

Modelling the phase and chemical equilibria of aqueous solutions of alkanolamines and carbon dioxide using the SAFT- γ SW group contribution approach



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ARTICLE INFO

Article history:

Received 30 April 2015

Received in revised form 27 July 2015

Accepted 27 July 2015

Available online 5 August 2015

Keywords:

SAFT

Group contribution

Alkanolamines

Aqueous solutions

Carbon capture

ABSTRACT

The speciation reactions that take place in mixtures of water (H₂O), carbon dioxide (CO₂), and alkanolamines make the modelling of the chemical and fluid-phase equilibria of these systems challenging. We demonstrate for the first time that the statistical associating fluid theory (SAFT), formulated within a group-contribution (GC) framework based on transferable intermolecular square-well (SW) potentials (SAFT- γ SW), can be used to model successfully such complex reacting systems. The chemical reactions in these mixtures are described via a physical association model. The concept of second-order groups is introduced in the SAFT- γ SW approach in order to deal with the multifunctional nature of the alkanolamines. In developing the models, several compounds including ethylamine, propylamine, ethanol, propanol, 2-aminoethanol, and 3-amino-1-propanol are considered. We present calculations and predictions of the fluid-phase behaviour of these compounds and a number of their aqueous mixtures with and without CO₂. The group-contribution nature of the models is used to predict the absorption of CO₂ in aqueous solutions of 5-amino-1-pentanol and 6-amino-1-hexanol. The proposed predictive approach offers a robust platform for the identification of new solvents and mixtures that are viable candidates for CO₂ absorption, thereby guiding experimental studies.

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1. Introduction

The dependence of world economies on the combustion of fossil fuels, such as coal, oil, and natural gas, to fulfil increasing energy requirements has led to a rise in the annual global emissions of carbon dioxide (CO₂) of approximately 80% between 1970 and 2004 [1]. In conjunction with growing concerns on the impact of these emissions on the climate [2] there is evidence that the CO₂ released to the atmosphere interacts with the oceans, resulting in a decrease in pH (ocean acidification) [3] and, as a consequence, is a threat to marine food chains [4]. Thus, the need to develop technologies for the capture of CO₂ to prevent its release into the atmosphere is increasingly pressing. Indeed, the combustion of fossil fuels accounts for 86% of anthropogenic greenhouse-gas emissions, while the rest comes mostly from changes in land use, e.g., deforestation and chemical processing [5]. A viable medium-term solution for large point-source emission locations, such as

coal- or gas-fired power stations, is the use of solvent-based absorption processes to separate the CO₂ from the flue gas [6,7]. Such processes often rely on amine-based solvents, and make use of the reversibility of the chemical reactions that lead to the chemisorption of CO₂ in the liquid phase. These processes however incur a significant economic penalty due to the large energetic consumption that arises from the regeneration of the solvent. These energy requirements are usually met by diverting steam from the power plant turbines and are therefore accompanied by an overall decrease in the efficiency of the power plant [5,7]. Commonly-used solvents such as aqueous monoethanolamine (MEA) also suffer from susceptibility to degradation, especially given the presence of oxygen in flue gas [8]. A key challenge for CO₂ capture is thus the design of solvents and solvent blends that can improve the economic and environmental performance of capture processes. Many aspects of the choice of solvent affect the viability of the overall process, and thermodynamic properties play a particularly important role as they define the absorption capacity and selectivity of the solvent, as well as the energy required for regeneration. There is however a lack of predictive approaches that can be used to estimate the properties of potential solvents and solvent mixtures in

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the absence of experimental data. The aim of our current study is the development of appropriate models and methods for the predictive thermodynamic description of solvents and their mixtures with CO₂, in order to enable the computer-aided design of optimal solvents and solvent blends to separate CO₂ from the flue gas.

The modelling of aqueous mixtures of alkanolamines and CO₂ presents a number of challenges. The first difficulty arises from the complex chemical nature of alkanolamines, which feature at least two highly polarizable functional groups, a hydroxyl and an amino group. Hydrogen bonding and polarity are important factors in the thermodynamic behaviour of these compounds, which lead to highly non-ideal interactions with water (H₂O). A second challenge arises from the reactive nature of mixtures of alkanolamines with H₂O and CO₂. In particular, alkyl-functional primary and secondary amines react with CO₂ to form carbamates; the formation of carbamates is typically described by the zwitterion mechanism [9,10]. The characteristics of the reactions and in particular the equilibrium constants depend on the molecular structure of the solvent and the process conditions, such as the temperature (see Refs. [10–12] for detailed studies of the types of reactions involved in these mixtures). Carbamate formation is reversible, allowing a reacting amine-based solvent to be recycled in the carbon-capture processes.

Given the importance and complexity of these mixtures, a number of theoretical approaches have been applied to study the fluid-phase behaviour of the alkanolamines with CO₂. A particularly successful approach is the use of the eNRTL activity coefficient model, with a model of the chemical equilibrium that includes temperature-dependent equilibrium constants, coupled with a simple model of the gas phase (typically employing Henry's constant) [13–16]. As an alternative, the UNIQUAC activity coefficient model has been extended to study the absorption of CO₂ in aqueous solutions of alkanolamines [17,18]. These approaches are very well-suited to model mixtures for which extensive experimental data are available, and they are easily integrated within models of CO₂ capture processes, providing a seamless link between thermodynamic behaviour and process performance. However, the large number of parameters required to model all of the relevant neutral and ionic species and the corresponding chemical equilibria makes it difficult to develop predictive models for novel solvents within such a framework. For each potentially viable new solvent, developing a thermodynamic model requires extensive data on speciation over a range of temperatures, as well as chemical and fluid-phase equilibrium data. Furthermore, if solvent mixtures are of interest additional experimental data must be gathered. This makes the development and assessment of new solvents both costly and time-consuming and clearly highlights the need for more predictive models that do not require experimental data on the specific molecule to be investigated, be it a pure component or a component of a mixture.

In the search for more predictive approaches, a promising avenue of investigation is the field of group-contribution (GC) methods (see Ref. [19] for a recent review of the area). In these methods, it is assumed that the thermodynamic properties of a compound can be derived from the independent contributions made by the chemical functional groups that appear in the molecular structure. Importantly, the contribution of each chemical or functional group is assumed to be transferable and this allows the prediction of the thermodynamic properties of new compounds. Several GC approaches have been proposed, and a few representative examples are briefly mentioned here. GC methods were first developed as empirical relations for the prediction of pure-component properties, such as the approaches developed by van Krevelen and Chermis [20] and later by Joback and Reid [21]. The GC concept has also been widely used to study binary and multi-component mixtures, including prominent examples

such as the widely applied universal functional activity coefficient (UNIFAC) approach [22–25], as well as the analytical solution of groups (ASOG) method [26]. Within this methodology the activity coefficients of the components in a liquid phase are calculated based on the contributions of the functional groups present and on their composition. The application of the GC concept has been extended to model the gas and liquid phases using the same equation of state (EoS) by developing predictive mixing rules for the molecular parameters in the EoS based on the activity coefficient GC methods. The predictive Soave–Redlich–Kwong (PSRK) [27], the generalized volume-translated Peng–Robinson (VTPR) EoS of Ahlers and Gmehling [28–30], and the second-order modified Huron–Vidal (MHV2) [31,32] approaches are of this type. Other methods have focused on applying the group contribution idea to determine binary interaction parameters for use with conventional mixing rules; this is the case of the predictive Peng–Robinson 1978 (PPR78) EoS [33,34] and the related PR₂SRK EoS [35,36], which follow the work of Abdoul and co-workers [37]. A final class of approaches involves the direct description of the parameters of an equation of state within a GC formalism; these ideas have been implemented within the GC-EoS [38,39] and the group contribution associating EoS (GCA-EoS) [40], both based on a generalized van der Waals EoS. Further examples of the latter type of methodologies are GC versions of the simplified perturbed hard chain theory (GSPHCT) [41], of the lattice-fluid theory (GCLF-EoS) [42], and of the statistical associating fluid theory (SAFT) EoS, based on a homonuclear adaptation of the SAFT-VR approach, as developed in Refs. [43–47], on a heteronuclear reformulation of the SAFT-VR approach using various intermolecular potentials [48–57], or on a group-contribution version of PC-SAFT [58,59].

Despite the significant body of work on GC methods, the application of these methods to the modelling of carbon dioxide + water + alkanolamine mixtures has been limited. The phase behaviour of mixtures of primary, secondary, and tertiary alkanolamines with hydrocarbons and alcohols [60] as well as mixtures containing alkanolamines and H₂O [61] has for example been described using the GCA-EoS [40], where successful predictions of the solubility of hydrocarbons in aqueous solutions of alkanolamines have been presented [61]. The GC-SAFT-VR approach [50,51] has been applied to describe mixtures of primary and secondary amines with alcohols and hydrocarbons, as well as some alkanolamines [62]. The GC-PPC-SAFT [44–46] EoS has also been applied to mixtures of primary, secondary, and tertiary amines with alkanes and alcohols [63] including some pure alkanolamines [64]. Hybrid approaches have been developed to model aqueous solutions of alkanolamines and CO₂, so that some elements of the UNIFAC model are enhanced with empirical correlations based on additional experimental information [65,66]. For example, H₂O, monoethanolamine, and CO₂ mixtures have been successfully modelled using UNIFAC extended to electrolytic systems with chemical equilibrium constants and Henry's law constants for CO₂ derived from experimental data [66]. To the best of our knowledge, however, no attempt has been presented so far to model both the chemical and phase equilibria of aqueous mixtures of alkanolamines with CO₂ based entirely on a group contribution approach. This is partly because the modelling of multifunctional molecules such as alkanolamines is an even greater challenge with GC methods than with standard thermodynamic approaches. The assumption of the transferability of the group parameters from molecule to molecule, regardless of the environment, which is central to the GC paradigm, often breaks down in such cases. Indeed, when two highly polarizable functional groups are in close proximity, it is expected that a new set of group parameters may be required to describe their behaviour accurately, i.e., that the parameters may not be transferable. The other significant issue is that

there is no systematic framework to model reaction equilibrium within thermodynamic GC methods.

Recent developments in the simultaneous modelling of chemical and phase equilibria for aqueous mixtures of alkanolamines and CO₂ offer a promising direction for research. Traditional chemical approaches [67–69,22–25,70,15,16] have been used extensively to deal with the occurrence of chemical reactions and formation of new species. The concentrations of the species that are assumed to be in chemical equilibrium for these reactions are expressed in terms of temperature, density, composition, and the corresponding equilibrium constants. The species that are not at equilibrium can be treated naturally within such a framework through the use of kinetic rate expressions and appropriate mass balances. An alternative is to model the reactions not through the formation of new species but in terms of the aggregation of the reactants driven by the presence of strong intermolecular interactions [71,72]. Despite the differences in the physical and chemical perspectives, which were a source of heated debate in the early 20th century [73], the current opinion is that the chemical and physical descriptions are equivalent under appropriate assumptions [74]. Physical theories rooted in statistical mechanics, such as SAFT [75,76], have been shown to provide an equivalent description to chemical and quasi-chemical approaches as long as the reactions do not lead to significantly different chemical species [77]. The use of a physical approach precludes the need for information on the equilibrium constants of the chemical reactions or on the concentrations of the product species during the development of models of the relevant compounds. This reduced dependence on experimental information makes it possible to develop models based solely on equilibrium concentration data for the reactants. This type of physical approach was employed successfully for mixtures relevant to carbon-capture processes within the framework of SAFT in previous work [78,79], where the statistical associating fluid theory for potentials of variable range (SAFT-VR) [80,81] with square well (SW) intermolecular potential interactions was applied to describe aqueous mixtures of different alkanolamines with CO₂. SAFT-VR SW is a homonuclear version of the SAFT theory in which intermolecular parameters are used to represent whole molecules rather than specific functional groups. The approach was further applied successfully to the modelling of the absorption of CO₂ in several aqueous solutions of multifunctional amines [79]. This implicit treatment of the reactions was shown to provide a satisfactory prediction of the speciation in these systems, in spite of the inherent assumption that key ionic species (the protonated amine and carbamate) are present as tightly bound pairs. The dielectric constant of the MEA solvent medium at ambient conditions is considerably lower than that for H₂O. This means that the ionic interactions will be less screened than in pure H₂O and we would therefore also expect that ion pairing would be strong. The approach can be used to provide useful insights into the thermodynamic behaviour and characteristics of these complex systems over a wide range of temperatures, pressures, and compositions. The fact that the model parameters are compound-specific only allows the modelling of compounds and mixtures for which data are available. In an attempt to establish a comparable methodology, but with enhanced predictive capabilities and with the ultimate aim of developing a formulation platform for solvent design, in our current work we assess the viability of developing an accurate representation of the thermodynamic behaviour of aqueous mixtures of alkanolamines with CO₂ within the context of a GC approach. Specifically, the SAFT- γ SW group-contribution approach [48,49] is used, wherein the interactions between functional segments are modelled using a square-well intermolecular potential. SAFT- γ SW has already been used to describe successfully a wide range of fluids that include pure component systems and mixtures including *n*-alkanes, branched alkanes, *n*-alkylbenzenes, unsaturated hydrocarbons, 2-ketones, carboxylic acids, and

primary amines [48,49], and also aqueous mixtures of hydrocarbons and 1-alkanols [82]. In our current paper, the application of the SAFT- γ SW framework is extended to aqueous mixtures of amines and alkanolamines with and without CO₂.

We focus specifically on the primary alkanolamines such as 2-aminoethanol (monoethanolamine or MEA) and 3-amino-1-propanol (MPA) because of the current interest in their use as solvents for CO₂ chemical absorption processes [83,84]. Models for these molecules and their mixtures with H₂O and CO₂ are obtained from the study of pure alkylamines and alkanolamines, as well as from representative mixtures where experimental data are available. A physical association scheme is used to treat chemical reactions. We use the concept of second-order groups [70,85–88] to deal with the multifunctional nature of the molecules. A table of group parameter values is developed within this framework that provides the predictive capabilities necessary to identify promising solvents. Our current paper is organized as follows: in Section 2 we outline the main expressions of the SAFT- γ SW theory as well as the methods employed in the development of the models; in Section 3, we present our findings to establish the foundations for the description of the fluid-phase behaviour of aqueous multi-functional alkanolamines and CO₂ within the SAFT- γ SW framework; concluding remarks are given in Section 4.

2. Methodology

The statistical association fluid theory (SAFT) [75,76] is an EoS based on the first-order thermodynamic perturbation theory (TPT1) of Wertheim for the explicit treatment of associating [89–92] and chain fluids [93,94]. The theory has been shown to be very successful in modelling a variety of complex associating fluids and fluid mixtures [95–98]. In its original incarnation the SAFT EoS was developed for a homonuclear representation of associating chains (i.e., molecules formed from identical segments) and the early work on GC-based SAFT approaches retained such a molecular representation. Representative examples of these approaches are the papers of Tobaly and co-workers [44,45] and Vijande et al. [43]. The formulation of SAFT is not restricted by a molecular model and it indeed has been extended to describe the thermodynamic properties of heteronuclear chain fluids (i.e., comprising segments of different size and/or energy-related parameters). One of these earlier extensions of Wertheim's approach considered purely repulsive heteronuclear molecules formed from hard-sphere segments of different diameters that were either tangentially bonded [99,100] or in a fused configuration [101]. Heteronuclear versions of the SAFT equation of state have also been developed for attractive van der Waals [102], square-well (SW) [103–105], and Lennard-Jones (LJ) [106,107] segments. This work has formed the basis for the development of GC SAFT approaches in which each type of segment of the heteronuclear molecular chain corresponds to a chemical functional group. It has been shown (perhaps unsurprisingly) that a fused heteronuclear representation is more suitable in the description of the properties of real compounds [48], and this concept has been pursued in several approaches of this type [47,49,50–55,57,58,88].

2.1. Model

Within the framework of SAFT- γ SW [48,49] molecules are modelled according to a group contribution scheme, in terms of the distinct chemical groups that they comprise. The representation is based on heteronuclear molecular chains, where each segment or group of identical segments corresponds to a given chemical functional group. The monomeric segments are allowed to overlap, resulting in a fused heteronuclear group-contribution molecular

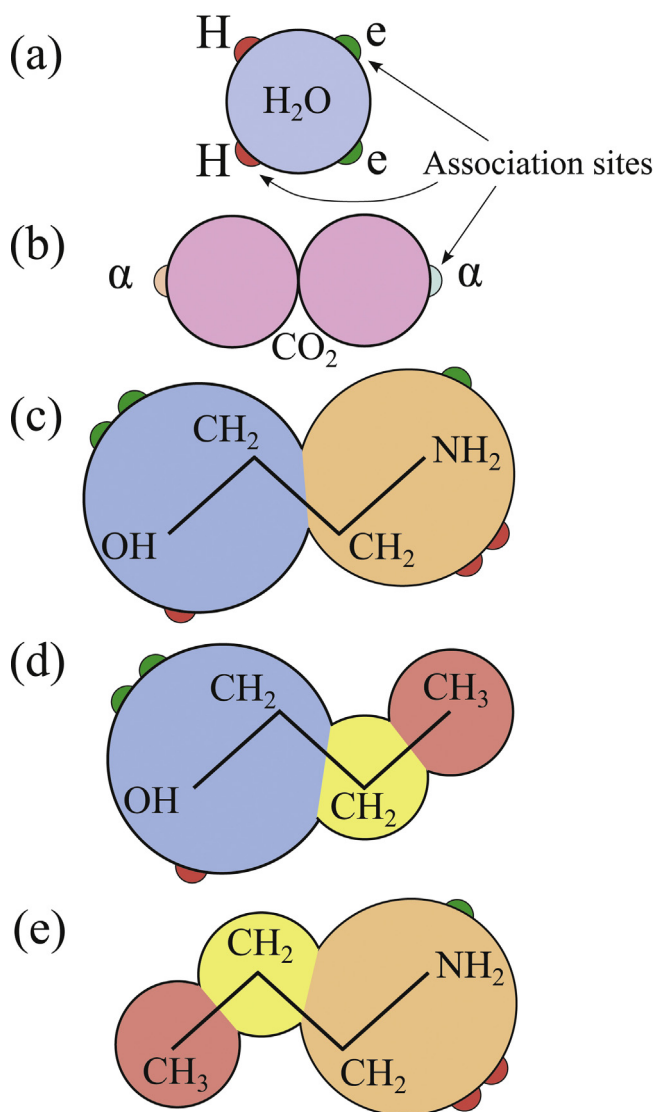


Fig. 1. Schematic representation of the heteronuclear molecular models employed to describe: (a) water; (b) carbon dioxide; (c) monoethanolamine (MEA); (d) propanol; (e) propylamine within the SAFT- γ SW framework. The distinct groups (H_2O , CO_2 , CH_2OH , CH_2NH_2 , CH_2 , and CH_3) are highlighted with different colours and the association sites are indicated as the small semi-circular segments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

model. Some schematic examples of molecular models for the compounds studied in our current work are presented in Fig. 1. The interactions between segments are modelled by means of the SW intermolecular potential. We should note, however, that the theoretical framework is general and can be extended to other types of interaction potentials [53,54,80,108–111]. A given chemical group k is fully characterized within SAFT- γ SW by the number ν_k^* of identical segments it comprises, the hard-core diameter of each segment σ_{kk} , and the well-depth ϵ_{kk} and range λ_{kk} of the attractive dispersion interactions. The degree to which each functional group contributes to the overall molecular properties is characterized in terms of the shape factor S_k . In the case of associating groups, additional off-centre square-well association sites are placed on the appropriate segments to mediate the directional interactions that arise, including hydrogen bonding. The total number of association site types for group k is represented by $N_{\text{ST},k}$ and the number of sites for each association site type by $n_{a,k}$ ($a = 1, \dots, N_{\text{ST},k}$). The sites are labelled as e or H , typically representing either a lone-pair

of electrons on an electronegative atom or hydrogen atoms in the functional group. For the purposes of our current work one e site is considered for each lone pair and one H site for each hydrogen atom, and only e - H bonding is permitted. For CO_2 two sites, namely α_1 and α_2 , are included to mediate the reaction of the amine and CO_2 . We do not consider α_1 - α_2 bonding (nor any interactions other than that between the amine lone-pair e site of the CH_2NH_2 group and the α_1 and α_2 sites of CO_2). A complete description of the association interactions requires the determination of two additional parameters for each pair of site types on a given segment type k , namely the energy $\epsilon_{kkab}^{\text{HB}}$ and range r_{kkab}^c of the association between sites of type a and b . The a and b sites are located at a specific distance from the centre of the segment, as will be discussed in Section 2.2.

To characterize the interactions between different segments, a number of unlike interaction parameters need to be specified. The unlike segment diameter parameters of types k and l is obtained as an arithmetic mean of the like segment diameters, $\sigma_{kl} = (\sigma_{kk} + \sigma_{ll})/2$. Likewise, the range of the unlike dispersion interactions is determined from $\lambda_{kl} = (\sigma_{kk}\lambda_{kk} + \sigma_{ll}\lambda_{ll})/(\sigma_{kk} + \sigma_{ll})$. The energy of the unlike dispersion interactions can be obtained by means of a geometric mean, $\epsilon_{kl} = \sqrt{\epsilon_{kk}\epsilon_{ll}}$. For the association interactions between a site of type a on group k and site of type b on group l , the unlike energy can be obtained as a geometric mean, $\epsilon_{klab}^{\text{HB}} = \sqrt{\epsilon_{kkaa}^{\text{HB}}\epsilon_{llbb}^{\text{HB}}}$, while the range r_{klab}^c is calculated by application of an appropriate combining rule for the bonding volume, K_{klab} , as explained in detail in Refs. [78,82]. Typically, however, the unlike interaction parameters ϵ_{kl} , $\epsilon_{klab}^{\text{HB}}$, and r_{klab}^c characterizing the potentials between different chemical groups are treated as adjustable parameters to reproduce accurately the fluid-phase behaviour of complex compounds and mixtures. For many mixtures, the commonly-employed combining rules are known to be inappropriate, particularly due to polarization effects [112], and allowing the unlike interactions to deviate from the fixed prescription ensures a greater reliability of the parameters. Where no experimental data are available to estimate the unlike-interaction parameters, the combining rules can be used to obtain a first estimate. In many cases, this would lead to a reduction in the accuracy of the predictions, but it allows one to provide a useful assessment of the potential performance of new molecules or mixtures, especially when combined with a sensitivity analysis that can quantify the impact of parametric uncertainty.

It should be noted that the SAFT- γ SW group-contribution approach is a generalization of the homonuclear SAFT-VR SW formulation [80,81] and for molecules comprising identical segments the two theories become identical. This facilitates the direct use of models readily available for molecular groups with SAFT-VR SW, such as H_2O and CO_2 , within the context of SAFT- γ SW.

2.2. Theory

Within the SAFT- γ SW approach the Helmholtz free energy A of a fluid mixture of N chain molecules is expressed as a sum of separate contributions through the dimensionless Helmholtz free energy, $a = A/(Nk_B T)$:

$$a = a^{\text{IDEAL}} + a^{\text{MONO.}} + a^{\text{CHAIN}} + a^{\text{ASSOC.}} \quad (1)$$

Here, a^{IDEAL} corresponds to the ideal contribution, $a^{\text{MONO.}}$ to the contribution due to the interaction between monomeric segments, a^{CHAIN} to the contribution due to the formation of heterosegmented chains, and $a^{\text{ASSOC.}}$ to the contribution to the free energy due to intermolecular association; T is the absolute temperature, and k_B is the Boltzmann constant.

The free energy of an ideal-gas mixture is given by [113]

$$a^{\text{IDEAL}} = \sum_{i=1}^{N_C} x_i \ln(\rho_i \Lambda_i^3) - 1, \quad (2)$$

where N_C is the total number of components, $x_i = N_i/N$ is the mole fraction for N_i molecules of component i , $\rho_i = N_i/V$ is the corresponding number density, and Λ_i^3 represents the thermal de Broglie volume of species i , which incorporates all of the kinetic (translational, rotational, and vibrational) contributions to the partition function of the molecule. The contribution to the free energy due to these degrees of freedom can be evaluated from experimental ideal heat capacity data, although it does not need to be specified explicitly for phase equilibrium studies.

The monomer contribution is obtained from a Barker–Henderson [114] high-temperature perturbation expansion up to second order, so that

$$a^{\text{MONO.}} = a^{\text{HS}} + \beta a_1 + \beta^2 a_2, \quad (3)$$

where β is defined as $\beta = 1/(k_B T)$. The free energy of the reference hard-sphere mixture a^{HS} is obtained from the expressions of Boublík [115] and Mansoori et al. [116]. The first-order term a_1 is the mean-attractive energy, and the second-order term a_2 describes the fluctuations of the attractive energy due to the action of the attractive well [113]. The exact determination of a_2 requires a knowledge of higher-order (up to four-body) correlation functions. In practice this term is approximated using a local compressibility approximation. For details the reader is referred to the original SAFT- γ SW papers [48,49].

For the calculation of the contributions to the free energy due to chain formation and association, a number of effective molecular parameters are defined, based on the group-specific parameters, namely the average molecular segment size $\bar{\sigma}_{ii}$, as well as the average range $\bar{\lambda}_{ii}$ and well-depth $\bar{\epsilon}_{ii}$ of dispersion interactions. These average parameters are obtained by means of appropriate mixing rules based on the group-specific parameters, as defined in Refs. [48,49]. All unlike effective molecular parameters are obtained from appropriate combining rules [48], so that their introduction does not lead to an increase of the number of adjustable parameters required in the theory.

The contribution to the free energy due to the formation of chains of SW segments can be written as [94,117]

$$a^{\text{CHAIN}} = - \sum_{i=1}^{N_C} x_i \left(\sum_{k=1}^{N_G} \nu_{k,i} \nu_k^* S_k - 1 \right) \ln(g_{ii}^{\text{SW}}(\bar{\sigma}_{ii}; \zeta_3)), \quad (4)$$

where N_C is the total number of groups, $\nu_{k,i}$ is the number of groups of type k in component i , and $g_{ii}^{\text{SW}}(\bar{\sigma}_{ii}; \zeta_3)$ is the SW radial distribution function at the effective contact distance $\bar{\sigma}_{ii}$ and packing fraction ζ_3 of the mixture. The SW radial distribution function is obtained from a high-temperature expansion [118,119,114] to first order (for further details see Refs. [80,81]).

The contribution to the free energy due to the association mediated by $N_{\text{ST},k}$ site-types on group type k can be calculated within the framework of the theory of Wertheim as [89–92,120]

$$a^{\text{ASSOC.}} = \sum_{i=1}^{N_C} x_i \sum_{k=1}^{N_G} \nu_{k,i} \sum_{a=1}^{N_{\text{ST},k}} n_{ka} \left[\ln X_{ika} + \frac{1 - X_{ika}}{2} \right]. \quad (5)$$

The first sum is over species i , the second is over groups k , and the third is over site types a in group k . In this expression X_{ika} is the fraction of groups in molecules of species i not bonded at a site of

type a of group k , and is obtained from the numerical solution of a mass-action equation [120]:

$$X_{ika} = \frac{1}{1 + \sum_{j=1}^{N_C} \sum_{l=1}^{N_G} \sum_{b=1}^{N_{\text{ST},k}} \rho \chi_j \nu_{lj} n_{lb} X_{jlb} \Delta_{ijklab}}, \quad (6)$$

where Δ_{ijklab} characterizes the association strength between site a on group k of molecule i and site b on group l of molecule j . It is determined from the contact value $g_{ij}^{\text{SW}}(\bar{\sigma}_{ij}; \zeta_3)$ of the radial distribution function of the monomer fluid as

$$\Delta_{ijklab} = f_{ijklab} g_{ij}^{\text{SW}}(\bar{\sigma}_{ij}; \zeta_3) K_{ijklab}, \quad (7)$$

where it should be noted that the SW radial distribution function $g_{ij}^{\text{SW}}(\bar{\sigma}_{ij}; \zeta_3)$ is evaluated at the effective contact distance $\bar{\sigma}_{ij}$ and actual packing fraction ζ_3 . The Mayer f -function f_{ijklab} of the site-site interaction is given as a function of the association energy as $f_{ijklab} = [\exp(\epsilon_{klab}^{\text{HB}}/(k_B T)) - 1]$. The site-site bonding volume is represented by K_{ijklab} . Although the degree of hydrogen bonding in the system is fully characterized by the strength of the site-site interaction and the overall bonding volume, it is often more convenient and physically intuitive to describe the volume accessible to bonding in terms of the cut-off r_{ijab}^c and of the distance $r_{ijab}^d/\bar{\sigma}_{ij} = 0.25$ from the centre of the sphere of interaction.

2.3. Parameter estimation

Appropriate values for the SAFT intermolecular model parameters for specific groups are determined by comparison with experimental fluid-phase equilibrium data. As is common practice, experimental vapour pressure and saturated-liquid density data are used in the determination of the group parameters. By obtaining the parameters for the various groups, e.g., CH_3 , CH_2 , CH_2OH , CH_2NH_2 , a group-group parameter database can be constructed. An important aspect of parameter estimation within SAFT- γ SW is that the unlike group interaction parameters can often be obtained from the pure-component experimental data for molecules comprising the appropriate groups, without the need for mixture data. This is a unique feature of heteronuclear approaches within a GC framework and is in contrast to other GC techniques such as UNIFAC [22,23] that rely exclusively on mixture data. For example, the parameters for the CH_3 – CH_2 interaction can be obtained solely from fluid-phase equilibria data relating to pure n -alkane [48].

The temperature range of the vapour–liquid equilibrium data considered for the parameter estimation is between the triple point and $0.9 T_c^{\text{exp}}$, where T_c^{exp} is the experimental critical temperature of the substance under study. Temperatures closer to the critical point are not included in favour of providing an optimal representation of the subcritical temperature region. This is because SAFT- γ SW is a classical EoS and cannot provide an accurate simultaneous description of the thermodynamic properties both close to and far from the critical region, but also because the subcritical region is of greater interest for the mixtures considered in our study. Although renormalization group theory treatments have been applied to SAFT-VR SW to tackle this issue [121–125] these have not yet been extended to the SAFT- γ SW version.

The estimation of the group parameters is carried out using the numerical solvers of the commercial software package gPROMS® [126]. The objective function employed is based on the maximum likelihood formulation:

$$\Phi = \frac{N_p}{2} \ln 2\pi + \frac{1}{2} \min_{\mathbf{v}} \left\{ \sum_{u=1}^{N_E} \sum_{v=1}^{N_{V_u}} \sum_{w=1}^{N_{M_{uv}}} \left[\ln \left(g_{uvw}^2 + \frac{(z_{uvw}^{\text{exp.}} - z_{uvw}^{\text{calc.}}(\mathbf{v}))^2}{g_{uvw}^2} \right) \right] \right\}, \quad (8)$$

where the vector of estimated parameters is denoted by \mathbf{v} , $z_{uvw}^{\text{calc.}}$ are the calculated and $z_{uvw}^{\text{exp.}}$ the experimental property values. In Eq. (8), N_p corresponds to the total number of experimental points

considered, N_E the number of experiments performed, N_{V_u} the number of variables measured in the u th experiment, and $N_{M_{uv}}$ the number of measurements of the v th variable in experiment u . The uncertainty in the experimental measurements is reflected in the constant relative variance, $g_{uvw} = 0.01 z_{uvw}^{\text{exp.}}$, which is used for the vapour pressure and density data. For compositional data, a constant variance of $g_{uvw} = 0.01$ is employed. To assess the quality of the descriptions of the pure-component fluid-phase equilibrium data obtained with the optimal parameter values, we use the average absolute deviations (%AAD):

$$\% \text{AAD } Z_i = \frac{100}{n_{Z_i}} \sum_{e=1}^{n_{Z_i}} \left| \frac{Z_{ie}^{\text{exp.}}(T_e) - Z_{ie}^{\text{calc.}}(T_e)}{Z_{ie}^{\text{exp.}}(T_e)} \right|, \quad (9)$$

where Z_{ie} is the vapour pressure or liquid density of component i at data point e (temperature T_e), and n_{Z_i} is the total number of data points for that component. The accuracy of the description of the fluid-phase behaviour is evaluated for the compounds included in the estimation process and for other compounds used to test the predictive capabilities of our approach.

As in previous work [82], the estimation of group parameters based on fluid-phase equilibrium data for binary mixtures is undertaken by means of a multistart, gradient-based, algorithm embedding a reliable pressure (P, T) flash algorithm [127,128] for the minimization of an objective function based on the absolute squared deviation for vapour and liquid compositions.

3. Results

The initial focus of our investigation is on the fluid-phase behaviour of pure primary n -alkylamines, for which we revisit previous SAFT- γ SW models [49], and some short alkanolamines selected based on the availability of experimental data (Table 1). We then study aqueous mixtures of n -alkanes, n -alkan-1-ols, and n -alkylamines, which are useful to determine the intermolecular model parameters characterizing the groups characteristic of the mixtures of interest. The investigation is then extended to ternary aqueous mixtures of alkanolamines with CO_2 , based on the description of binary mixtures of CO_2 with the alkanes and alkanols. To the best of our knowledge, there is no CO_2 + alkylamine binary (H_2O -free) mixture data, so the parameters related to the interactions between the amine group and CO_2 are obtained directly from a consideration of ternary mixture data for these systems. An initial GC model of some of these mixtures based on the SAFT- γ SW EoS has been proposed previously [129]. We revisit the group model parameters reported previously for aqueous solutions of n -alkan-1-ols by improving the overall performance over a wider range of thermodynamic conditions. The work is complemented by presenting calculations for new mixtures that were not previously shown, including ternary mixtures of H_2O + CO_2 + alkanolamines. All of the relevant parameters are presented in Tables 2, 3, and 4. We assess the quality of the results by comparison with published experimental data.

3.1. Pure components

Pure H_2O and CO_2 are described by means of homonuclear molecular groups comprising one and two identical segments, respectively. SAFT- γ SW models for these molecules are therefore indistinguishable from SAFT-VR SW homonuclear models. Use is thereby made here of the models that were developed in previous SAFT-VR SW studies [130–132]. Interaction parameters for the chemical groups CH_3 , CH_2 , CH_2OH are also taken from previous work and for details the reader is redirected to the original

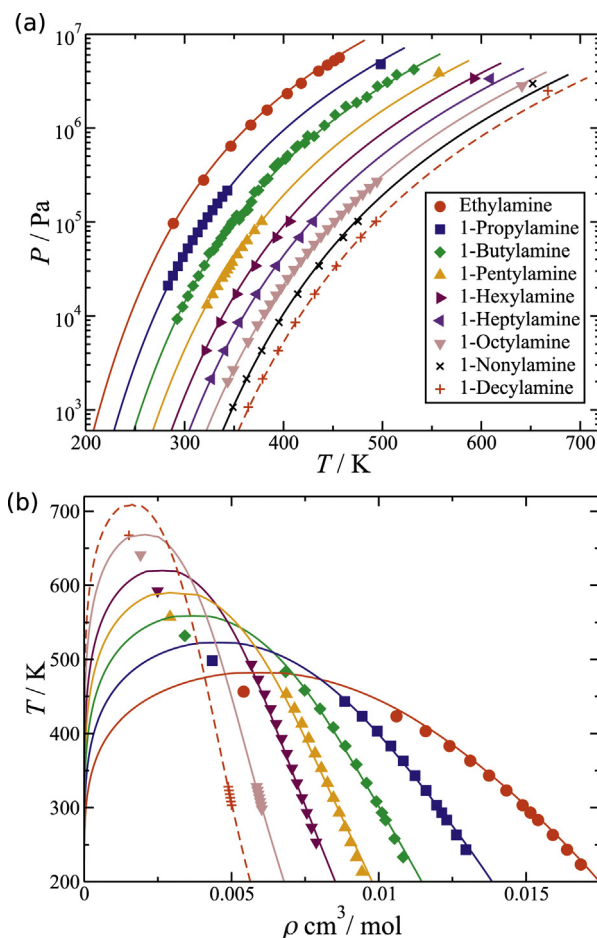


Fig. 2. (a) Vapour pressure in a pressure–temperature PT representation (noting the logarithmic scale for the pressure) and (b) coexisting densities in a temperature–density $T\rho$ representation for primary n -alkylamines (ethylamine to 1-decylamine) used for the determination of the parameters corresponding to the CH_2NH_2 chemical group. The symbols correspond to experimental data (see Table 1 for details of the appropriate sources); the critical points correspond to correlated experimental data from NIST [133] and the curves represent the SAFT- γ SW calculations.

publications [48,49,82]. For completeness all of the intermolecular and group parameters are presented in Table 2.

The modelling of the chemical family of the primary n -alkylamines is carried out by defining a new chemical group, the CH_2NH_2 group, which is a more coarse-grained representation than the NH_2 group considered in previous work [49]. The CH_2NH_2 group is modelled as an associating group with the 3B association scheme [143], featuring two association sites of type H , and one association site of type e . This group is relevant to the description of the phase behaviour of pure primary n -alkylamines and alkanolamines as well as their aqueous mixtures. The parameters of the new CH_2NH_2 group as well as those relating to its interactions with the CH_2 and the CH_3 groups are estimated by using pure-component experimental data for nine primary n -alkylamines, namely: ethylamine [134,135], 1-propylamine [135,136], 1-butylamine [135,137], 1-pentylamine [138,139], 1-hexylamine [139,140], 1-heptylamine [140], 1-octylamine [141,142], 1-nonylamine [140], and 1-decylamine [140,142] as in previous work [49]. The optimal parameters for the CH_2NH_2 group are presented in Table 2 and those for the unlike interactions with the CH_3 and CH_2 groups in Table 3. The resulting description of the fluid-phase equilibria and the degree of agreement with experimental data are seen in Fig. 2 and Table 1, respectively. The description obtained with our transferable GC parameters is of equivalent quality to that obtained

Table 1
Average absolute deviations %AADs of the vapour pressure P_s and saturated-liquid density ρ_l calculated with the SAFT- γ SW GC framework compared to experimental data (where n is the number of data points) for primary n -alkylamines. Two different descriptions of the amine group are considered: one representing a NH_2 group, based on previous work [49], and one representing the more coarse-grained CH_2NH_2 group, based on our current work.

Component	%AAD P_s			%AAD ρ_l								
	Reference	T range/K	n	CH_2NH_2		NH_2		Reference	T range/K	n	CH_2NH_2	
Ethylamine	Berthoud [134]	282–403	6	4.10	1.57	Liessmann et al. [135]	223–403	11	0.88	0.68		
1-Propylamine	Wolff et al. [136]	283–343	13	0.93	1.35	Liessmann et al. [135]	243–443	12	0.48	0.33		
1-Butylamine	Daubert [137]	308–462	35	5.99	5.23	Liessmann et al. [135]	233–458	11	0.66	0.51		
1-Pentylamine	Antosik et al. [138]	322–377	13	1.33	0.44	Costello et al. [139]	213–453	13	1.14	0.99		
1-Hexylamine	Ralston et al. [140]	320–405	6	4.65	3.53	Costello et al. [139]	253–493	13	0.86	0.85		
1-Heptylamine	Ralston et al. [140]	326–430	7	2.66	2.13	–	–	–	–	–		
1-Octylamine	Steele et al. [141]	343–494	22	1.59	1.45	Oswal et al. [142]	298–328	7	0.18	0.19		
1-Nonylamine	Ralston et al. [140]	324–475	11	3.29	2.34	–	–	–	–	–		
1-Decylamine	Ralston et al. [140]	329–493	11	1.68	1.60	Oswal et al. [142]	303–328	6	0.14	0.15		
Average	–	–	–	2.99	2.18	–	–	–	0.62	0.53		

within the traditional SAFT-VR SW approach for homonuclear models based on a determination of (non-transferable) parameters on a molecule-by-molecule basis [144]. A comparison of the description provided by the new CH_2NH_2 group with the description obtained with the smaller NH_2 group [49] is presented in Table 1, where the %AADs for vapour pressures and coexisting liquid densities of pure primary n -alkylamines are assessed for both models. Comparing to previous work with SAFT- γ SW [49], the use of the CH_2NH_2 group rather than the NH_2 group is found to provide a similar description of the fluid-phase equilibria of pure primary n -alkylamines; the description using the CH_2NH_2 group is found to be only marginally poorer. However, as we will show, the new group provides a significant improvement in the description of the thermodynamic behaviour of aqueous mixtures of the primary n -alkylamines. On this basis, the CH_2NH_2 group is also expected to offer a better description of the phase behaviour of other mixtures. A similar conclusion has been made for equivalent coarse-grained models of aqueous mixtures with n -alkanols [82], where the CH_2OH group has been used and shown to lead to a better description of the fluid-phase behaviour.

Having developed the group parameters for the CH_2NH_2 functional group and the unlike interaction energies with the CH_3 and CH_2 groups, we proceed to determine the unlike interaction parameters between the CH_2NH_2 and CH_2OH groups. In this case we obtain the unlike interaction energies from experimental data of the fluid-phase equilibria of pure alkanolamines, namely 2-aminoethanol (MEA) and 3-amino-1-propanol (MPA), which comprise both the CH_2NH_2 and CH_2OH functional groups. In addition to the unlike dispersion interaction between these groups, unlike association is expected to occur between the hydrogen atoms and the lone pairs of the electronegative atoms on both groups. Following the previously developed association scheme employed in the modelling of these systems with the SAFT-VR SW approach [78], an asymmetric association scheme is assumed for the sites in the OH and NH_2 groups, i.e., $\epsilon_{\text{CH}_2\text{NH}_2, \text{CH}_2\text{OH}, e, H}^{\text{HB}} \neq \epsilon_{\text{CH}_2\text{NH}_2, \text{CH}_2\text{OH}, H, e}^{\text{HB}}$ and $r_{\text{CH}_2\text{NH}_2, \text{CH}_2\text{OH}, e, H}^{\text{C}} \neq r_{\text{CH}_2\text{NH}_2, \text{CH}_2\text{OH}, H, e}^{\text{C}}$. A total of five unlike parameters ($\epsilon_{\text{CH}_2\text{NH}_2, \text{CH}_2\text{OH}, e, H}^{\text{HB}}$, $\epsilon_{\text{CH}_2\text{NH}_2, \text{CH}_2\text{OH}, H, e}^{\text{HB}}$, $r_{\text{CH}_2\text{NH}_2, \text{CH}_2\text{OH}, e, H}^{\text{C}}$, $r_{\text{CH}_2\text{NH}_2, \text{CH}_2\text{OH}, H, e}^{\text{C}}$, and $\epsilon_{\text{CH}_2\text{NH}_2, \text{CH}_2\text{OH}, e, H}^{\text{C}}$) are hence estimated from the fluid-phase equilibria of MEA and MPA. The parameter

estimation is based on existing experimental data (MEA [133] and MPA [145,146]) and the resulting optimal parameter sets are presented in Tables 3 and 4. A visual comparison with the experimental data is shown in Fig. 3.

3.2. Aqueous mixtures of alkanes

The next phase of our current study is to use the parameters obtained from pure-component systems in a transferable manner to represent the corresponding mixtures. Mixtures of n -alkanes and H_2O have been studied previously with SAFT- γ SW [82]. In general it is well known that the extreme nature of the phase separation [150] makes it challenging to model mixtures of H_2O with non-polar compounds. Because of the large differences in the dielectric constant of the two phases as well as in the dipole moment of H_2O and the hydrophobic molecules, it is especially difficult to obtain phase-independent unlike interaction parameters [112] and thus to model simultaneously the equilibrium phases. In previous work [82], emphasis was placed on obtaining an accurate description of the alkane-rich phases (both liquid and vapour), while small absolute (but not relative) deviations for the aqueous phase composition were achieved. The systems of interest in our current work are typically aqueous mixtures containing a high proportion of H_2O , alkylamine, and CO_2 . Consequently, in order to provide an improved overall description of the fluid-phase equilibria at the conditions of interest, refinements have been made to the unlike parameters presented in the previous study [129] relating to the interactions between H_2O and the alkyl groups, CH_3 and CH_2 , namely $\epsilon_{\text{CH}_3, \text{H}_2\text{O}}$, $\epsilon_{\text{CH}_2, \text{H}_2\text{O}}$ and $\lambda_{\text{CH}_3, \text{H}_2\text{O}}$, $\lambda_{\text{CH}_2, \text{H}_2\text{O}}$.

The estimation of these parameters is based on solubility data for the H_2O -rich and n -alkane-rich liquid phases for aqueous mixture of n -heptane at conditions of three-phase equilibria over a temperature range from 280 to 400 K using correlated experimental data [148]. The final set of interaction parameters are gathered in Table 3 and a visual comparison of the performance of SAFT- γ SW with the new group parameters with respect to the experimental data for aqueous solutions of n -heptane is shown in Fig. 4. The adequacy of the SAFT- γ SW models developed in our current work is additionally demonstrated in Fig. 4 with a comparison of the

Table 2
SAFT- γ SW like-interaction parameters for the functional groups present in aqueous solutions of alkanolamines and CO_2 (CH_3 , CH_2 , CH_2NH_2 , CH_2OH , H_2O , and CO_2 groups).

Group	ν^*	S	$\sigma/\text{\AA}$	λ	$(\epsilon_{\text{kk}}/k_B)/\text{K}$	$(\epsilon_{\text{kkeH}}^{\text{HB}}/k_B)/\text{K}$	$r_{\text{kkeH}}^{\text{C}}/\text{\AA}$	Site e	Site H	Site α_1	Site α_2
CH_3	1	0.66667	3.81048	1.4130	252.601	–	–	–	–	–	–
CH_2	1	0.33333	4.02758	1.6606	240.482	–	–	–	–	–	–
CH_2NH_2	1	0.90747	3.80800	1.4836	439.350	1021.375	2.4450	1	2	–	–
CH_2OH	1	0.56570	4.31736	1.6519	399.959	2555.721	2.3598	2	1	–	–
H_2O	1	1.00000	3.03420	1.7889	250.000	1400.000	2.1082	2	2	–	–
CO_2	2	1.00000	2.78649	1.5157	179.270	–	–	–	–	1	1

Table 3

SAFT- γ SW unlike dispersion energy (ϵ_{kl}/k_B)/K for the CH₃, CH₂, CH₂NH₂, CH₂OH, H₂O, and CO₂ functional groups. The numbers in parentheses correspond to the unlike values of the range of the SW potential λ_{kl} ; in all other cases the combining rule, $\lambda_{kl} = (\lambda_{kk}\sigma_{kk} + \lambda_{ll}\sigma_{ll})/(\sigma_{kk} + \sigma_{ll})$, is used. The table is symmetric (i.e., $\epsilon_{kl} = \epsilon_{lk}$).

Group	CH ₃	CH ₂	CH ₂ NH ₂	CH ₂ OH	H ₂ O	CO ₂
CH ₃	252.601	–	–	–	–	–
CH ₂	261.520	240.482	–	–	–	–
CH ₂ NH ₂	254.736	297.873	439.350	–	–	–
CH ₂ OH	279.939	283.702	143.247	399.959	–	–
H ₂ O	460.312	460.276	286.857	328.263	250.000	–
	(1.257)	(1.257)	(1.740)			
CO ₂	196.296	189.721	480.501	245.442	224.400	179.270
			(1.293)			

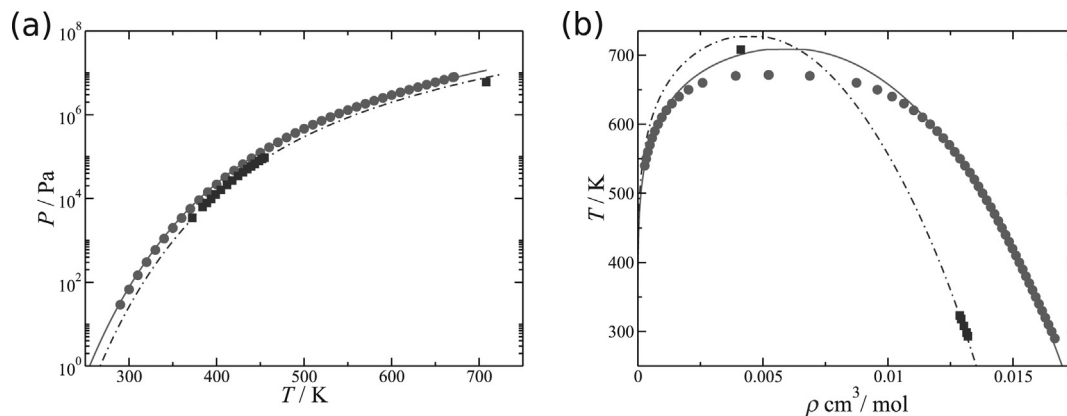


Fig. 3. (a) Vapour pressures PT (noting the logarithmic scale for the pressure) and (b) coexisting densities $T\rho$ phase diagrams for 2-aminoethanol (MEA, red circles and continuous curves) and 3-amino-1-propanol (MPA, blue squares and dot-dashed curves) used to estimate the dispersion energy as well as the cross association parameters between the chemical groups CH₂NH₂ and CH₂OH. The symbols correspond to experimental data (2-aminoethanol [133] and 3-amino-1-propanol [145,146]) and the curves represent our SAFT- γ SW calculations. The critical point for 3-amino-1-propanol is from the correlation reported in NIST [133]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

prediction of the fluid-phase equilibria with the experimental data for aqueous mixtures of *n*-hexane [147] and *n*-octane [149]).

3.3. Aqueous mixtures of alcohols and amines

Transferable parameters to describe the unlike interactions between H₂O and the CH₂OH and CH₂NH₂ groups are obtained using binary data for mixtures of H₂O and *n*-alcohols or primary *n*-alkylamines. Aqueous mixtures of *n*-alkanols have been previously studied with SAFT- γ SW [82]. However, since the parameters relevant to the interactions between the CH₃ and CH₂ chemical groups and H₂O have been revised in our current work, the parameters describing the interactions between the CH₂OH group

and H₂O also need to be re-determined. A preliminary effort in obtaining the pertinent parameters for H₂O + *n*-alkanol systems was presented earlier [129]. However, the parameters are revised here to improve the reliability of the description over a wider temperature range by including experimental data up to 420 K. The unlike association interactions between H₂O and a group *l*, with $l \in \{\text{CH}_2\text{OH}, \text{CH}_2\text{NH}_2\}$ are assumed to be asymmetric, which leads to a total of six adjustable parameters for the characterization of aqueous solutions of *n*-alkanols and six parameters for aqueous solutions of primary *n*-alkylamines, namely the unlike dispersion energies ($\epsilon_{\text{H}_2\text{O},l}$), the range of unlike dispersion interactions ($\lambda_{\text{H}_2\text{O},l}$) the energy and range of association between sites of type *H* of H₂O and *e* of CH₂OH or CH₂NH₂ ($\epsilon_{\text{H}_2\text{O},l,H,e}^{\text{HB}}$ and $r_{\text{H}_2\text{O},l,H,e}^{\text{C}}$), and the energy and range of association between sites of type *e* of H₂O and *H* of CH₂OH or CH₂NH₂ ($\epsilon_{\text{H}_2\text{O},l,e,H}^{\text{HB}}$ and $r_{\text{H}_2\text{O},l,e,H}^{\text{C}}$). The unlike parameters corresponding to the interactions between the CH₂OH group and H₂O are estimated using experimental data relating to binary aqueous mixtures of *n*-alkanols [151,152] and those corresponding to the interactions between the CH₂NH₂ group and H₂O using the corresponding data for binary aqueous mixtures of primary *n*-alkylamines [154–156]. More specifically, the parameter estimation for aqueous mixtures of *n*-alkanols is carried out by comparison to experimental vapour-liquid equilibrium data for ethanol (over a temperature range of $T = 350\text{--}420$ K) and 1-propanol (over a temperature range of $T = 360\text{--}420$ K); that for aqueous mixtures of *n*-alkylamines is based on vapour-liquid equilibrium data for ethylamine, 1-propylamine, and 1-butylamine at a pressure of $P = 10^5$ Pa. The optimal parameters for CH₂OH and CH₂NH₂ with H₂O are reported in Tables 3 and 4. A visual comparison of the SAFT- γ SW calculations with experimental data as well as with the description of the modified Dortmund UNIFAC approach [153] is presented in Fig. 5 for aqueous mixtures of *n*-alkanols, and

Table 4

SAFT- γ SW unlike association energy ($\epsilon_{klab}^{\text{HB}}/k_B$)/K for the CH₂NH₂, CH₂OH, H₂O, and CO₂ functional groups. The indexes *a* and *b* correspond to the different types of association sites (*e*, *H*, α_1 , α_2). The numbers in parentheses correspond to the unlike association range $r_{klab}^{\text{C}}/\text{\AA}$. Any parameter not shown takes a value of zero (i.e., $\epsilon_{klab}^{\text{HB}} = 0$); for like site-site interactions see Table 2.

Association site	CH ₂ OH		CH ₂ NH ₂	
	(<i>e</i>)	(<i>H</i>)	(<i>e</i>)	(<i>H</i>)
CH ₂ OH (<i>e</i>)	–	2555.721 (2.3598)	–	1696.979 (2.5282)
CH ₂ OH (<i>H</i>)	2555.721 (2.3598)	–	903.303 (3.9520)	–
H ₂ O (<i>e</i>)	–	1905.280 (2.4669)	–	1365.326 (2.3082)
H ₂ O (<i>H</i>)	2122.971 (2.0186)	–	1261.968 (2.5200)	–
CO ₂ (α_1)	–	–	4175.000 (1.9699)	–
CO ₂ (α_2)	–	–	4870.194 (1.9790)	–

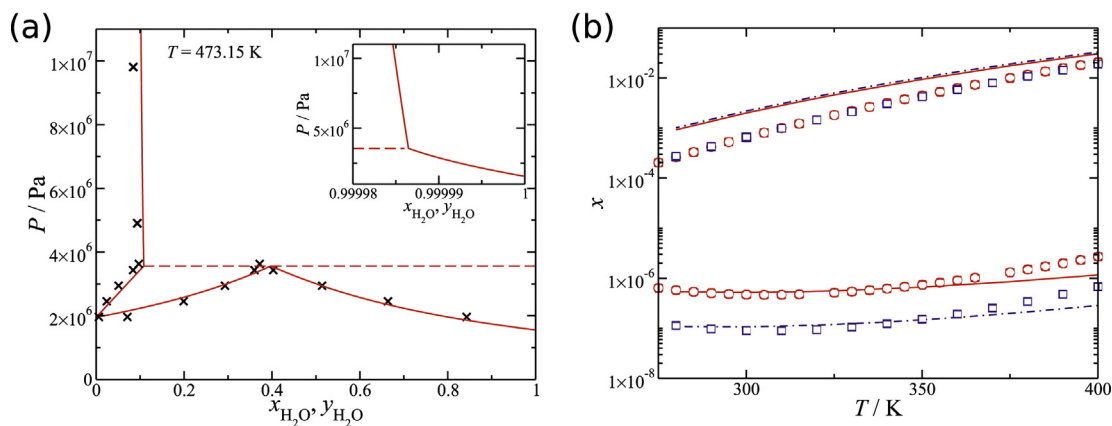


Fig. 4. (a) Pressure-composition isotherm (at $T=473.15$ K) for the vapour–liquid and liquid–liquid equilibrium regions of an aqueous mixture of *n*-hexane. The symbols correspond to experimental data [147], and the curves represent the SAFT- γ SW calculations. (b) Mutual solubilities of *n*-alkane in the H_2O -rich liquid phase (bottom) and H_2O in the *n*-alkane-rich liquid phase (top) at conditions of three-phase equilibria for *n*-heptane (red circles and continuous curves) and *n*-octane (blue squares and dot-dashed curves) aqueous mixtures as a function of temperature. The symbols correspond to the correlated experimental data for *n*-heptane [148] and *n*-octane [149], and the curves represent our SAFT- γ SW calculations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in Fig. 6 for aqueous mixtures of primary *n*-alkylamines. The accuracy of the representation of the fluid-phase equilibria with the SAFT- γ SW framework is equivalent to that provided by the modified Dortmund UNIFAC approach for the case of ethanol, although noticeable deviations can be seen with our approach at higher temperatures in the case of 1-propanol. For the aqueous mixtures of the alkylamines considered, however, SAFT- γ SW provides an improved performance. It should be noted that the focus of the current contribution is on compounds of low molecular weight, since heavier compounds are in principle of less interest in carbon-capture processes, due to their significantly higher viscosity.

3.4. Aqueous mixtures of alkanolamines

The group interaction parameters developed up to this point can be used to predict the fluid-phase behaviour of aqueous mixtures of MEA and MPA. Unfortunately, only limited agreement of the predicted phase behaviour with experimental data for aqueous MEA [153,158,157] can be achieved using the parameter values presented in the previous sections (cf. Fig. 7). On the other hand good agreement with the experimental data for aqueous MPA [157,158] is found as can be seen in Fig. 8. It should be emphasized here that these results are fully predictive, having been obtained entirely

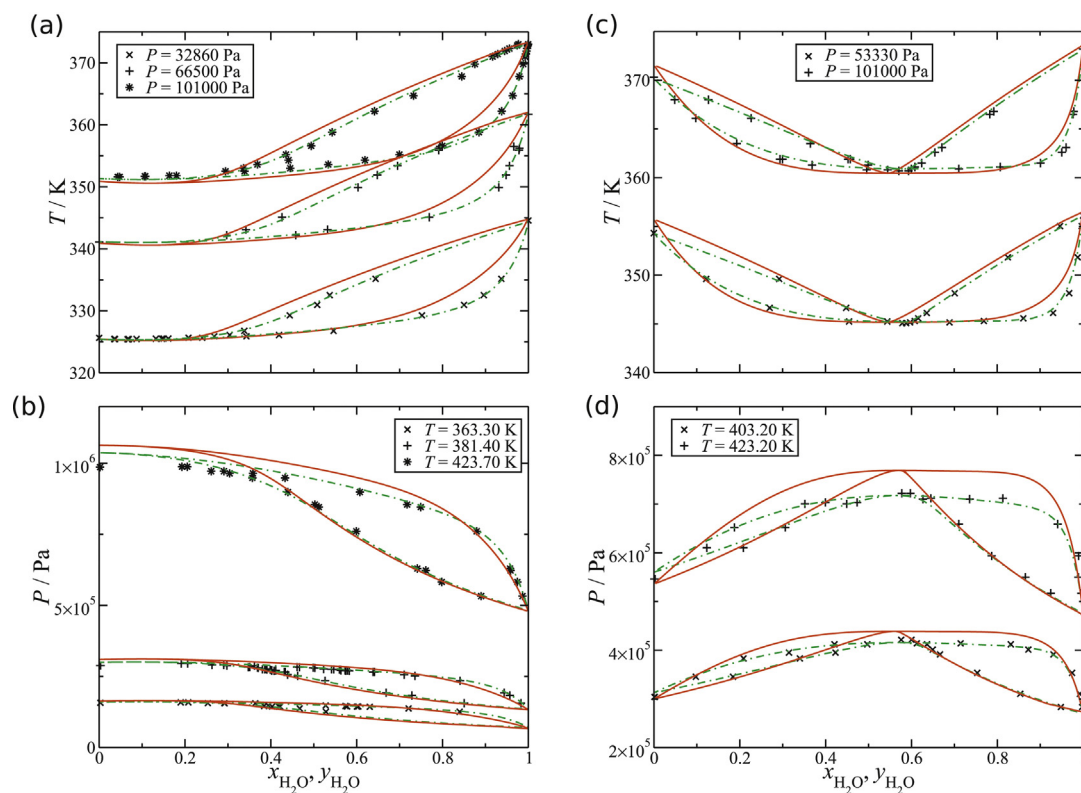


Fig. 5. Isobaric temperature-composition and isothermal pressure-composition slices of the vapour–liquid equilibria for aqueous mixtures of (a,b) ethanol and (c,d) 1-propanol. The symbols correspond to experimental data (ethanol [151] and propanol [152]), the continuous curves represent the SAFT- γ SW calculations, and the dashed curves those obtained using the Dortmund UNIFAC approach [153].

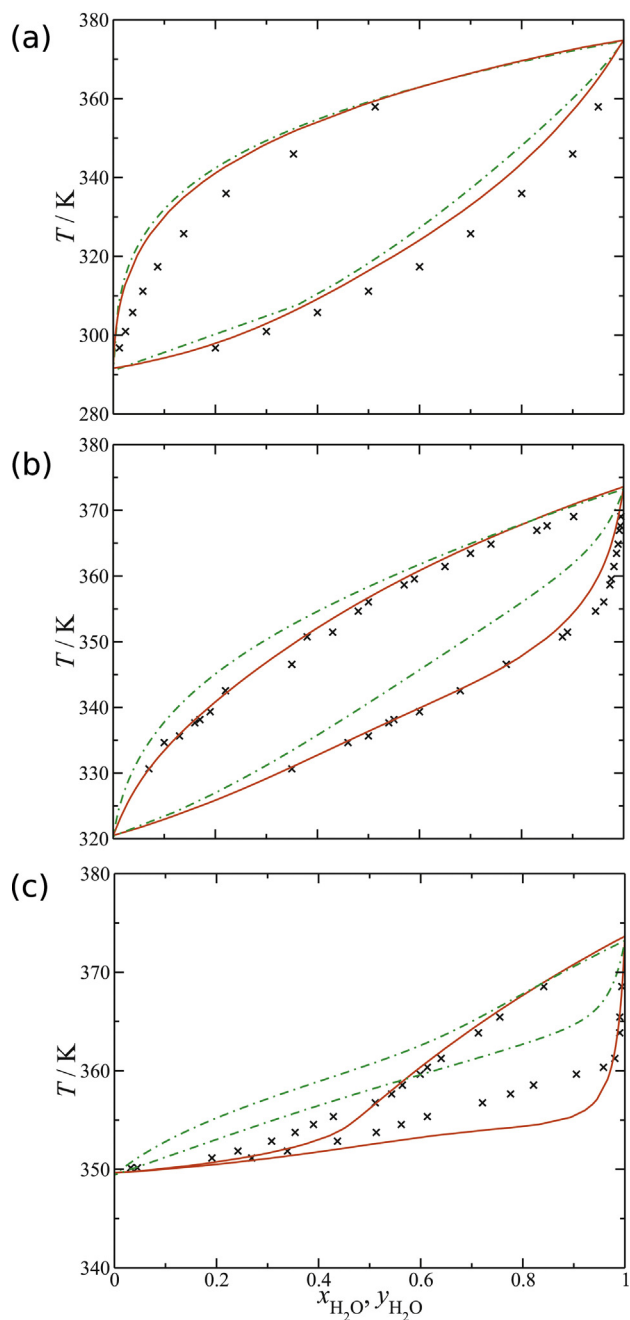


Fig. 6. Isobaric (at $P = 10^5$ Pa) temperature-composition slices of the vapour-liquid equilibrium for aqueous mixtures of (a) ethylamine, (b) 1-propylamine, and (c) 1-butylamine. The symbols correspond to experimental data (ethylamine [154], 1-propylamine [155], and 1-butylamine [156]), the continuous curves represent the SAFT- γ SW predictions using first-order groups, the dashed curves correspond to the SAFT- γ SW calculations using second-order groups, and the dot-dashed curves those obtained with the Dortmund UNIFAC approach [153].

using group parameters developed based on the data for pure alkanolamines and selected aqueous mixtures of alkanes, alkanols, and alkylamines, but no data for $\text{H}_2\text{O} + \text{alkanolamine}$ mixtures (cf. Tables 2, 3, and 4). In the case of aqueous mixtures of MPA, the group parameters appear to provide a reasonably accurate description of the fluid-phase behaviour. The difference between MEA and MPA is that MPA contains an additional CH_2 group sandwiched between the CH_2NH_2 and the CH_2OH chemical groups. The less accurate description obtained for MEA can thus be partially explained by the close proximity of the CH_2NH_2 and CH_2OH groups, which can be expected to lead to mutual polarization of the two moieties.

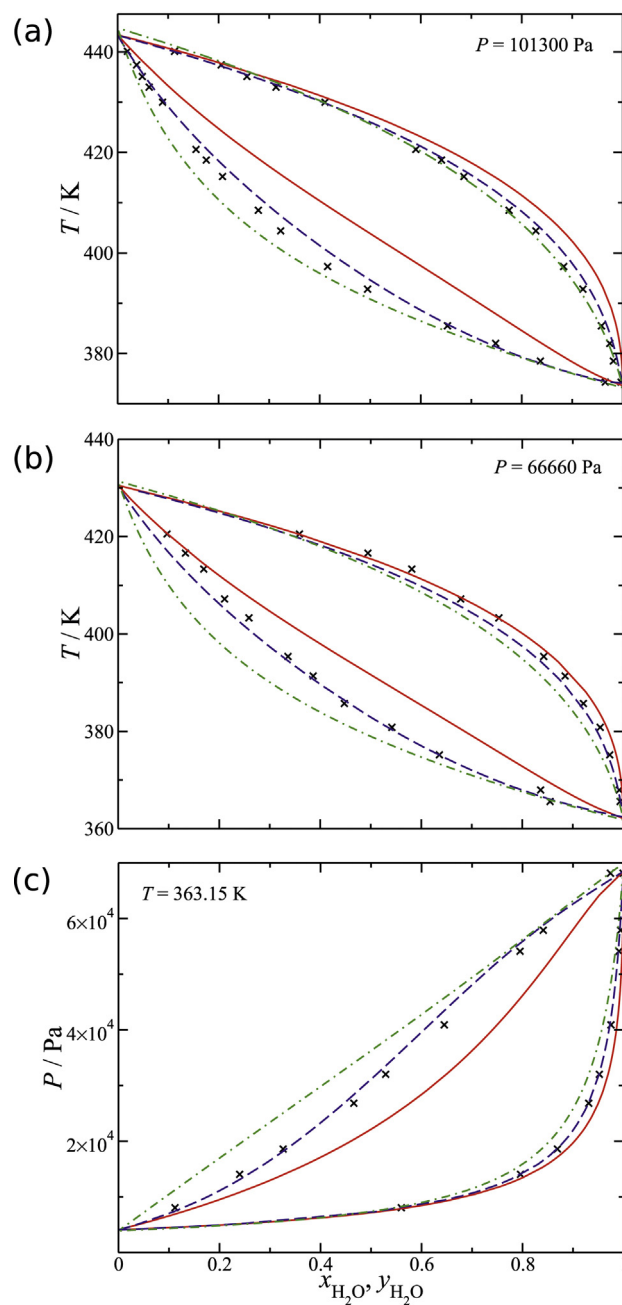


Fig. 7. (a,b) Isobaric temperature-composition and (c) isothermal pressure-composition slices of the vapour-liquid equilibria for aqueous mixtures of 2-aminoethanol (MEA). The symbols correspond to experimental data (isobars [157] and isotherm [158]), the continuous curves represent the SAFT- γ SW predictions using first-order groups, the dashed curves correspond to the SAFT- γ SW calculations using second-order groups, and the dot-dashed curves represent the results using the modified Dortmund UNIFAC approach [153].

Table 5

SAFT- γ SW unlike dispersion energy (ϵ_{kl}/k_B)/K for the second-order $\text{CH}_2\text{NH}_2[\text{CH}_2\text{OH}]$ group with H_2O and CO_2 . The numbers in parentheses correspond to the unlike values of the range of the SW potential λ_{kl} . The table is symmetric (i.e., $\epsilon_{kl} = \epsilon_{lk}$).

Group	$\text{CH}_2\text{NH}_2[\text{CH}_2\text{OH}]$
H_2O	444.924 (1.279)
CO_2	383.850 (1.293)

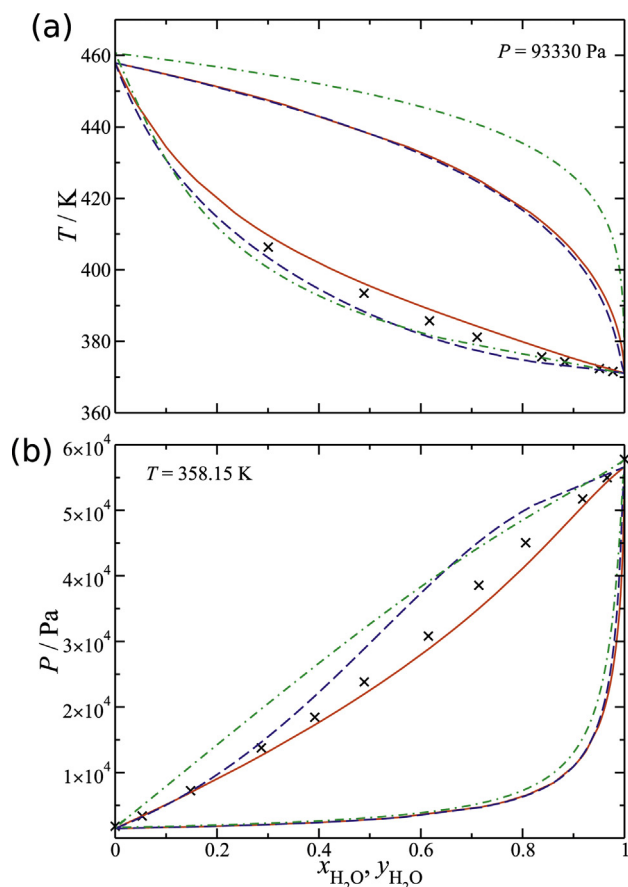


Fig. 8. (a) Isobaric temperature-composition and (b) isothermal pressure-composition slices of the vapour-liquid equilibria for aqueous mixtures of 3-amino-1-propanol (MPA). The symbols correspond to experimental data (isobar [157] and isotherm [158]), the continuous curves represent the SAFT- γ SW predictions using first-order groups, the dashed curves correspond to the SAFT- γ SW calculations using second-order groups, and the dot-dashed curves represent the results using the modified Dortmund UNIFAC approach [153].

Any such polarization would certainly be expected to affect the interactions of these groups with H_2O . In the case of MEA, we hence re-evaluate the unlike energetic parameters between the CH_2NH_2 group and H_2O using the experimental data for aqueous mixtures of MEA, and obtain an excellent description of the experimental data with the estimated parameters (cf. Fig. 7); we refer to the new parameters as second-order group parameters. For clarity we label the second-order CH_2NH_2 group as $\text{CH}_2\text{NH}_2[\text{CH}_2\text{OH}]$, where the square brackets indicate that this group should be used when the CH_2NH_2 group is covalently bonded to a CH_2OH group.

Table 6

SAFT- γ SW unlike association energy ($\epsilon_{klab}^{\text{HB}}/k_{\text{B}}$)/K for the second-order $\text{CH}_2\text{NH}_2[\text{CH}_2\text{OH}]$ group with H_2O and CO_2 . The index a and b correspond to the different types of association sites (e, H, α_1, α_2). The numbers in parentheses correspond to the unlike association range $r_{klab}^c/\text{\AA}$. Any parameter not shown takes a value of zero (i.e., $\epsilon_{klab}^{\text{HB}} = 0$); for like site-site interactions see Table 5.

Association site	$\text{CH}_2\text{NH}_2[\text{CH}_2\text{OH}]$	
	(e)	(H)
H_2O (e)	–	1322.697 (2.3082)
H_2O (H)	1542.734 (2.5200)	–
CO_2 (α_1)	4875.000 (1.9699)	–
CO_2 (α_2)	5175.024 (1.9790)	–

These second-order group parameters provide a representation of the fluid-phase equilibria that is as good as that obtained with mixture-specific homonuclear SAFT-VR SW models [78,79]. The parameters associated with the second-order group are presented in Tables 5 and 6. All other parameters for this group are the same as for the first-order CH_2NH_2 group. In the case of MPA, a second-order group parameter correction is not required, as can be seen from Fig. 8. This is consistent with the chemical nature of MPA, where the presence of the CH_2 group between the CH_2NH_2 and CH_2OH groups reduces the polarization effects. In other words, the second-order group parameters are designed to capture the behaviour of MEA in H_2O . The purpose of second-order groups is to provide more accurate structural information for compounds where the description with the first-order groups is insufficient due to proximity effects leading to a breakdown of the assumption of the transferability of the parameters [85,87,70,88].

3.5. Mixtures of CO_2 with alkanes or alkanols

Having determined all the unlike interaction parameters that characterize aqueous solutions of alkanolamines, we now develop the unlike interaction parameters between CO_2 and the functional groups of the alkanolamines, namely CH_2 , CH_2OH , and CH_2NH_2 . As was the case for H_2O , the fact that CO_2 is represented at the molecular level means that experimental data for mixtures are required to estimate the unlike parameters between CO_2 and the other functional groups. The unlike interactions between CO_2 and the methyl (CH_3) and methanediyl (CH_2) functional groups are determined based on isothermal experimental data for the vapour-liquid equilibrium of $\text{CO}_2 + n$ -propane at 293.15 K [160] and $\text{CO}_2 + n$ -nonane at 298.20 K [161]. The temperatures are chosen to be below the critical point of CO_2 (303.15 K) to avoid any bias due to the expected over-prediction of the critical point of the fluid-phase behaviour of the binary mixtures. The performance of SAFT- γ SW in the description of the vapour-liquid equilibria of binary mixtures of CO_2 with selected alkanes, namely ethane, n -propane, and n -nonane, is shown in Fig. 9.

The optimal values of the unlike dispersion energies between the CO_2 and the CH_3 and CH_2 groups are then transferred to the study of binary mixtures of CO_2 with n -alkanols, for the determination of the unlike interaction parameters between the CO_2 and CH_2OH groups. It is assumed that no association occurs between CO_2 and the CH_2OH group, and the unlike dispersion energy $\epsilon_{\text{CO}_2, \text{CH}_2\text{OH}}$ is then estimated from the experimental isothermal vapour-liquid equilibrium data [162,163] for the binary mixtures of CO_2 with ethanol and 1-propanol at temperatures of $T = 293.15$ K and $T = 303.15$ K (all other unlike parameters are determined by means of combining rules) [49]. The resulting description of the experimental data with the SAFT- γ SW approach is presented in Fig. 10, and the values of the optimal parameters are summarized in Table 3.

3.6. Aqueous mixtures of MEA and CO_2

To the best of our knowledge no experimental data are available for the binary mixtures of CO_2 and the alkanolamines considered in our current work. However, vapour-liquid equilibrium (VLE) data are available for the ternary aqueous mixtures: $\text{MEA} + \text{CO}_2 + \text{H}_2\text{O}$ [164,165] and $\text{MPA} + \text{CO}_2 + \text{H}_2\text{O}$ [166]. These data are used to estimate the unlike binary parameters characterizing the interactions of CO_2 with the CH_2NH_2 and the $\text{CH}_2\text{NH}_2[\text{CH}_2\text{OH}]$ groups, since all other unlike interactions have been previously presented and the unlike interaction between CO_2 and H_2O used is the one developed previously within the framework of the homonuclear SAFT-VR SW models [78]. Aqueous mixtures of alkanolamines and carbon dioxide are known to be reactive, leading to the formation of new

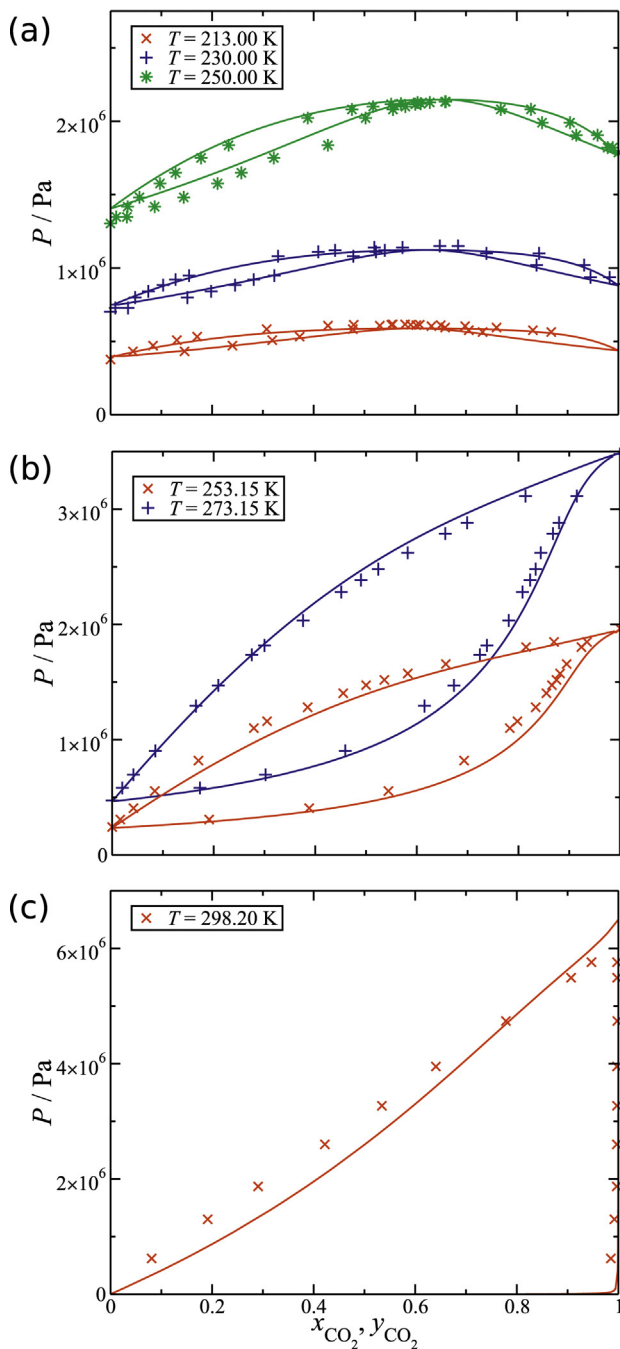


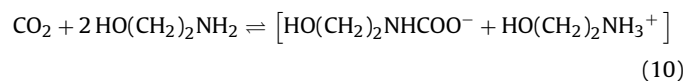
Fig. 9. Isothermal pressure-composition slices of the vapour-liquid equilibrium of binary mixtures of *n*-alkanes and carbon dioxide: (a) ethane, (b) *n*-propane, and (c) *n*-nonane. The symbols correspond to experimental data (ethane [159], *n*-propane [160], and *n*-nonane [161]), and the curves to SAFT- γ SW calculations.

species via complex reaction schemes [11,10,12]. It has been shown [78] that it is possible to treat these reactions and new species implicitly, through the incorporation of association sites on the CO₂ molecule to mediate the interactions with the amine group [78,144]. This implicit treatment of the reactions provides a convenient and straightforward method for an early assessment of new solvents for use in the context of carbon-capture processes, as only a comparatively small number of parameters (with respect to equivalent chemical approaches) have to be estimated from fluid-phase equilibrium data for the reactants alone (i.e., MEA, CO₂, and H₂O in the current context) to develop the potential models. It should be noted that, as in previous work [78,79], we do not consider ionic

speciation explicitly, but assume the formation of tight ion pairs by association of the ionic species into aggregates leading to no net overall charge.

Following the procedure developed in Ref. [79], the interactions between the amine group in the MEA molecule and the two acceptor sites of the CO₂ molecule (labeled α_1 and α_2) are not considered to be identical (i.e., $\epsilon_{\text{CH}_2\text{NH}_2, \text{CO}_2, e, \alpha_1}^{\text{HB}} \neq \epsilon_{\text{CH}_2\text{NH}_2, \text{CO}_2, e, \alpha_2}^{\text{HB}}$), and the unlike association interaction ranges are also assumed to be different (i.e., $r_{\text{CH}_2\text{NH}_2, \text{CO}_2, e, \alpha_1}^c \neq r_{\text{CH}_2\text{NH}_2, \text{CO}_2, e, \alpha_2}^c$). Hence, six parameters need to be determined to describe the MEA+CO₂ binary interactions: $\epsilon_{\text{CH}_2\text{NH}_2, \text{CO}_2}^c$, $\lambda_{\text{CH}_2\text{NH}_2, \text{CO}_2}$, $\epsilon_{\text{CH}_2\text{NH}_2, \text{CO}_2, e, \alpha_1}^{\text{HB}}$, $\epsilon_{\text{CH}_2\text{NH}_2, \text{CO}_2, e, \alpha_2}^{\text{HB}}$, $r_{\text{CH}_2\text{NH}_2, \text{CO}_2, e, \alpha_1}^c$, and $r_{\text{CH}_2\text{NH}_2, \text{CO}_2, e, \alpha_2}^c$. The model parameters are estimated through comparison with CO₂ solubility data for a 30 wt% aqueous solution of MEA as a function of partial pressure of CO₂ for a single isotherm at $T=353.15$ K [164], using CO₂ loadings up to $\theta_{\text{CO}_2} = 0.7$. Since our focus is on MEA, where the CH₂NH₂ group is bonded directly to the CH₂OH group, the model parameters are those of the second-order group, CH₂NH₂[CH₂OH]; the values of the unlike interaction parameters are presented in Tables 5 and 6. MEA has been extensively studied as an amine absorbent for carbon capture processes for over 60 years, and extensive data are therefore available [164,167–172]. Given the broad agreement among the various data sources, we assess the description for only a few representative data points. In Fig. 11 the partial pressure of CO₂ is plotted as a function of the CO₂ loading, which is defined as the number of moles of CO₂ absorbed in the liquid phase per mole of amine in that phase. Despite the fact that the estimation of the parameters is based on only one isotherm, the same set of parameters leads to a good description of the partial pressure of CO₂ for two other isotherms at $T=313.15$ K and 393.15 K over the range of pressures that is most relevant for carbon capture, up to $\theta_{\text{CO}_2} \approx 0.5$ (see Fig. 11). Some deviations are observed for isotherms at $T=313.15$ K and 393.15 K for larger θ_{CO_2} values, indicating that temperature-dependent parameters may be required to achieve higher accuracy but this is beyond the scope of our current work [173]. The SAFT- γ SW GC models are found to provide an improvement compared to that obtained with the SAFT-VR SW homonuclear molecular model developed specifically for this ternary mixture and also compared to the correlations of Gabrielsen et al. [174]. We focus on pressure ranges that would be encountered in carbon capture processes; typically flue gas is at atmospheric pressure, representing a low partial pressure of CO₂, and it is therefore preferable for it not to be compressed.

The fraction of molecules (not) bonded at a given site is evaluated as part of the determination of the Helmholtz free-energy in the SAFT approach. This information can be used to predict the degree of speciation in the mixture [79]. The mole fractions of the two main species formed, carbamate and bicarbonate, [11] as a function of CO₂ loading are presented for two temperatures ($T=313.15$ and $T=333.15$ K) in Fig. 12. The relative proportions of the species present in the system can be obtained from an analysis of the fraction of molecules not bonded at the given association sites [120,117]. As has already been mentioned, we do not consider ionic speciation explicitly but only the association of the ionic species as tight ion pairs that have no net overall charge. Two key reactions are considered:



where the ion pairs (represented between square brackets) are assumed to be associated species. The concentration of carbamate

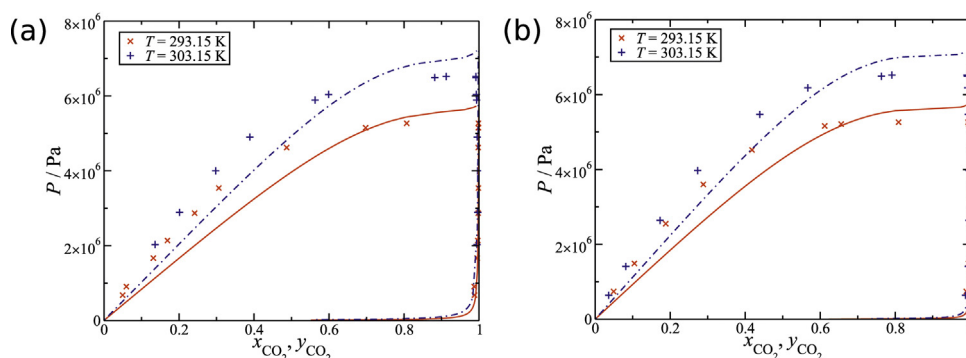


Fig. 10. Isothermal pressure-composition slices of the vapour-liquid equilibrium of binary mixtures of carbon dioxide with (a) ethanol and (b) 1-propanol. The symbols correspond to experimental data (ethanol [163] and 1-propanol [162]) and the curves to SAFT- γ SW calculations.

(Eq. (10)) can be inferred from the concentration of CO₂ molecules bonded at both sites, while the concentration of bicarbonate (Eq. (11)) can be obtained from the concentration of CO₂ molecules bonded at only one site. It can be shown that this is equivalent to the following expressions:

$$[\text{HO}(\text{CH}_2)_2\text{NHCOO}^-] = x_{\text{CO}_2} [(1 - X_{\alpha_1, \text{CO}_2})(1 - X_{\alpha_2, \text{CO}_2})], \quad (12)$$

and

$$[\text{HCO}_3^-] = x_{\text{CO}_2} [X_{\alpha_1, \text{CO}_2} + X_{\alpha_2, \text{CO}_2} - 2X_{\alpha_1, \text{CO}_2}X_{\alpha_2, \text{CO}_2}], \quad (13)$$

where x_{CO_2} is the overall mole fraction (concentration) of CO₂ in the system, and $X_{\alpha_i, \text{CO}_2}$ is the fraction of CO₂ molecules not bonded at site α_i . These expressions for the concentrations of carbamate and bicarbonate (Eq. (12) and Eq. (13)) are an improved re-interpretation of the expressions reported in a previous study [79]. It is important to note here that while reaction mechanisms or products do not need to be postulated *a priori*, the SAFT- γ SW approach is able to provide an accurate characterization of the degree of speciation of the mixture being studied. A caveat, however, in the context of the MEA + CO₂ + H₂O system, is that our models do not fully capture the various reaction mechanisms (we

focus on the main species formed), so that use of the model far outside the region where they were developed may not be reliable (e.g., in the limit of low H₂O concentration).

We continue our investigation with the determination of the unlike interaction parameters between the CO₂ and the CH₂NH₂ group when it is *not* covalently bonded to a CH₂OH group. We follow the procedure used to obtain the parameters for the CH₂NH₂[CH₂OH] group, except that now the unlike association interaction ranges are kept the same as with CH₂NH₂[CH₂OH] group when it is interacting with CO₂. The parameter estimation is performed with solubility data in a 30 wt% aqueous solution of MPA as a function of partial pressure of CO₂ for two isotherms ($T = 313.15$ and 393.15 K) [166]. The values of the unlike interaction parameters are presented in Tables 3 and 4. The partial pressure of CO₂ is plotted in Fig. 13 as a function of the CO₂ loading, again defined as the number of moles of CO₂ absorbed in the liquid phase per mole of MPA in the liquid. The overall performance is satisfactory for the purposes of our current study. Despite the relatively small number of parameters required, and the fact that they are temperature and pressure independent, the SAFT- γ SW models provide a reliable description of the observed phase behaviour across a

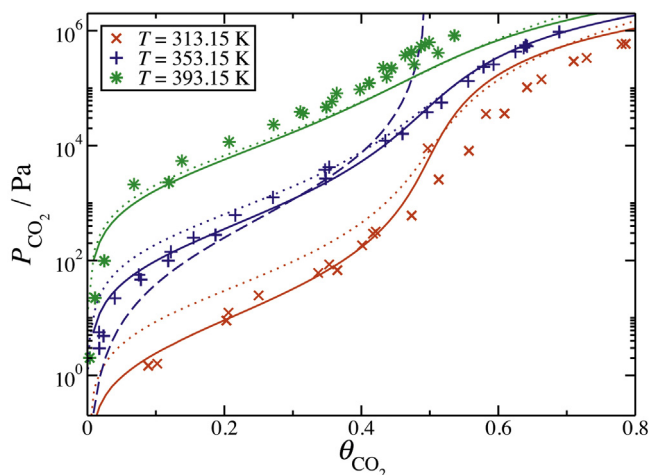


Fig. 11. Solubility of CO₂ in a 30 wt% MEA aqueous solution at $T = 313.15$ K (red crosses), 333.15 K (blue pluses), and 393.15 K (green asterisks) as a function of the partial pressure of CO₂ at vapour-liquid equilibrium for the ternary mixture of MEA + H₂O + CO₂. The solubility is represented as CO₂ 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 [164,165,170,172]. The continuous curves correspond to the SAFT- γ SW GC calculations for the ternary mixture of MEA + H₂O + CO₂, and the dotted curves to the SAFT-VR SW homonuclear calculations [79], and the dashed curve corresponds to a correlation presented by Gabrielsen et al. [174] at $T = 353.15$ K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

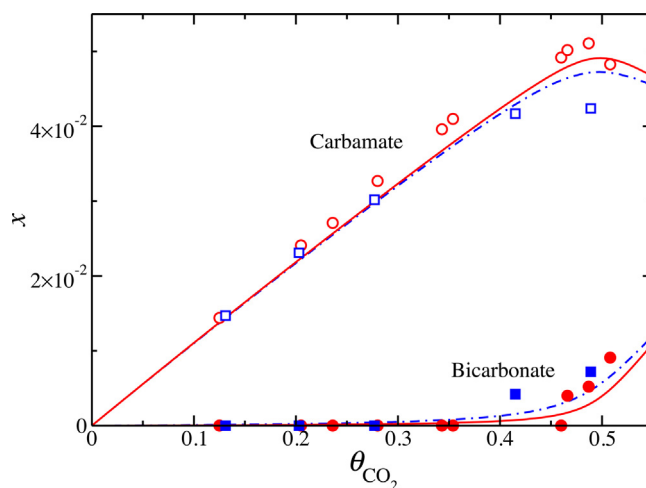


Fig. 12. Predicted mole fraction of carbamate and bicarbonate in the liquid phase of a 30 wt% MEA aqueous solution at $T = 313.15$ K (red circles) and 333.15 K (blue squares) at vapour-liquid equilibrium for the ternary mixture of MEA + H₂O + CO₂ as a function of the CO₂ loading, θ_{CO_2} , defined as 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 [164,165] 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. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

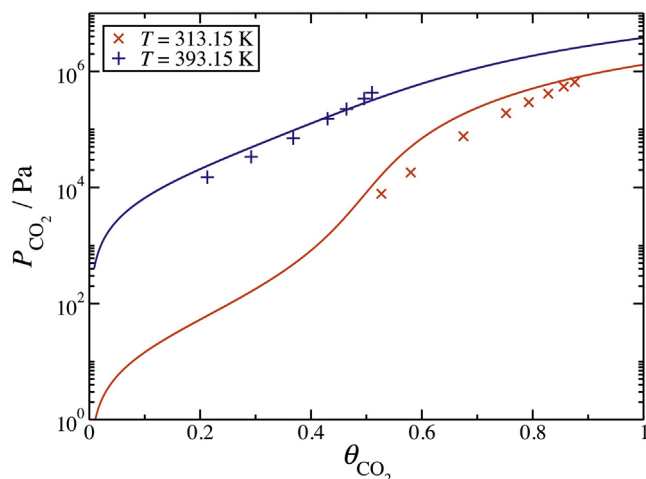


Fig. 13. Solubility of CO₂ in a 30 wt% MPA aqueous solution at $T=313.15$ K (red crosses), and 393.15 K (blue pluses) as a function of the partial pressure of CO₂ at vapour–liquid equilibrium for the ternary mixture of MPA + H₂O + CO₂. The solubility is represented as CO₂ loading, θ_{CO_2} , defined 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 [166] and the curves correspond to the SAFT- γ SW calculations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

relatively broad range of temperatures and compositions. In the case of a solvent such as MEA, with such a wealth of data, more detailed models can of course be developed [15–18]. However, for solvents like MPA for which little or no data are available, the use of transferable parameters within a group contribution formalism opens new avenues. The ability to predict speciation rather than to be dependent on the availability of such data is also a significant benefit of our methodology in the context of solvent design.

We conclude this section by investigating the predictive capabilities of our approach. Since the model parameters required to describe the vapour–liquid equilibria of ternary mixtures of any primary alkanolamines + H₂O + CO₂ have been determined, we can now examine their transferability for longer

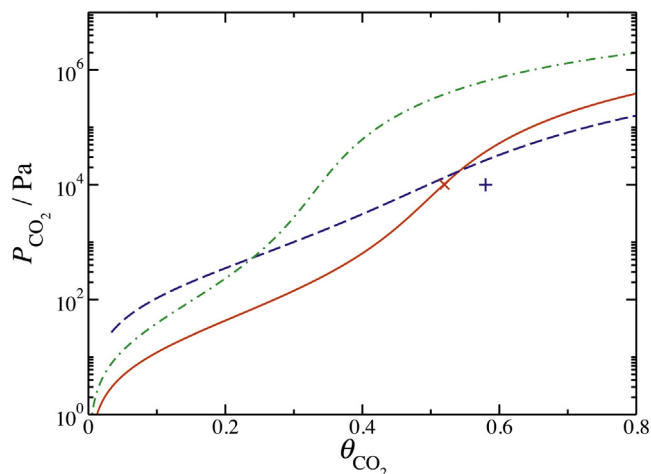


Fig. 14. Solubility of CO₂ in a 26 wt% aqueous solution of 5-amino-1-pentanol (red continuous curve and cross) and in a 6 wt% aqueous solution of 6-amino-1-hexanol (blue dashed curve and plus) at $T=303.15$ K as a function of the partial pressure of CO₂ at vapour–liquid equilibrium for the ternary mixture of amine + H₂O + CO₂. The corresponding solubility of CO₂ in a 18.5 wt% MEA and 11.4 wt% MPA aqueous solution at $T=313.15$ K is also shown (green dot-dashed curve). The solubility is represented as 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 [175] and the curves correspond to the SAFT- γ SW predictions.

alkanolamines, namely 5-amino-1-pentanol (NH₂(CH₂)₅OH) and 6-amino-1-hexanol (NH₂(CH₂)₆OH). Limited solubility data are available for the corresponding ternary mixtures comprising these amines [175]. The partial pressure of CO₂ as a function of the CO₂ loading for these systems is shown in Fig. 14. We use the first-order CH₂NH₂ group and find that the predictive capability of the SAFT- γ SW models for the 5-amino-1-pentanol solutions to be excellent. The performance is also satisfactory in the case of 6-amino-1-hexanol, albeit less accurate. Overall, our approach is robust and the description based on the temperature independent group parameters developed in our current work for primary alkanolamines provides a physically consistent and reasonably accurate representation of mixture properties over a wide range of temperatures, pressures, and compositions. Moreover, the predictive capabilities of our approach are not limited to ternary systems. The SAFT- γ SW description of an isotherm for the quaternary H₂O + CO₂ + MEA + MPA mixture is presented in Fig. 14. All the group parameters needed to model this four-component mixture with the implicit treatment of ionic species have been obtained in previous sections and thus the thermodynamic description is fully predictive. Thus, by adopting a simplified view of the speciation chemistry in these complex mixtures, the SAFT- γ SW models are found to provide a useful predictive framework for new solvent molecules, and new solvent formulations, even in the absence of experimental data.

4. Conclusions

We have presented the development of a group-contribution approach to predict the thermodynamic behaviour and fluid-phase equilibria of mixtures relevant to CO₂ capture by chemical absorption. The approach can be applied even in the absence of experimental data and provides a useful tool to support the development of novel solvents and solvent mixtures. We have focused on aqueous solutions of primary alkanolamines to establish the basis of this predictive framework. The pertinent group parameters are estimated from pure-component experimental data where possible and from binary mixture data in the case of single-group components such as CO₂ and H₂O. To account for proximity (polarization) effects in small multifunctional molecules such as MEA, we have used the concept of second-order groups. The interactions between the CH₂NH₂ functional group and H₂O are thus represented through two different sets of parameters. The first set characterizes the CH₂NH₂–H₂O unlike interaction when the amine group is in close proximity to non-polar groups, such as the methanediyl CH₂ group. The second set captures the change in the interaction between the CH₂NH₂ functional group and H₂O when the former group is covalently bonded to CH₂OH group (as in the case of MEA); the hydroxyl group is expected to polarize the amine group to a certain extent.

A significant challenge in developing group-contribution models for these mixtures is the presence of chemical reactions. We have shown how the main reaction products can be represented implicitly using physical models of association directly within the SAFT- γ SW framework. This greatly simplifies the representation of the mixtures, because speciation products are not modelled explicitly. Despite this assumption, we have shown that the SAFT- γ SW models developed for mixtures of MEA and MPA with H₂O and CO₂ can be used to describe the vapour–liquid equilibria over a wide range of temperatures, and specifically in the range of interest for operation of absorption/desorption processes. Moreover, a comparison of our predictions with experimental data for the concentrations of carbamate and bicarbonate reveals that these models provide an excellent representation of the speciation observed in such systems. Overall our models are found to be in very good

agreement with the available experimental data for the selection of compounds studied. The findings establish a broad set of chemical groups that are necessary for the description of the thermodynamic and phase-equilibrium properties of multifunctional amines as pure fluids and in aqueous mixtures containing CO₂. This provides a tool to assess novel solvents and solvent mixtures on the basis of their relative absorption performance, as we have demonstrated with the SAFT- γ SW predictions of the absorption of CO₂ in aqueous mixtures of 5-amino-1-pentanol and 6-amino-1-hexanol. Our methodology differs from modelling approaches (e.g., eNRTL) that rely on a detailed knowledge of the reaction chemistry and speciation: while such approaches provide accurate calculations for specific solvents and are therefore very appropriate for detailed process design, they require a large set of experimental data for model parameterization. Given the need for predictive models to explore the vast number of possible solvent molecules yet to be synthesized, our work motivates the extension of the group-parameter table to include secondary and ternary amines, as well as other chemical functionality.

Acknowledgments

The authors are thankful to Andrew Haslam for a critical reading of the manuscript. The authors are also grateful to the Commission of the European Union (project FP7-ENERGY-2011-282789) and the Engineering and Physical Sciences Research Council (EPSRC) of the UK (grants EP/E016340, EP/J014958/1 and EP/J003840/1) for financial support to the Molecular Systems Engineering (MSE) group.

Data statement: Data underlying this article can be accessed on Zenodo at <https://zenodo.org/record/29874>, and used under the Creative Commons Attribution licence.

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