

## Modelling the Fluid Phase Behaviour of Multifunctional Alkanolamines and Carbon Dioxide Using the SAFT- $\gamma$ Approach

Alexandros Chremos<sup>a</sup>, Esther Forte<sup>a,b</sup>, Vasileios Papaioannou<sup>a</sup>, Amparo Galindo<sup>a</sup>, George Jackson<sup>a</sup>, Claire S. Adjiman<sup>a,\*</sup>

<sup>a</sup>Department of Chemical Engineering, Centre for Process Systems Engineering, Imperial College, South Kensington Campus, London SW7 2AZ, UK.

<sup>b</sup>Department of Chemistry, BP Centre for Petroleum & Surface Chemistry, University of Surrey, Guildford, GU2 7XH, UK  
[c.adjiman@imperial.ac.uk](mailto:c.adjiman@imperial.ac.uk)

Given growing concerns on climate change, and particularly greenhouse gas emissions, the development of technologies for the capture of carbon dioxide (CO<sub>2</sub>) to prevent its release into the atmosphere is increasingly pressing. A likely medium-term solution for large-point emission sources, such as coal- or gas-fired power stations, is the use of solvent-based absorption processes. However, such processes, which often rely on the use of aqueous alkanolamine solutions as a solvent, incur a large economic penalty and it is necessary to identify alternatives that can reduce this cost. A key challenge for CO<sub>2</sub> capture is thus the design of solvents and solvent blends with thermodynamic properties which would improve the economic performance of capture processes. Given the importance of being able to predict the thermodynamic properties of such solvents, we have developed molecular models for use with the statistical associating fluid theory (SAFT). Specifically, the purpose is to identify mixtures that are good candidates for CO<sub>2</sub> absorption using transferable intermolecular potential models and a group contribution framework within SAFT. In the proposed approach chemical equilibrium is treated with a physical approach, so that reaction products are treated implicitly. We investigate the applicability of the SAFT- $\gamma$  (group contribution) equation of state to carbon dioxide, water and alkanolamine mixtures, and discuss how SAFT- $\gamma$  opens avenues for thermodynamic property prediction, decreasing the dependence on experimental data. The aqueous solvents examined include ethylamine, propylamine, ethanol, propanol, monoethanolamine (MEA) and 3-amino-1-propanol. We present calculations and predictions of the fluid phase behaviour of these components and of a number of their aqueous mixtures.

### Introduction

Understanding and predicting the phase behavior of fluid systems is central to chemical process design, particularly in oil and petrochemical industries (separation and refining processes, natural gas processing, etc.). More recently, in light of growing concern surrounding anthropogenic carbon dioxide (CO<sub>2</sub>) emissions, there has been a great deal of interest in alkanolamine-based chemisorption processes as part of the effort to mitigate emissions, particularly from large fixed-point sources such as fossil-fuel fired power-stations (Mac Dowell et al., 2010a). To achieve such goals, accurate thermodynamic models are needed. Unfortunately, experimental information for these systems is not always available and measurements that can be used to complete the existing physical property database are time-consuming and expensive to perform. Thus, the development of reliable tools with predictive capabilities is important to complement the existing data to help identify promising molecules and systems that could be the subject of experimental investigations.

In this paper, we describe the use of the statistical associating fluid theory for square-well potentials (SW) within a group-contribution (GC) framework (SAFT- $\gamma$  SW) proposed by Lympieriadis et al. (2007) and later extended to a wider set of groups (Lympieriadis et al., 2008) to calculate the equilibrium fluid-phase

behaviour of aqueous mixtures of multi-functional alkanolamines. The results are useful towards investigating and predicting the phase behavior of amine-based aqueous mixtures with CO<sub>2</sub>. In Section 2, we briefly describe the methodology used. In Section 3, we present a set of our findings that establish the foundations for the description of the fluid phase behaviour of aqueous multi-functional alkanolamines and CO<sub>2</sub>. In Section 4 we summarize our results.

## Methodology

A popular approach to overcome the reliance on experimental data and increase the predictive capability of a given thermodynamic methodology is its formulation within a group contribution approach (Papaioannou et al., 2010). Within the scope of GC methods, molecules are deconstructed into distinct functional groups that characterise their chemical composition. The underlying assumption is that these groups give rise to the same thermodynamic contribution independently of the molecule in which they appear. Once the parameters for a group have been determined via regression to experimental data, the group can be used as a building block to form a molecule. With appropriate use of group contribution methodologies the properties of a system of interest can be obtained even in cases where the thermodynamic behaviour might be unknown if the parameters characterizing the groups forming the molecules have been characterised. In this sense, group contribution methods are essentially predictive, since there is a dependency on experimental data only at the early stage of obtaining the group parameters from a set of selected systems.

Molecular-based equations of state, such as those derived from the SAFT approach by Chapman et al. (1989, 1990), provide a framework in which the effects of asymmetries in molecular shape and attractive interactions on the thermodynamic properties of complex fluids can be separated and quantified. Such approaches have increasingly been formulated within a group-contribution framework. Within the SAFT formalism molecules are modeled as chains of spherical segments with off-center bonding sites to mediate short-range intermolecular association (hydrogen bonding). In SAFT the Helmholtz free energy  $A$  of a homonuclear associating chain model molecule is written as the sum of separate contributions:

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{mono.}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc.}}{NkT}, \quad (1)$$

where  $N$  is the number of molecules,  $k$  the Boltzmann constant, and  $T$  the absolute temperature.  $A^{ideal}$  is the ideal free energy,  $A^{mono.}$  the contribution to the free energy due to the interaction between monomeric segments,  $A^{chain}$  the contribution due to the formation of a chain of  $m$  monomers, and  $A^{assoc.}$  the contribution due to association (e.g., due to hydrogen bonding). For full details of the implementation of the approach within a heteronuclear GC formalism (SAFT- $\gamma$  SW) the reader is directed to the original publications by Lympieradis et al. (2007) – the initial development as well as the advanced implementation (2008).

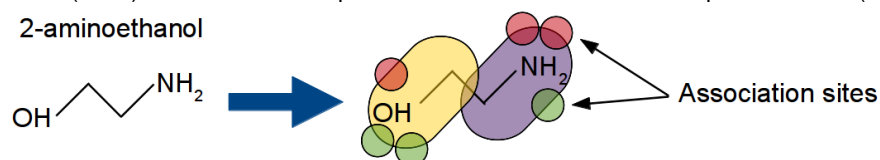


Figure 1: Schematic representation of the grouping to describe 2-aminoethanol (monoethanolamine MEA) within the SAFT- $\gamma$  SW framework; the various groups are highlighted with different colours and the association sites are indicated as the circles

The theory is developed by considering molecules in terms of their distinct chemical groups which contribute to the overall properties in the same way, regardless of the specific molecular environment in which they are found. This concept is illustrated in Figure 1 for 2-aminoethanol. In the SAFT- $\gamma$  (Lympieradis et al., 2007, 2008) group contribution version of SAFT, the common assumption that the segments making up a molecule are identical is lifted: the basic molecular model is therefore heteronuclear rather than homonuclear. Appropriate values for the SAFT intermolecular model parameters for specific groups are determined by estimation from 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. The thermodynamic properties are estimated based on the interaction parameters between each pair of those groups. By obtaining the parameters for groups, e.g., CH<sub>3</sub>, CH<sub>2</sub>, CH<sub>2</sub>OH, CH<sub>2</sub>NH<sub>2</sub>, a group-group parameter database can be constructed.

## Results

We use SAFT- $\gamma$  SW to obtain the parameters of the CH<sub>2</sub>NH<sub>2</sub> chemical group, which is useful to describe the phase behaviour of alkyl amines and amino alcohols as well as aqueous mixtures of 2-aminoethanol and 3-amino-1-propanol. The parameter estimation procedure is based on the phase behaviour of the nine n-alkylamines from ethylamine to n-decylamine. As a result of this parameter estimation, the parameters for the CH<sub>2</sub>NH<sub>2</sub> group, as well as the parameters related to its interactions with CH<sub>2</sub> and CH<sub>3</sub> groups have been obtained. The resulting descriptions of the fluid phase behaviour are shown in Figures 2 (a) & (b). The description is of equivalent quality to that obtained within the traditional SAFT-VR approach with homonuclear models based on estimations on a molecule-by-molecule basis (Mac Dowell et al., 2011). We should also note that in contrast to the earlier work by Lymeriadis et al. (2008), we consider here a CH<sub>2</sub>NH<sub>2</sub> group rather than a separate NH<sub>2</sub> group, as this is found to improve the transferability of the description for mixtures. The optimal parameters for the CH<sub>2</sub>NH<sub>2</sub> group as well as the parameters for CH<sub>3</sub> and CH<sub>2</sub> are shown in Table 1 and 2.

Table 1: SAFT- $\gamma$  SW like intermolecular potential group parameters for CH<sub>3</sub>, CH<sub>2</sub>, CH<sub>2</sub>NH<sub>2</sub>, CH<sub>2</sub>OH, and H<sub>2</sub>O.  $S_k$  is the shape factor;  $\sigma_{kk}$  is the group hard-core diameter;  $\epsilon_{kk}$  and  $\lambda_{kk}$  are the dispersion energy and range of the square-well potential, respectively; and  $\epsilon_{kkab}^{HB}$  and  $r_c$  are the site-site association energy and range.

Group	$S_k$	$\sigma_{kk} / \text{\AA}$	$\lambda_{kk}$	$(\epsilon_{kk}/k) / \text{K}$	$(\epsilon_{kkab}/k) / \text{K}$	$r_{c,kkab} / \text{\AA}$	Sites a	Sites b
CH <sub>3</sub>	0.66667	3.811	1.4130	252.601	-	-	-	-
CH <sub>2</sub>	0.33333	4.028	1.6606	240.482	-	-	-	-
CH <sub>2</sub> NH <sub>2</sub>	0.90747	3.808	1.4836	439.350	1021.375	2.4450	1	2
CH <sub>2</sub> OH	0.56570	4.317	1.6519	399.959	2555.721	2.3598	2	1
H <sub>2</sub> O	1.00000	3.034	1.7889	250.000	1400.000	2.1082	2	2

Table 2: SAFT- $\gamma$  SW unlike dispersion interaction energy group parameters,  $\epsilon_{kl}/k$ , for CH<sub>3</sub>, CH<sub>2</sub>, CH<sub>2</sub>NH<sub>2</sub>, CH<sub>2</sub>OH, and H<sub>2</sub>O in units of K. The numbers in parenthesis correspond to the unlike values of the range of the square-well potential,  $\lambda_{kl}$ . In all cases where no parenthesis are shown the combining rule,  $\lambda_{ij} = (\lambda_{ii}\sigma_{ii} + \lambda_{jj}\sigma_{jj}) / (\sigma_{ii} + \sigma_{jj})$ , is used. The table is symmetric (i.e.,  $\epsilon_{ij} = \epsilon_{ji}$ ).

Group	CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>2</sub> NH <sub>2</sub>	CH <sub>2</sub> OH	H <sub>2</sub> O
CH <sub>3</sub>	-	-	-	-	-
CH <sub>2</sub>	261.520	-	-	-	-
CH <sub>2</sub> NH <sub>2</sub>	254.736	297.873	-	-	-
CH <sub>2</sub> OH	279.939	283.702	143.247	-	-
H <sub>2</sub> O	460.312 (1.257)	460.276 (1.257)	286.857 (1.740)	299.263	-

Table 3: SAFT- $\gamma$  SW unlike site-site association energy group parameters,  $\epsilon_{ijab}^{HB}/k$ , for CH<sub>2</sub>NH<sub>2</sub>, CH<sub>2</sub>OH, and H<sub>2</sub>O in units of K. The numbers in parenthesis correspond to the unlike association range  $r_{c,ijab} / \text{\AA}$ . Any parameter not shown takes a value of zero (e.g.,  $\epsilon_{ijab}^{HB} = 0$ ); for like site-site interactions see Table 1.

Group	CH <sub>2</sub> NH <sub>2</sub> (a)	CH <sub>2</sub> NH <sub>2</sub> (b)	CH <sub>2</sub> OH (a)	CH <sub>2</sub> OH (b)
CH <sub>2</sub> OH (a)	-	1696.979 (2.528)	-	-
CH <sub>2</sub> OH (b)	903.303 (3.952)	-	-	-
H <sub>2</sub> O (a)	-	1 <sup>st</sup> order: 1365.326 (2.308) 2 <sup>nd</sup> order: 1520.482 (2.308)	-	1645.280 (2.467)
H <sub>2</sub> O (b)	1 <sup>st</sup> order: 1261.968 (2.520) 2 <sup>nd</sup> order: 1579.563 (2.520)	-	2472.971 (2.019)	-

In order to describe the fluid phase behaviour of amino alcohols, the parameters of two groups are necessary: the CH<sub>2</sub>NH<sub>2</sub> and the CH<sub>2</sub>OH chemical moieties. The parameters for the CH<sub>2</sub>OH group including its interactions with CH<sub>2</sub>, CH<sub>3</sub> groups as well as with H<sub>2</sub>O have been obtained previously (Papaioannou et al., 2011) and for pure component for water (Clark et al., 2006). Adjustments to the unlike interaction parameters between H<sub>2</sub>O and CH<sub>3</sub>, CH<sub>2</sub>, as well as CH<sub>2</sub>OH groups have been made from those presented in this earlier study to provide an overall improved description of the phase behaviour of aqueous solutions of short-chain alcohols, which are most relevant to the systems of interest here. The unlike interaction parameters between the CH<sub>2</sub>NH<sub>2</sub> and CH<sub>2</sub>OH groups are obtained with a parameter estimation based on

the thermodynamic behaviour of pure 2-aminoethanol (MEA) and 3-amino-1-propanol; cf. Tables 1, 2, and 3. A comparison with experimental data is shown in Figures 2 (c) & (d).

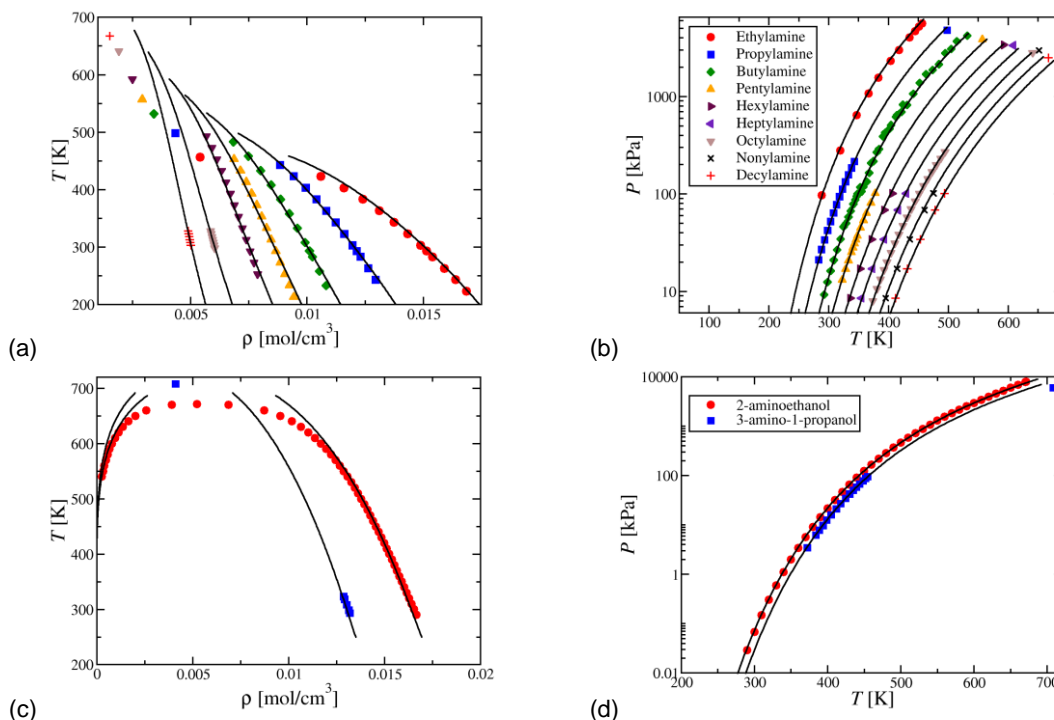


Figure 2: (a & b) Temperature-density and pressure-temperature representations of the fluid phase behaviour for primary amines used for the determination of the parameters for the  $\text{CH}_2\text{NH}_2$  chemical group. (c & d) Temperature-density and pressure-temperature representations of the fluid phase behaviour for 2-aminoethanol and 3-amino-1-propanol used for the determination of the dispersion energy as well as the cross association related parameters between the chemical groups  $\text{CH}_2\text{NH}_2$  and  $\text{CH}_2\text{OH}$ . The points correspond to experimental data and the continuous curves represent the SAFT- $\gamma$  SW calculations.

The next phase of our investigation is to transfer the parameters that we have obtained to mixtures. We focus on aqueous mixtures of the amino alcohols and in particular on MEA and 3-amino-1-propanol. Towards that goal we have investigated the transferability of our parameters for the description of alkanols and alkylamines. A visual comparison with experimental data as well as with the predictions of the modified Dortmund UNIFAC approach (Gmehling et al., 1993) is presented in Figure 3 for aqueous mixtures of ethylamine, 1-propylamine, ethanol, and 1-propanol.

The parameters obtained from previous estimations can be used to predict the phase behaviour of aqueous mixtures of MEA and 3-amino-1-propanol; the main difference on going from MEA to 3-amino-1-propanol is the addition of a  $\text{CH}_2$  group between the  $\text{CH}_2\text{NH}_2$  and the  $\text{CH}_2\text{OH}$  chemical groups. We refer to the set of parameters that characterize the amine group as 1<sup>st</sup> order. The 1<sup>st</sup> order approach provides very good agreement with experiments for 3-amino-1-propanol and a modest agreement for MEA, cf. Figure 4. It should be emphasised here that the results presented under our 1<sup>st</sup> order approach are totally predictive, obtained solely based on the group-parameters developed as described previously. Regarding the less accurate description for MEA, part of the problem is that the  $\text{CH}_2\text{NH}_2$  and  $\text{CH}_2\text{OH}$  groups are expected to polarise each other due to their close proximity, and thus the effective interaction of those groups with water is not expected to remain the same. In other words, the groups' properties are affected by their close proximity and thus a 2<sup>nd</sup> order correction is required, similar to the strategy followed in KT-UNIFAC (Wang et al., 2002). In the case of MEA, we have re-evaluated the unlike energetic parameters between the amine group and  $\text{H}_2\text{O}$ , providing an excellent description of the experimental data, cf. Figures 4 (a) & (b). The second-order parameters provide a representation of the fluid phase equilibria which is as

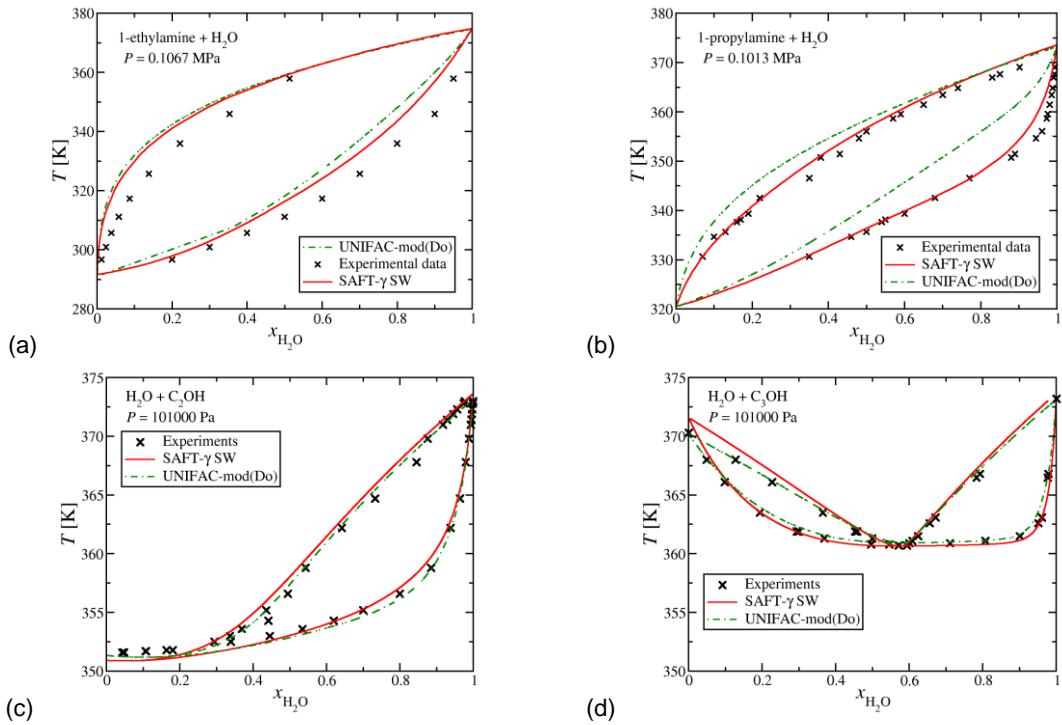


Figure 3: Isobaric temperature-composition slice of the vapour-liquid equilibrium of aqueous mixtures of (a) ethylamine; (b) 1-propylamine; (c) ethanol; (d) 1-propanol. The points correspond to experimental data, the continuous curves represent the SAFT- $\gamma$  SW calculations, and the dashed curves to calculations with the Dortmund UNIFAC approach (Gmehling et al., 1993)

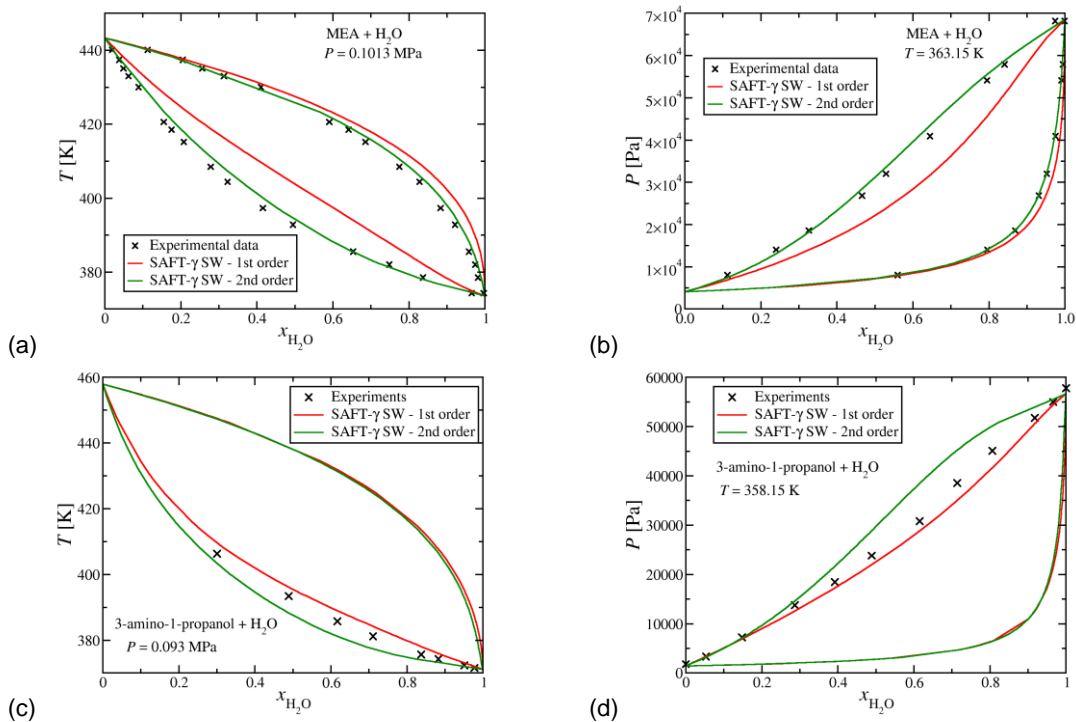


Figure 4: Isobaric temperature-composition and isothermal pressure-compositions slices of the vapour-liquid equilibrium of aqueous mixtures of (a) & (b) MEA; (c) & (d) 3-amino-1-propanol. The points correspond to experimental data, the continuous curves represent the SAFT- $\gamma$  SW calculations with first- and second-order group interactions

good as with mixture-specific homonuclear models by Mac Dowell et al. (2010b) and more recently by Rodriguez et al. (2012). In the case of 3-amino-1-propanol, a second order correction is not required, as can be seen from Figures 4 (c) & (d). This is in line with the chemical nature of 3-amino-1-propanol, where the presence of a CH<sub>2</sub> group between the CH<sub>2</sub>NH<sub>2</sub> and CH<sub>2</sub>OH groups reduces the effects of polarisability.

## Conclusions

New parameters for a CH<sub>2</sub>NH<sub>2</sub> group and a CH<sub>2</sub>OH group, as well as their interactions with other groups such as CH<sub>3</sub>, CH<sub>2</sub> and H<sub>2</sub>O have been presented, based on the SAFT- $\gamma$  SW equation of state, in which molecules are modelled using fused heteronuclear segments interacting via square-well potentials. The method is found to be in very good agreement with the available experimental data for the range of compounds studied. The findings establish a significant set of chemical groups that are necessary for the description of multifunctional amines as pure and in aqueous mixtures and for their future application in the prediction of the phase behaviour of mixtures containing CO<sub>2</sub>.

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