degeneracy can be addressed by choosing parameter values (or a range of values) that make physical sense, for example in SAFT-VR Mie one can set λ_r to 6, following the arguments presented in [86] and [87]. Furthermore, properties not included in the objective function can be analysed in a predictive fashion to discriminate between models (for example, the heat of vaporization [108] and surface tension [108, 110]).

To develop mixture models based on homonuclear versions of SAFT, additional parameters often need to be estimated based on multi-component (usually binary) phase-equilibrium data, such as vapour–liquid equilibrium or liquid–liquid equilibrium. It is usually sufficient to estimate unlike energy parameters for dispersive interactions (ε_{ij} between compounds i and j) and, if relevant, for association interactions (ε_{abij}^{HB} between sites of type a on compound i and sites of type b on compound j). Occasionally, the unlike range parameters also need to be estimated from the data to increase model accuracy (e.g. see [45]). Once again, any unlike parameter not regressed to experimental data can be obtained from the like parameters using combining rules. For example, the unlike size parameter (σ_{ij}) required to describe the interactions between a compound i with diameter σ_i and a compound j with diameter σ_j can be obtained by taking the average of the like segment diameters:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad (1.5)$$

The combining rules for other unlike parameters can be found in [56] for SAFT-VR SW, in [84] for SAFT-VR Mie, in [103] for SAFT- γ SW and in [34] for SAFT- γ Mie.

1.2.4 SAFT Models for Physical Absorption Systems

In this section, we present a few examples of SAFT models that have been developed based on the SAFT-VR and SAFT- γ platforms to treat the species present in physisorption processes.

Pereira *et al.* [25] considered the separation of CO₂ from methane (CH₄), a mixture relevant to the treatment of natural gas streams, using solvents consisting of different n -alkanes. Molecular models were developed within the framework of SAFT-VR SW [55, 56]. Following the approach proposed in [44] and [111], the SAFT parameters describing n -alkane mixtures were determined as a function of the average number of carbon atoms in the mixture. Molecular models for CO₂ and CH₄ were transferred from previous work [43, 112], using parameters that were scaled to reproduce the critical temperature and critical pressure of CO₂. To determine the unlike interaction parameters between CH₄, CO₂ and the n -alkanes, mixtures consisting of CH₄, CO₂ and n -decane (C₁₀) were studied and a single parameter for each pair of species, describing the unlike interaction energy, ε_{ij} , was used to describe accurately the vapour–liquid equilibria. Due to the transferability of SAFT-VR parameters within a homologous

series (e.g. see [43, 112]), the predicted phase behaviour of various $\text{CO}_2 + n$ -alkane mixtures (up to hexadecane) was found to be in very good agreement with experiment. A good prediction of the ternary phase behaviour of the $\text{CH}_4 + \text{CO}_2 + \text{C}_{10}$ mixture was also achieved and the cross-interaction parameters were found to be transferable to other mixtures of $\text{CH}_4 + \text{CO}_2 + n$ -alkane. The molecular nature of SAFT-VR allowed for the formulation of a full CAMPD problem on the basis of these models, as discussed further in Section 1.4.

Burger *et al.* [26] developed SAFT- γ Mie models for solvents consisting of the following functional groups: CH_3 , CH_2 , and two different oxygen functional groups, cO (an oxygen located between two CH_2 groups) and eO (an oxygen next to a CH_3 group). These groups represent the families of linear alkanes and ethers, and include highly oxygenated compounds such as diethers and glymes. The inclusion of two oxygen groups makes it possible to distinguish between some structural isomers, for instance methylpropyl ether and diethyl ether. SAFT- γ Mie parameters for the relevant groups were obtained by fitting to vapour pressure and liquid density measurements for pure components and to binary phase equilibrium data. Using the parameters obtained, Burger *et al.* [26] predicted the phase behaviour of some of the pure solvents for which experimental data were available, as exemplified in Figure 1.4, where the predicted vapour pressures of six different ethers are compared to experimental data. The parameters describing the CO_2 and CH_4 functional groups were transferred directly from previous work [113, 114]. The parameters describing the unlike interactions between CO_2 and solvent functional groups were estimated by fitting to available mixture data, as shown in Figure 1.5, and used to predict the phase behaviour of binary mixtures of solvents and CO_2 . This application illustrates the highly predictive nature of the SAFT- γ Mie equation of state as a wide variety of solvents can be modelled with only a few parameters. The use of this approach within a CAMPD problem will be discussed in Section 1.4.

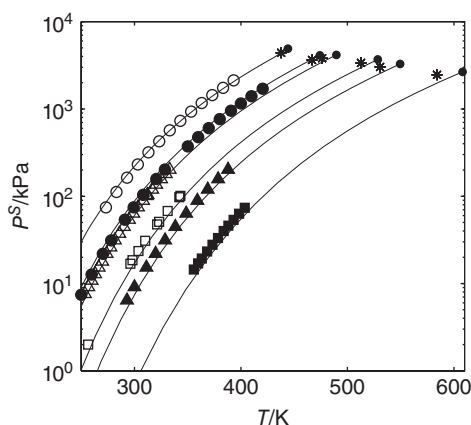


Figure 1.4 Logarithmic representation of the saturated vapour pressure, P^S , with respect to temperature T . The curves represent calculations with the SAFT- γ Mie EoS and the symbols denote the corresponding experimental data [115–119] for methyl ethyl ether (white circles), diethyl ether (black circles), methyl propyl ether (white triangles), methyl butyl ether (white squares), dipropyl ether (black triangles), and dibutyl ether (black squares). The figure is reproduced from [26].

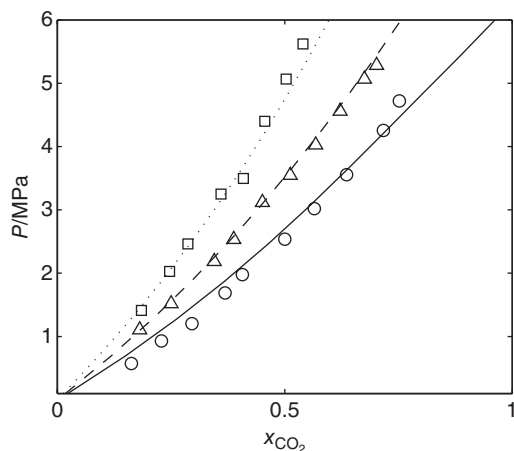


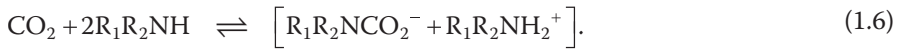
Figure 1.5 Pressure–mole fraction (liquid phase) isothermal slices of the vapour–liquid phase equilibrium envelope for the binary mixture of carbon dioxide and di(oxyethylene) dimethyl ether at different temperatures: $T = 298.15\text{ K}$ (—;○), $T = 313.15\text{ K}$ (---;△), $T = 333.15\text{ K}$ (···;□). The curves represent the calculations of the SAFT- γ Mie EoS and the symbols the corresponding experimental data [120]. The figure is reproduced from [26].

Another notable application of SAFT-based thermodynamic models to study the absorption of CO_2 in physical solvents is the use of GPC-SAFT [102]. Sauer *et al.* [102] developed parameters within the framework of GPC-SAFT for various non-polar and polar functional groups, by considering the vapour pressure and liquid density data of pure components. For polar groups, an additional term was required to characterize the dipole moment. The inclusion of parameters describing the dipolar interaction between functional groups can be useful when considering the design of solvents for physisorption of CO_2 . Because CO_2 possesses a strong quadrupole moment, it can interact favourably with polar groups [121], leading to an additional mode of absorption compared to non-polar solvents (which interact with CO_2 via weaker dispersion forces). This work facilitated a case study for the design of CO_2 capture solvents (both polar and non-polar) via physisorption [27], for which the full CAMPD problem is discussed in Section 1.4.

1.3 Describing Chemical Equilibria with SAFT

The predictive modelling of chemical equilibrium poses a greater challenge than phase equilibria for thermodynamic models. Of particular interest in chemisorption processes for CO_2 capture is the reaction between CO_2 and alkanolamines. Extensive theoretical and experimental work has been undertaken to determine the reaction kinetics and reaction mechanisms of these systems, e.g. [122–131]. Primary and secondary amines, for example monoethanolamine (MEA) and diethanolamine (DEA), react to form a carbamate. Although the exact reaction mechanism is still not fully understood [131], the most prominent mechanism is thought to involve the formation of a zwitterionic form of the carbamate [122, 129, 130], followed by a slow proton exchange reaction

with a base (water or another amine molecule). The overall reaction can be represented as [2]:



The other prominent reactions include carbamate hydrolysis:



and bicarbonate formation:



The carbamate hydrolysis reaction (1.7) only becomes important at high CO_2 loadings for non-sterically hindered amines (e.g. MEA), where the loading is defined as the moles of CO_2 absorbed per mole of amine solvent. In the case of MEA, the CO_2 loading due to chemisorption is therefore limited to 0.5, although additional CO_2 can be absorbed by physisorption, especially at high pressures. The hydrolysis reaction is important for sterically hindered amines, for example MDEA (*N*-methyl diethanolamine) and AMP (2-amino-2-methyl-1-propanol). For these amines, the carbamate bond is weakened by the presence of a bulky substituent group adjacent to the amino nitrogen site. Hence, carbamate reversion to the bicarbonate ion and the free amine via reaction 1.7 becomes favourable and CO_2 loadings due to chemisorption can approach one mole CO_2 per mole amine [2, 132, 133].

1.3.1 Chemical and Physical Models of Reactions

The two approaches that are commonly adopted to model reaction equilibrium, based on chemical or on physical theories, are briefly introduced in this section.

1.3.1.1 The Chemical Approach

The most widely used approach stems from chemical theory (see e.g. [94, 134–138]), where all relevant reaction products must be identified *a priori* and modelled explicitly. To illustrate this, we consider a mixture consisting of reactants A and B and the bimolecular reaction:



Within the chemical view, the mixture consists of three species: A, B and AB in chemical equilibrium with an equilibrium constant K defined as

$$K(T) = \frac{a_{\text{AB}}}{a_{\text{A}}a_{\text{B}}} \quad (1.10)$$

where a_i is the activity of component i and K is the temperature-dependent equilibrium constant, which is related to the standard change in Gibbs free energy (ΔG^\ominus) for the forward reaction, $K(T) = \exp(-\Delta G^\ominus/RT)$, where R is the gas constant. Thus, to model the system using a chemical approach, speciation data for all species in the mixture at various temperatures are required.

Electrolyte extensions to activity coefficient based models, for example eNRTL [139, 140] and extended UNIQUAC [141] have been used to treat CO_2 + amine + water (H_2O) systems for a few well-known solvents [136, 140, 142–146]. These methods have been shown to be highly successful in correlating the properties of mixtures for which appropriate experimental data are available, and can readily be combined with models of carbon-capture processes. We note that SAFT-type equations can in principle be used to model the chemical and phase equilibria of CO_2 capture mixtures using a chemical approach, by building on the extensions of SAFT EoSs that have been developed to treat explicitly the ionic species formed from reactions [73, 75–81]. No complete SAFT-based model of CO_2 + amine + H_2O mixtures has yet been proposed within this framework, but we note that [136] have developed a model based on chemical theory in which the PC-SAFT equation of state [58] is used to obtain gas-phase fugacity coefficients, and the eNRTL equation and Henry's law are used to compute the quantities needed for phase-equilibria calculations. The gas phase is assumed not to contain any ionic species.

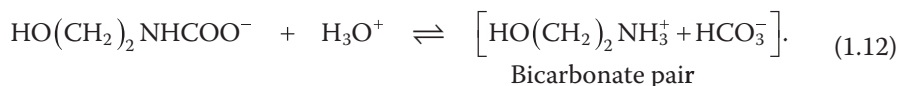
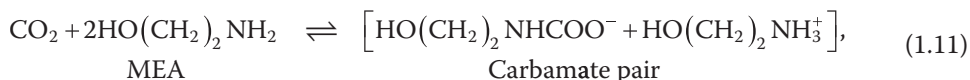
1.3.1.2 The Physical Approach

In physical approaches, an alternative description of the underlying physicochemical phenomena is used. Rather than considering the formation of new species explicitly, reaction products are treated as aggregates of the reactants that arise due to the presence of strong intermolecular forces, akin to the association approach used to model hydrogen bonding. This does not require the *a priori* specification of reaction products, as aggregates such as dimers, trimers or longer chains can form if the chosen association scheme (i.e. the number and types of sites) permits this. Reactions can thus be modelled within the SAFT framework by the addition of association sites that enable chemical binding. Referring again to equation (1.9), the impact of the formation of aggregate AB on the thermodynamic behaviour of a mixture of A and B can then be derived as a function of the concentrations of A and B and the mixture temperature and pressure, solely based on the SAFT parameters describing A and B and their interactions, particularly via the types, number, energy and bonding volume of association sites. With this modelling approach, it is possible to develop SAFT models using only experimental vapour–liquid equilibrium data and the initial concentrations of the reactants (here, CO_2 , water and solvent) as a function of temperature and pressure; neither the reaction products nor any equilibrium constants need to be specified [147]. Based on the association scheme chosen for the reactants, the concentration of all species present can be found via a statistical analysis of the SAFT thermodynamics at the given thermodynamic state, specifically of the fractions of association sites of different types not bonded [110, 148].

Economou and Donohue [149] have compared the analytical form of the expressions for the mole fraction of monomers and the association contribution to the compressibility factor obtained with chemical and physical approaches. Under appropriate assumptions, e.g. a constant binding energy and an equilibrium constant that is independent of the degree of association of the reactants, they showed that the description obtained by both theories is the same in terms of their functional form, provided that the correct reaction stoichiometry is given. The results were also shown to be numerically indistinguishable [149, 150]. In fact, the parameters obtained within the physical theory to describe the association interactions, namely the depth and range of the association potential, can be related to the equilibrium constant. A key advantage of the

physical approach over the chemical approach is that the parameters obtained are not functions of the thermodynamic state, whereas the equilibrium constant is a function of temperature, requiring the consideration of larger sets of experimental data.

To illustrate how reactions can be represented within a physical association framework, an example is shown for the reactions occurring when CO_2 is absorbed in an aqueous MEA solution, following the method of Mac Dowell *et al.* [151] and Rodriguez *et al.* [110], who developed models using a homonuclear SAFT approach, SAFT-VR SW. Different off-centre SW association sites are placed on the molecules in the mixture to mediate directional interactions, as shown in Figure 1.6. Sites labelled 'e' and 'H' represent lone pairs of electrons and hydrogen atoms, respectively, mediating hydrogen bonding and chemical binding. CO_2 has two association sites, α_1 and α_2 , which associate with the electron site corresponding to the amino group of MEA. This treatment mediates the following reactions:



Ion pairs are represented by square brackets and these are assumed to be tightly bound species. A CO_2 molecule for which both association sites are bonded is taken to exist in a carbamate structure. If only one association site is bonded (α_1 or α_2), the CO_2 molecule is assumed to be present as the bicarbonate HCO_3^- (cf. Figure 1.6). Inherent in the adoption of a physical approach is the assumption that ions aggregate to form

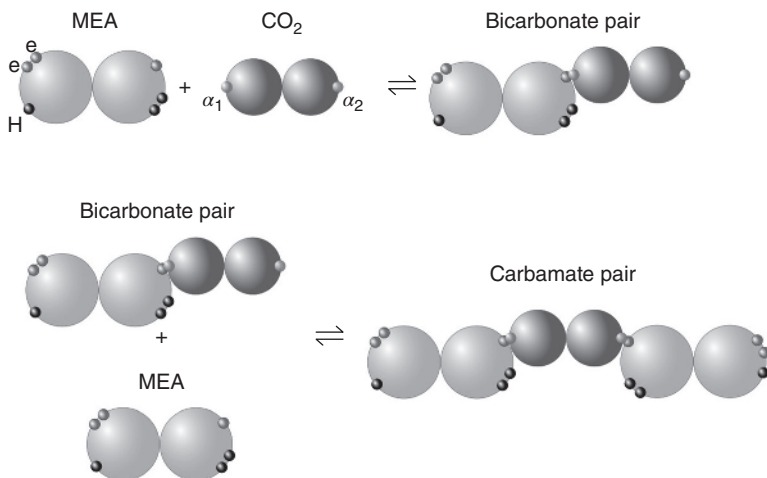


Figure 1.6 Schematic to show how the addition of association sites leads to the formation of the expected reaction products for CO_2 in an aqueous MEA solution: the bicarbonate pair (zwitterion) and carbamate pair. This association scheme was developed in [151] and [110].

species (e.g. carbamate) with no overall charge; this is justified by the low dielectric constant of the aqueous alkanolamines of interest compared to water, which leads to strong ion pairing.

This simple treatment of the complex reactions underlying CO₂ chemisorption can be used to predict the concentrations of carbamate and bicarbonate with remarkable accuracy for various CO₂ loadings and temperatures [107, 110], despite the fact that no speciation data was used in model development. However, one must be careful when using a physical approach if the reaction products are chemically very different from the reactants as the monomeric segments and association sites in the aggregate species may interact differently. In the case of amines reacting with CO₂ in water, the physical description appears to be a reasonable assumption as reaction products are not very different chemically and the reaction is fully reversible.

1.3.1.3 Comparison of Chemical and Physical Approaches

Most models developed to describe CO₂ in solutions of aqueous amines follow a chemical-based approach to treat the reactions. Models based on chemical theory are generally more detailed than those based on physical theory and are usually more accurate. A state-of-the-art model for mixtures of CO₂, water and MEA, for instance, is that of Zhang *et al.* [136], who modelled the relevant chemical equilibria explicitly by using the electrolyte NRTL model [135]. This model accounts for the long-range ion–ion interactions and short-range interactions between the nine major ionic and neutral species present in solution. The model of Zhang *et al.* [136] provides an accurate representation of the VLE, heat capacity and speciation in CO₂ + H₂O + MEA mixtures for a broad range of temperatures and pressures, and a good representation of the enthalpy of absorption at low temperatures and for loadings of up to 0.5 mol CO₂ per mol of amine, with larger deviations observed at higher temperatures and/or higher loadings. Due to the high level of detail that is embedded in this chemical model, the representation of the behaviour of this well-known solvent is more accurate than that achieved with a physical treatment using SAFT-VR SW [152].

This level of accuracy comes at a high cost in terms of experimental effort, however, as different types of data must be acquired across a wide range of conditions for model parameterization. Relevant properties include pure component and mixture VLE data, heat capacities, excess enthalpies, enthalpies of absorption and NMR spectroscopic data. Furthermore, in developing a chemical model, the reaction scheme must be postulated *a priori* and this becomes more challenging as the number of reactions increases since temperature-dependent data is required to derive an expression for each equilibrium constant. As a result of these data-intensive requirements, there is currently no chemical approach that enables the prediction of the thermodynamics of mixtures of CO₂ in solvents for which no data or very limited data are available. This reliance on extensive data sets presents a considerable hurdle to the application of a model-based CAMD approach to the identification of new solvents.

On the other hand, physical models based on a SAFT EoS can be developed even with limited data (or even no data) and can then be used to predict thermodynamic properties reliably, offering a way to compare the likely performance of different solvents. To develop a homonuclear model of a mixture of CO₂, amine and H₂O, a relatively small amount of data is required in terms of types of data and number of data points. Thus, it suffices to have equilibrium data on the concentrations of CO₂, H₂O and amine at a few temperatures and pressures, and no speciation data are required. This is a result of the

temperature-independence of the parameters in SAFT EoSs and of the fact that only three components (CO_2 , amine and H_2O) need to be modelled. Thanks to their strong molecular basis, SAFT parameters that are highly transferable from compound to compound can often be obtained: for example, some of the association parameters in MEA can be derived from models of alkylamines and models of alkanols [151, 152], and other parameters can be transferred from one alkanolamine to another [110]. As a result, SAFT models for new solvents can typically be derived using very limited data sets. In the case of heteronuclear models, Chremos *et al.* [107, 153] have shown that the physical approach can also be adopted successfully to model reactive systems within the SAFT- γ SW group contribution framework. This paves the way for the modelling of many solvents and countless solvent blends can be considered without extensive reliance on experimental data.

There is a clear synergy between physical SAFT-based models that can provide an initial assessment of the capture potential of new solvents, and chemical models that can provide a detailed representation of the behaviour of the solvent once the necessary experimental data are available for model regression. While physical models can play an important role at the conceptual design stage, helping to focus the experimental effort on the most promising candidate molecules, chemical models can assist in the detailed design of CO_2 capture processes. Owing to the explicit modelling of the reaction products, reaction kinetics can easily be integrated with models based on chemical theory in order to calculate non-equilibrium concentrations. Similarly, diffusion phenomena can be modelled more rigorously when all species are treated explicitly and the effect of ionic strength on mass transfer is taken into account. Thus, chemical approaches are invaluable in the development of the accurate process models that are needed for a full assessment of potential solvents. Since the development of accurate chemical models is well understood [136], we focus in the remainder of this section on the development of physical models of chemisorption thermodynamics.

1.3.2 Modelling Aqueous Mixtures of Amine Solvents and CO_2

The first SAFT models of aqueous mixtures of amines and carbon dioxide were developed by Button and Gubbins [154]. The original SAFT EoS [46, 47], in which molecules are described as chains of Lennard-Jones segments, was used to predict the VLE of mixtures containing CO_2 and MEA or DEA solutions. Four association sites were proposed to model CO_2 to account for interactions occurring due to its strong quadrupole moment. Water was also modelled with four association sites, one for each hydrogen and one for each lone pair of electrons on the oxygen atom. To treat MEA, five association sites were proposed, with two sites of type e (one representing the set of two lone pairs on the OH group and one representing the lone pair on the NH_2 group), and three sites of type H, to represent hydrogen bonding on the amino and hydroxyl groups of the molecules. The number of adjustable parameters used to define the molecular models was limited by assuming that the cross-association parameters between sites of types e and H were the same, regardless of whether they represent the bonding of the amino or hydroxyl groups. The number of adjustable parameters was also limited by taking cross-association parameters (describing the energy and range of association) to be the geometric mean of the pure component association parameters. Thus, only a single temperature-independent parameter needed to be estimated from phase-equilibrium

data for the MEA + H₂O and CO₂ + H₂O binary mixtures to determine the unlike dispersion energy. The unlike dispersion energy between CO₂ and MEA was taken as the geometric mean of the like pair values. Following this method, the liquid mole fractions in the ternary mixture were predicted with reasonable accuracy. However, small deviations in the liquid mole fractions lead to large deviations in the predicted CO₂ loadings, which were therefore predicted with limited accuracy.

Mac Dowell *et al.* [152] developed models within the framework of SAFT-VR SW [55, 56] to describe the fluid-phase behaviour of CO₂ + MEA + H₂O mixtures. Both a symmetric and an asymmetric association scheme for MEA were investigated. In the asymmetric model, the differences in association between the amine and hydroxyl functional groups are considered explicitly, whereas in a symmetric scheme these interactions are considered to be the same, as with the models proposed in [154]. The asymmetric model was found to provide a better description of the phase behaviour of mixtures than the symmetric model, especially in the description of the phase behaviour of MEA + CO₂ and of ternary mixtures of CO₂ + MEA + H₂O. The transferability of parameters in SAFT was exploited. For example, the unlike hydrogen-bonding interactions between MEA and H₂O were obtained from separate studies of aqueous solutions of ethanol and ethylamine.

A similar physical treatment of the reactions (see Section 1.3) was also successfully employed in subsequent work to model the phase behaviour of mixtures of CO₂ and water with alkylamines [151] within the SAFT-VR SW framework, including ammonia, NH₃, and *n*-alkylamines up to *n*-hexylamine (CH₃NH₂ to *n*-C₆H₁₃NH₂). The reactions between CO₂ and the amines were modelled by incorporating an association site on the CO₂ molecule which interacts with the electron site on the NH₃ and *n*-alkylamine molecules. The parameters describing the interaction between CO₂ and NH₃ were obtained by comparison to experimental data for the NH₃ + H₂O + CO₂ ternary mixture. These were then transferred to the other *n*-alkylamines. The phase behaviour of ternary mixtures of CO₂ + *n*-propylamine + H₂O, CO₂ + *n*-butylamine + H₂O and CO₂ + *n*-hexylamine + H₂O was then predicted. The ternary phase diagram for *n*-hexylamine + CO₂ + H₂O revealed the existence of separate regions of vapour–liquid and liquid–liquid coexistence. The demixing of the absorbent could have some promising advantages, e.g. the reduction in the energy penalty associated with solvent regeneration due to the reduced volume of the charged organic-rich phase. If the solution demixes into two liquid phases upon heating, an amine-rich phase with a high concentration of CO₂ and a water-rich phase with a low concentration of CO₂, only the CO₂-rich phase needs to be sent to the stripper [155]. Several experimental studies have been conducted to identify amine solvents with these phase characteristics (e.g. [156–159]). *n*-hexylamine was identified as a promising thermomorphic biphasic solvent [157–159] due to a liquid–liquid phase separation (LLPS), as predicted in [151], upon heating. The fact that Mac Dowell *et al.* [151] were able to anticipate the occurrence of a phase split illustrates the significant advantage of using a predictive thermodynamic model to identify promising CO₂ capture solvents.

The approach proposed in [151] was extended further in [110] to include different multi-functional amine solvents, such as diethanolamine (DEA), methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP). Extensive use was made of parameter transferability in developing the models, with the aim to minimize reliance on VLE data. A good description of the vapour pressures and liquid densities of the binary and

ternary mixtures was obtained. Speciation, as derived from the fractions of association sites α_1 and α_2 bonded on the CO_2 molecules, was successfully predicted for the $\text{MEA} + \text{CO}_2 + \text{H}_2\text{O}$ mixture.

Given the promising results obtained by transferring parameters from one homonuclear model to another, an initial investigation of the effectiveness of the SAFT- γ SW group contribution EoS was undertaken by Chremos *et al.* [107], developing models for the groups required to represent several primary alkanolamines (e.g. MEA and MPA), and models for a broader range of amines was developed in [153]. This work represents the first treatment of the chemical reaction equilibria involved in CO_2 capture within a group-contribution framework. In [107], an asymmetric association scheme was used to treat chemical reactions. To model ternary $\text{CO}_2 + \text{H}_2\text{O} + \text{primary alkanolamine}$ mixtures, a small set of functional groups was considered: CO_2 , H_2O , CH_2 , CH_3 , NH_2CH_2 and CH_2OH . Group parameters were developed based on data for pure alkylamines and alkanolamines, and mixture data where available. Thanks to the transferability of groups, this set of parameters was sufficient to describe any primary alkanolamine with an alkyl chain length of three or more carbons (from monopropanolamine onwards). The predicted solubility of CO_2 in aqueous MPA solution is in good agreement with experimental data, as illustrated in Figure 1.7. The predictive capabilities of the approach were also demonstrated for the absorption of CO_2 in aqueous solutions of alkanolamines (5-amino-1-pentanol and 6-amino-1-hexanol), which were not considered in the parameter estimation. The scarce data available were predicted with good accuracy.

The concept of second-order groups [95–97] was adopted in [107] to treat MEA due to the importance of proximity effects in this molecule. The CH_2 groups present in the

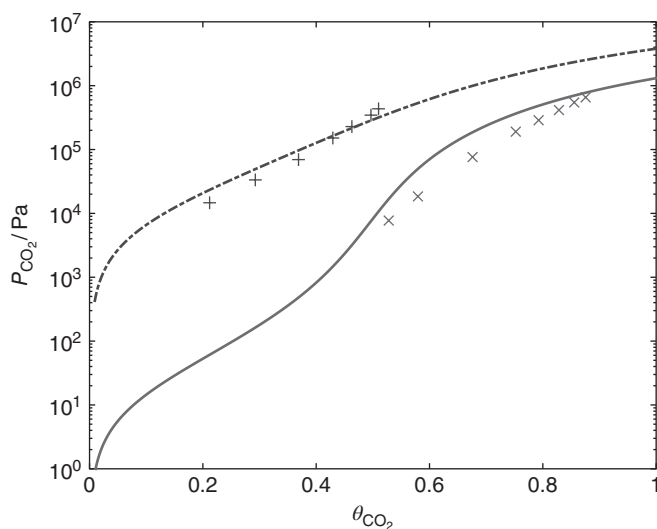


Figure 1.7 Solubility of CO_2 in a 30 wt% MPA aqueous solution at $T = 313.15\text{ K}$ (\times), and 393.15 K ($+$) as a function of the partial pressure of CO_2 at vapour–liquid equilibrium for the ternary mixture of $\text{MPA} + \text{H}_2\text{O} + \text{CO}_2$. The solubility is represented as CO_2 loading, θ_{CO_2} , defined as the number of moles of CO_2 absorbed in the liquid phase per mole of amine in the liquid. The symbols correspond to the experimental data [160] and the curves correspond to the SAFT- γ SW calculations. This figure has been reproduced from [107].

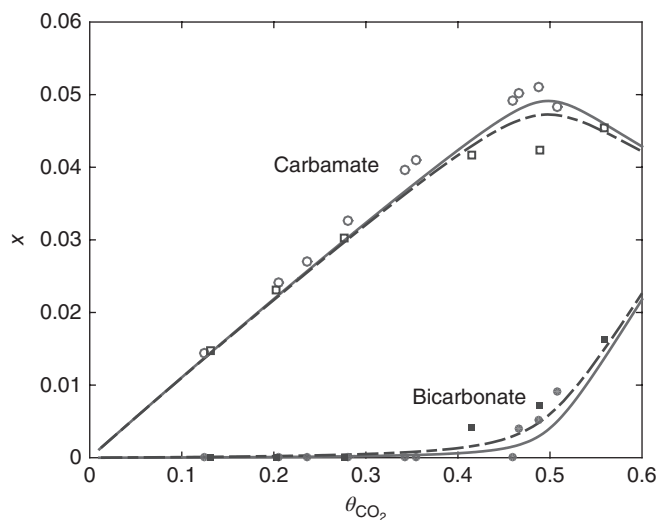


Figure 1.8 Predicted mole fraction, x , of carbamate and bicarbonate in the liquid phase of a 30 wt% MEA aqueous solution at $T = 313.15$ K (circles) and 333.15 K (squares) at vapour–liquid equilibrium for the ternary mixture of MEA + H₂O + CO₂ as a function of the CO₂ loading, θ_{CO_2} , defined as the number of moles of CO₂ absorbed in the liquid phase per mole of amine in the liquid. The symbols correspond to the experimental data [161,162] with open symbols corresponding to carbamate and filled symbols to bicarbonate. The curves correspond to the SAFT- γ SW predictions; continuous curves for 313.15 K and dot-dashed curves for 333.15 K. This figure has been reproduced from [107].

molecule are polarized due to the proximity of the NH₂ and OH groups. As a result, the model for MEA included the second-order CH₂NH₂[CH₂OH] group, which denotes a CH₂NH₂ group that is covalently bonded to a CH₂OH group. The parameters describing the unlike interactions between CH₂NH₂[CH₂OH], H₂O and CO₂ were re-evaluated by using experimental mixture data, keeping all other interaction parameters the same as the CH₂NH₂ group. An improved description of the MEA + H₂O system was then obtained, and the phase behaviour of the CO₂ + H₂O + MEA mixture was described with good accuracy. In addition, the concentrations of bicarbonate and carbamate were predicted accurately for this reactive mixture at different temperatures, as shown in Figure 1.8. The predictive capabilities of SAFT- γ were further illustrated by calculating the solubility of CO₂ in a quaternary H₂O + CO₂ + MEA + MPA mixture, which can be carried out without the specification of additional parameters.

1.4 Integrated Computer-aided Molecular and Process Design using SAFT

The SAFT thermodynamic platform described in Sections 1.2 and 1.3 has been successfully employed to design solvents for carbon capture. It can be used to predict the behaviour of fluid mixtures as a function of operating conditions, and is hence amenable to exploring interactions between molecular (solvent) choices and process variables. In this section, we present the CAMPD problem in greater detail and discuss some methodologies for solvent design that embed the SAFT EoSs.

The CAMPD problem is given by

$$\begin{aligned}
 \min_{\mathbf{u}, \mathbf{n}, \mathbf{y}} \quad & f(\mathbf{u}) && \text{(P)} \\
 \text{s.t.} \quad & \mathbf{g}_p(\mathbf{u}, \mathbf{n}) = 0 \\
 & \mathbf{g}(\mathbf{u}, \mathbf{n}) \leq 0 \\
 & \mathbf{C}\mathbf{y} \leq \mathbf{d} \\
 & \mathbf{n} + \mathbf{D}\mathbf{y} = 0 \\
 & \mathbf{u}^L \leq \mathbf{u} \leq \mathbf{u}^U \\
 & \mathbf{n}^L \leq \mathbf{n} \leq \mathbf{n}^U \\
 & \mathbf{y} = \{0, 1\}^q
 \end{aligned}$$

where $\mathbf{u} \in X \subset \mathbb{R}^c$ is a vector of continuous process (design) variables and $\mathbf{n} \in N \subset \mathbb{R}^m$ is a vector of continuous variables that represent the number of groups of each type in the molecule. \mathbf{y} is a q -dimensional vector of binary variables. $f: X \rightarrow \mathbb{R}$ is the process objective. \mathbf{g}_p is a set of process and property constraints, \mathbf{g} represents process constraints, $\mathbf{C}\mathbf{y} \leq \mathbf{d}$ represents molecular feasibility constraints (such as the octet rule [15]) and $\mathbf{n} + \mathbf{D}\mathbf{y} = 0$ is a set of constraints that ensures that \mathbf{n} take on integer values only. $(\mathbf{u}^L, \mathbf{n}^L)$ and $(\mathbf{u}^U, \mathbf{n}^U)$ are lower and upper bounds on the continuous design variables, respectively.

1.4.1 CAMPD of Physical Absorption Systems

The solution of the CAMPD problem (P), in the context of carbon capture via absorption, yields the optimal solvent structure and operating conditions of the process. A realistic process must include both the absorption of CO_2 and regeneration and subsequent recycle of the solvent. As an example we consider a simple process flowsheet for the physical absorption of carbon dioxide from high pressure natural gas, as shown in Figure 1.9. The feed enters at the bottom of the absorber (with N stages) at a temperature T_F and a vapour composition \mathbf{x}_F^V . The clean natural gas exits at the top of the absorber. A solvent stream is contacted with the gas stream, with the clean solvent entering the absorber at the top and the loaded solvent leaving from the bottom stage. In this pressure-driven process, the spent solvent is regenerated at a lower pressure in a flash drum. The recycled solvent is mixed with fresh solvent to make up for solvent losses.

Problem (P), which involves both continuous and integer decisions, belongs to the class of mixed integer non-linear problems (MINLP). As with other MINLPs, the discrete decisions lead to a combinatorial explosion of the solution space [163]. Furthermore, for any given combination of the binary variables, the solution of the resulting non-linear problem (NLP) can be very challenging. As the process and thermodynamic models consist of a large number of coupled non-linear equations, its solution requires a good initial guess. Incompatible combinations of process and molecular variables can also result in numerical failure. For example, the evaluation of the absorber model may fail if, for the solvent under consideration, there are conditions within the process design space at which only one phase is present. Finally, the non-convexity of

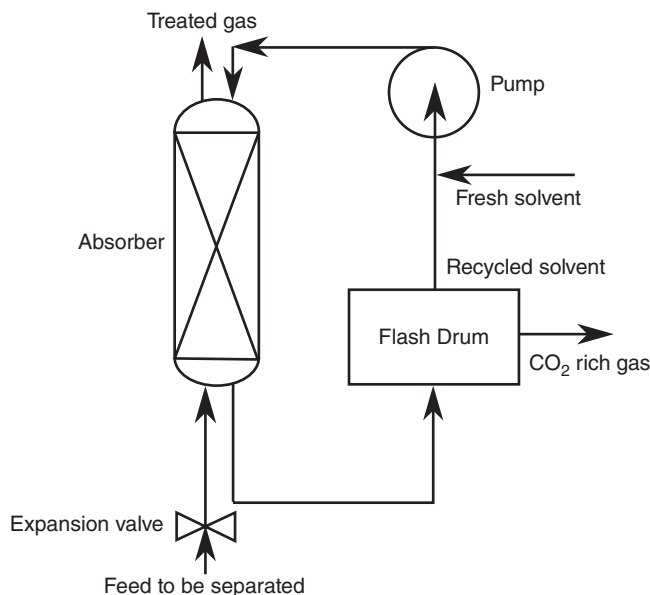


Figure 1.9 A simple flowsheet for a carbon-capture process.

the feasible space is yet another challenge in converging to the optimal solution. To overcome some of these challenges, several strategies have been adopted to solve the CAMPD problem for carbon capture.

Pereira *et al.* [25] solved a simplified version of the CAMPD problem arising from the absorption of CO_2 from a methane stream by a reformulation into a continuous optimization problem, which was made possible by restricting the solvent design space to mixtures of n -alkanes. The required thermophysical properties were obtained by applying the principle of congruence within the homologous family of alkanes, and adopting a SAFT-VR SW model of n -alkanes using the chain length [44], and transferable parameters to model their mixtures with CO_2 and methane (cf. Section 1.2.4). The average chain length of the alkanes in the solvent blend was represented by a continuous variable, n_C , that could be directly related to SAFT parameters, thereby removing the need for binary variables. The results of this study suggest that the optimal n -alkanes in the blend and the optimal process conditions vary with the concentration of CO_2 in the feed. The results indicated that process and molecular level decisions interact strongly, and that the optimal molecule is sensitive to both process specifications (inputs) and process variables. This was further confirmed by studying a modified flowsheet that includes an additional heat exchanger [164]. While this investigation showed that the SAFT-VR EoSs can be used for the design of a blend of solvents, searching within a homologous series is restrictive and the extension of this approach to a broader range of solvents requires tackling the integer nature of the problem.

Another approach to solving the CAMPD MINLP, the continuous molecular targeting CAMD (CoMT-CAMD) approach, was proposed in [17]. The separation of carbon dioxide from hydrogen and water was studied. In the first step of the study, the parameters of a hypothetical optimal solvent p^* and the corresponding process variables that

optimize the process objective were determined. The hypothetical solvent \mathbf{p}^* was represented in terms of the continuous parameters of the homonuclear PC-SAFT EoS [58], rather than via its molecular structure, so that an NLP was obtained. In the second stage, solvents in a database were examined to find the solvent with parameters \mathbf{p} that is closest to \mathbf{p}^* . This solvent is expected to exhibit a similar performance in the process as the hypothetical solvent. In more recent work [27], the second stage was replaced by an integer optimization problem to find \mathbf{n} by setting the vector \mathbf{p} equal to $\sum_i (n_i \mathbf{p}_i)$, where \mathbf{p}_i represents the parameters of group i in the GPC-SAFT equation [102], the group contribution version of the PC-SAFT EoS. The two-stage approach circumvents the solution of the highly nonlinear MINLP (P). However, the combination of parameters \mathbf{p}^* is not necessarily attainable by a real solvent that obeys molecular feasibility constraints. Furthermore, the use of group parameters to form molecular parameters results in an averaging of group properties and the need for unlike molecular parameters which has been found to be less accurate than a heteronuclear GC version of SAFT [102].

With a view to maintain a tight integration between the molecular and process design problems, Burger *et al.* [26] developed a two-stage hierarchical optimization methodology, HiOpt, in their CAMPD study of the removal of CO₂ from a high-pressure methane stream, based on the flowsheet shown in Figure 1.9. Hierarchical optimization is an approach in which models of increasing complexity are developed and optimized for the solution of challenging optimization problems. In the first step, a reduced, or simplified, process model was constructed assuming isothermal operation, an absorber with an infinite number of theoretical stages, no solvent losses from the absorber, an ideal vapour phase in the flash drum, and 100% recovery of any CO₂ and methane in the loaded solvent in the vapour stream leaving the flash drum. A mixed-integer multi-objective optimization (MOO) problem was solved to minimize the solvent flowrate and solvent losses, while maximizing the treated gas flowrate. The decision variables included a reduced set of degrees of freedom for the process and discrete variables \mathbf{y} , representing the structure of the solvent. Points lying on the Pareto front of the MOO problem were used as initial guesses for the optimization of the full MINLP CAMPD problem (P). The identification of these starting facilitates convergence of the MINLP solver to a solution. The authors used the heteronuclear SAFT- γ Mie equation of state [34] for property prediction. The solvent search space comprised of the families of linear n -alkanes and linear ethers with various numbers of ether groups (requiring the groups CH₃, CH₂, cO, eO, as described in Section 1.2.4). Penta(oxymethylene)dimethyl ether was identified as an optimal solvent [26]. The optimal process conditions using this solvent are shown in the last row of Table 1.3.

A comparison between two cases with different solvent design spaces is shown in Table 1.3. The objective to be maximized in both cases is the net present value of the process, NPV, in billion USD. It may be seen that in the work of Pereira *et al.* [25], where the solvent design space was restricted to blends of n -alkanes, the NPV was 22% lower, than in the work of Burger *et al.* [26] even though the concentration of CO₂ in the feed to be separated, $x_{\text{FeCO}_2}^{\text{V}}$, is lower and therefore the separation to achieve the same purity of 3 mol% of CO₂ in the clean gas stream is less demanding. This clearly highlights the important role of the solvent in determining process performance, as the expansion of the design space to include linear alkylethers results in a significant improvement in the NPV.

Table 1.3 Comparison of CAMPD results using a solvent design space of a blend of alkanes and ethers and alkanes. Two different values of the feed mole fraction of CO₂, $x_{\text{CO}_2}^{\text{V}}$, were used. The optimal values of the absorber, P_{abs} , the solvent flowrate, F_{sol} , and the net present value, NPV, are reported.

Ref.	$x_{\text{CO}_2}^{\text{V}}$	Solvent design space	P_{abs} /MPa	F_{sol} /kmol s ⁻¹	NPV/10 ⁹ USD
[25]	0.10	alkane blends	3	1.78	1.342
[26]	0.20	ethers + alkanes	3.84	0.84	1.721

1.4.2 CAMPD of Chemical Absorption Systems

The use of optimization techniques to design solvents has not been restricted to physical absorption systems alone. CAMPD systems for chemisorption have been made possible due to the development of group-contribution methods capable of assessing combined physical and chemical equilibrium of systems of reactive solvents and CO₂.

As has been discussed in Section 1.3.2, the use of physical association to describe the phase and chemical equilibrium at the heart of chemisorption paves the way for solvent design by making it possible to construct predictive thermodynamic models of reactive mixtures. The suitability of such models to provide a rapid and early assessment of absorption performance based on a process model has recently been demonstrated through an extensive comparison of predicted and pilot-plant data for an absorber using monoethanolamine solutions [165]. Two modelling strategies were investigated: one in which no pilot-plant data is used, and one in which one set of data from one pilot-plant run is used to fit one model parameter related to mass transfer. It was found that in the absence of data, the proposed approach provides a useful bound on achievable process performance, while quantitative agreement between pilot-plant data and predicted absorption profiles can be obtained by extrapolating from a single pilot-plant run. Typical results from such an approach are illustrated in Figure 1.10. This indicates that physical absorption models based on the SAFT EoSs are a valuable tool to guide the identification of promising solvents prior to experimentation.

In a first integrated design strategy employing such models, multi-functional amine solvents have been designed by developing a three-step methodology [29]. Novel solvent structures and existing amine solvents were screened in a first step. The solutions of a MOO problem, along with database screening, were used to identify solvents with favourable thermodynamic, reactivity and sustainability characteristics. Computationally simple group-contribution models were used to predict the properties of pure solvent candidates in the first step. In the second step, high-performing molecules were further screened based on their VLE behaviour, which was predicted using the SAFT-VR SW and SAFT- γ SW EoSs for mixtures of CO₂, water and amines as discussed in Section 1.3.2. Finally, the performance of selected solvents was evaluated through simulations of process flowsheets of various configurations. The results of the study showed that both the solvent structure and the process flowsheet configuration can have a huge impact on the cost and energy requirements of the carbon-capture system. For instance, a carbon-capture flow sheet where a portion of the solvent stream was cooled between absorber stages, reduced the energy demand of the process to less than 80% of its value without cooling.

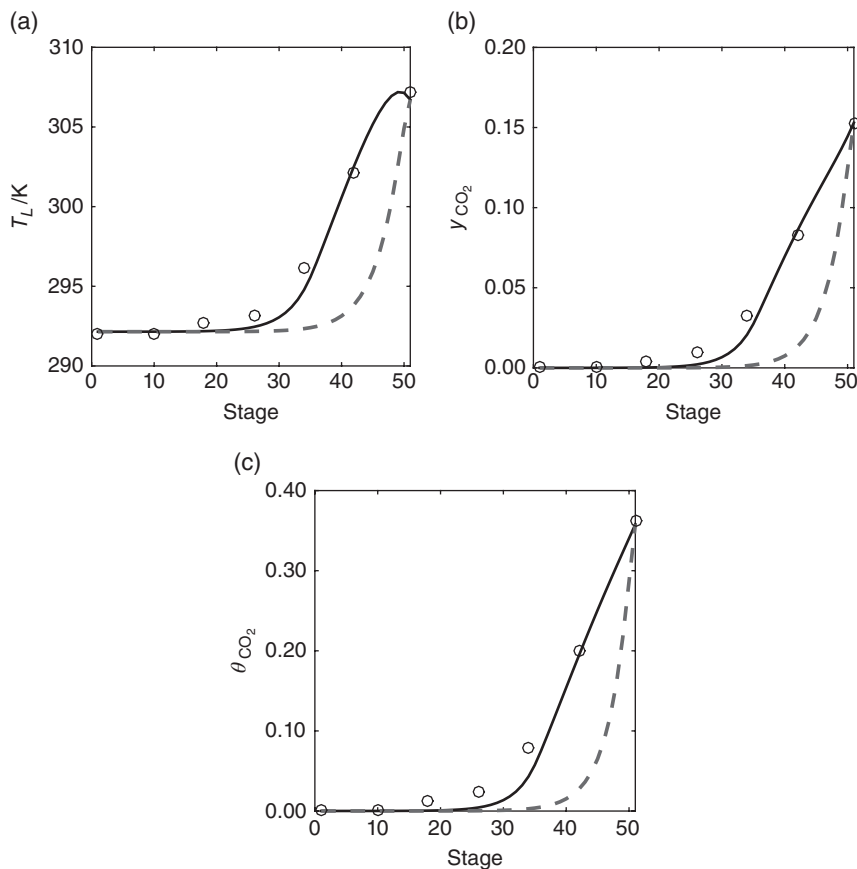


Figure 1.10 Comparison of the pilot-plant data (circles) for the chemisorption of CO_2 in aqueous monoethanolamine from Run T13 in [166] and predicted results using a SAFT-VR SW thermodynamic model (curves) for Run T13. The dashed curves represent the results obtained without any use of pilot-plant data in model development and the continuous curves the results obtained by fitting one model parameter to one run (Run T22). (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. Figure reproduced from [165].

1.5 Conclusions

The applicability of molecular systems engineering concepts to CO_2 capture has been discussed in this chapter. Molecular systems engineering, through its combination of molecular-based predictive models and computer-aided molecular and process design, offers the potential to design improved solvents in order to guide experimental investigations. It helps to reduce the time and investment needed to arrive at improved processes. The development of EoSs rooted in formal molecular theories, their extension to describe reaction equilibria, and the development of solution methodologies for the integrated solvent and process design problem all play an important role in realizing this potential.

Recent advances in the SAFT equations of state, in particular the development of a group-contribution framework, have put the reliable prediction of a wide range of thermodynamic properties for novel solvents and their mixtures within reach. Of interest in physical absorption, the prediction of the dependence on temperature, pressure and composition of the fluid-phase equilibria of mixtures containing CO₂, alkanes and potential solvents has become feasible in the absence of experimental data, even under conditions of high pressure and/or high CO₂ concentrations. The use of the Mie potential in the SAFT- γ Mie equation ensures that a thermodynamically consistent model is available to obtain the thermodynamic properties relevant to process design to a good level of quantitative accuracy. In the context of chemical absorption, the physical approach to association embedded within the SAFT framework provides an advantageous platform for the prediction of the phase and chemical equilibria of mixtures of CO₂, amines and water. As with models that account for phase equilibria only, the thermodynamic behaviour of mixtures containing novel molecules can be predicted by using the SAFT- γ SW equation of state. These models thus enable the solution of CAMPD problems involving the processing of CO₂. This approach is the foundation of a molecular systems engineering of carbon-capture systems and new groups and their parameters are currently being developed [45, 107, 114, 167], so that an increasingly wide range of structures can be described within the SAFT framework.

In tandem with these developments, several promising methodologies have been put forward to solve CAMPD problems that span larger and larger search spaces. Different approaches to problem decomposition have been proposed, resulting either in the approximate solution of the CAMPD problem [25, 27, 29, 164], or in the generation of starting points that facilitate convergence to the full solution [26]. These approaches have led to the identification of promising solvents for physical absorption and for chemical absorption of CO₂ capture. The HiOpt approach [26] makes it possible to tackle the non-linearity of the MINLP problem to achieve convergence in a larger solvent design space, but more powerful algorithms may be required to design solvents from larger search spaces, to deal with more complex flowsheets and to design solvent blends. The reliable solution of optimization problems that integrate choices of solvent structure, solvent blend-composition, process variables and topology, while employing molecular-based thermodynamic models, remains an exciting challenge in molecular systems engineering.

List of Abbreviations

AMP	2-amino-2-methyl-1-propanol
CAMD	computer-aided molecular design
CAMPD	computer-aided molecular and process design
CCUS	carbon capture, utilization and storage
CoMT-CAMD	continuous molecular targeting CAMD
DEA	diethanolamine
EoS	equation of state
GC	group contribution
MDEA	<i>N</i> -methyl diethanolamine

MEA	monoethanolamine
MINLP	mixed integer non-linear problems
MOO	mixed-integer multi-objective optimization
MPA	3-amino-1-propanol
MPA	monopropanolamine
MSE	molecular systems engineering
NLP	non-linear problem
SAFT	statistical associating fluid theory
SW	square-well
TPT	thermodynamic perturbation theory

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