

Prediction of thermodynamic properties and fluid-phase behaviour of aqueous solutions of linear, branched, and cyclic amines

Felipe A. Perdomo | Siti H. Khalit | Claire A. Adjiman
| Amparo Galindo | George Jackson

Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.

¹Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.

Correspondence

George Jackson, Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.
Email: g.jackson@imperial.ac.uk

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The SAFT- γ Mie group-contribution equation of state is used to represent the fluid-phase behaviour of aqueous solutions of a variety of linear, branched, and cyclic amines. New group interactions are developed in order to model the mixtures of interest, including the like and unlike interactions between alkyl primary, secondary, and tertiary amine groups (NH₂, NH, N), cyclic secondary and tertiary amine groups (cNH, cN), and cyclohexylamine groups (cCHNH, cCHN) with water (H₂O). The group-interaction parameters are estimated from appropriate experimental thermodynamic data for pure amines and selected mixtures. By taking advantage of the group-contribution nature of the method, one can describe the fluid-phase behaviour of mixtures of molecules comprising those groups over broad ranges of temperature, pressure, and composition. A wide range of aqueous solutions of amines are studied including linear, branched aliphatic, and cyclic amines. Liquid-liquid equilibria (LLE) bounded by lower critical solution temperatures (LCSTs) have been reported experimentally and is reproduced here with SAFT- γ Mie approach. The main feature of the approach is the ability not only to represent accurately the experimental data

employed in the parameter estimation, but also to predict the vapour-liquid, liquid-liquid, and vapor-liquid-liquid equilibria, and LCSTs with the same set of parameters. Pure compound and binary phase diagrams of diverse types of amines and their aqueous solutions are assessed in order to demonstrate the main features of the thermodynamic and fluid-phase behaviour.

KEYWORDS

keyword 1, keyword 2, keyword 3, keyword 4, keyword 5, keyword 6, keyword 7

1 | INTRODUCTION

Amines are defined as organic compounds comprising one or more nitrogen atoms with a pair of valence electrons. They are classified according to the nature and number of substituents, including aliphatic amines, whether they only contain hydrogen or alkyl (branched or cyclic) substituents, and aryl amines when the nitrogen atom is bonded to an aromatic ring. There are other subcategories when the organic compound contains other functional groups as well as the amine group. For instance, alkanolamines comprise both alcohol and amine groups. In pure amines, such as primary and secondary amines, the physical properties are strongly affected by the presence of hydrogen bonds donors on the NH_2 and NH groups.

Amines are also bases, as they possess an electron lone pair, which they can share with other atoms. The greater the electron density associated with the lone pairs, the more basic the amine. Additionally, within the different types of amine, the ability of the nitrogen atom to donate its lone pair of electrons is modified by the presence of other functional groups bonded to the nitrogen atom, groups that donate or supply electrons increase the basicity of the amine, while groups that decrease the electron density around the nitrogen decrease the basicity of the molecule. [1]

In water, the ammonium salts of amines undergo solvation effects (due to hydrogen bonding) that increase the electron density on the amine nitrogen to a greater degree than the inductive effect of alkyl groups. Amine groups strongly interact with surrounding water molecules in aqueous mixtures through amine-water intermolecular hydrogen bonds that give rise to complex hydration structures [2, 3]. As a consequence of their basicity, aqueous solutions of organic amines are employed in a broad range of important industrial chemical applications such as in dyes, pesticides, varnishes, ion-exchange resins, surfactants, and perfumes [4, 5, 6]. The broad variability in the miscibility of aqueous solutions of amines has also been used in extraction processes for metal salts [7, 8], carboxylic [9], and dicarboxylic acids [10].

In particular, aliphatic amines have been the subject of intensive research, both for their interesting stereochemical properties and for their usefulness as model systems in studies of enzymatic reactions [11]. They are widely used as neutralizing agents for acid-functional raw materials in cosmetics [12] and to improve the solubility and enhance the permeation of pharmaceutical compounds [13]. Importantly, they are very effective absorbents of acid gases, such as hydrogen sulphide (H_2S) and carbon dioxide (CO_2), and as such a wide variety of aliphatic amines have been used as gas sweeteners and CO_2 capture solvents [14, 15].

It is well known that physico-chemical properties in complex fluids are strongly influenced by a molecule's stereochemistry and structure [16, 17]. As expected, variations of the molecular framework or of the moieties constituting different amines give rise marked differences in the macroscopic properties of the solutions. In aqueous solutions of amines the

solubility of the amine in water is strongly affected by its molecular weight; the amines's molecular weight can play a more important role than whether the amine is primary, secondary, or tertiary [18, 19].

The presence of a lower critical solution temperature (LCST) is another important feature of the mutual solubility of aqueous solutions of amines: such mixtures are partially miscible at intermediate temperatures but due to the presence of an LCST become completely miscible at lower temperatures. The accurate determination of the liquid-liquid equilibria (LLE) of amine-water systems throughout the domain of both total and partial solubility limits is a demanding task for any thermodynamic model due to the balance complex molecular detail that needs to be accounted for. In spite of the paucity of studies on modelling the phase behaviour of aqueous solutions of amines an important example worthy of mention is the work of Hartono et al. [20] who modelled the vapour-liquid equilibria (VLE) of aqueous solutions of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ). These authors used the UNIQUAC, NRTL, and Wilson models to calculate the activity coefficients of the species in the mixture, correlated these to experimental data and determined a set of interaction parameters that allow one to predict the VLE of aqueous solutions of AMP and PZ. These models provide a good description of the binary VLE data and interaction parameters were then used to predict the phase behaviour of the ternary system AMP + PZ + H₂O. The UNIQUAC approach is seen to provide the best representation of the experimental data. The NRTL activity-coefficient model has also been applied to determine the thermodynamic properties of binary mixtures of cyclic amines and water. Li et al.[21] determined the NRTL parameters for VLE and excess enthalpy data for N-methylpiperazine (MPZ) + H₂O system allowing for a good representation of the fluid-phase behaviour though the average relative deviation of the mole fraction of MPZ in vapor phase is found to be higher than 10%.

Even though these approaches have been shown to give a good representation of the VLE in aqueous solutions of amines, the parameters are restricted to a limited domain of pressures and temperatures and do not explicitly take into account the complex intermolecular interactions (such as solvation and association) that take place in the liquid phase and play an important role in determining the thermodynamic properties of this type of systems such as the presence of an LCST.

In order to provide a good understanding of the link between the macroscopic behaviour of aqueous solutions of amines and the specific molecular interactions relevant in these mixtures, approaches such as molecular-simulation methods [3, 22] or molecular based EOSs are better suited to the task. In these approaches one can account for highly polarizable functional groups to consider the physical-chemical forces (such as hydrogen bonding) that play an important role in determine the structure and phase equilibria of the system, including an explicit description of molecular association and solvation.

In particular, molecular theories of associating fluids, such as the statistical associating fluid theory (SAFT) [23, 24, 25], can be used to provide a versatile platform for the accurate description of the phase behaviour of aqueous solutions of amines. The SAFT family of EOSs is well-known for its ability to model complex mixtures of associating fluids and has been used in a number of studies to describe the fluid-phase behaviour of amines. The version of the theory developed for potentials of variable range (SAFT-VR) [26, 27] has been employed to model the fluid-phase behavior of aqueous mixtures of ammonia (NH₃) and *n*-alkyl amines [28]. The models developed within the SAFT description allow one to account for both the molecular association and the non-spherical chain-like nature of the amines, thereby making the models transferable to the entire *n*-alkylamine series, including delivering a description of the liquid-liquid equilibria seen in solutions of *n*-hexylamine. The amines were modelled as homonuclear chain molecules formed from spherical segments with additional association sites incorporated to mediate the effect of hydrogen-bonding interactions. The same approach has been used to represent the thermodynamic behaviour of aqueous mixtures of multifunctional alkanolamines [29], and later similar systems were studied [30] with a reformulation of SAFT as a group-contribution (GC) approach. In this case, the SAFT- γ SW group-contribution approach [31, 32] was used to describe the interactions

between the various functional groups characterising the molecules with an intermolecular potential of the square-well (SW) form; the concept of second-order groups was employed to deal with the multifunctional nature of the alkanolamines molecules.

In our current paper we implement the SAFT- γ Mie group-contribution [33, 34, 35] approach to provide a more realistic representation of the molecular interactions based on the Mie (generalized Lennard-Jones) potential for a wide variety of amines and their respective mixtures with water. The amine compounds are modelled as chain molecules formed from different types of fused Mie segments with short-range association sites where appropriate. This allows one to account for not only the hydrogen bonding and molecular length, but also the influence of unsaturation, molecular volume and shape of the variety of functional groups present in amine systems on the thermodynamic properties of the solutions.

The use of the SAFT- γ group-contribution approach is particularly advantageous when there is limited availability and reliability in the experimental data; reliable experimental data for amines (e.g., cyclic amines and cyclohexylamines) is often very scarce. With the SAFT- γ group-contribution approach the interaction parameters between functional groups can be estimated entirely from the experimental data of homologous series of related chemical families, the data for which are typically more accessible. In the following sections we describe in detail how the interaction parameters for the various functional chemical groups can be successfully transferred to represent the thermodynamic properties and fluid-phase behaviour for aqueous solutions of representative linear, branched, and cyclic amines.

2 | THERMODYNAMIC MODEL: SAFT- γ MIE

We consider a variety of aqueous amine systems comprising species with both short and large molecular structures, which feature strong intermolecular interactions that give rise to complex hydrogen-bonded structures. Several of the molecules considered and their SAFT- γ Mie representation are shown in Figure 1.

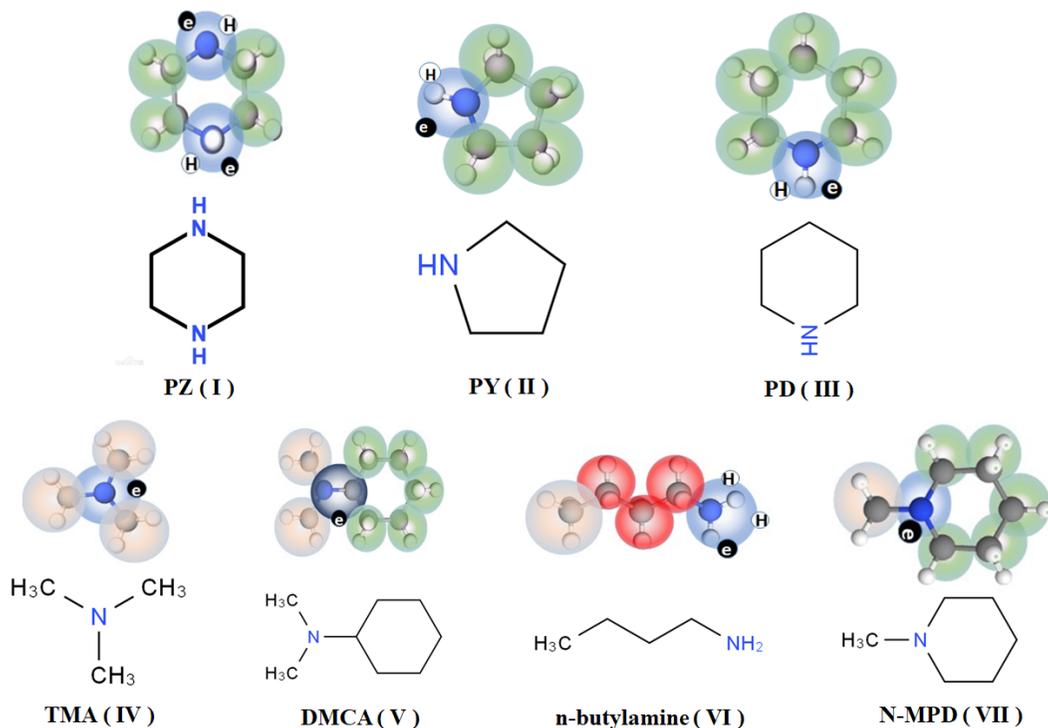


FIGURE 1 Representative alkyl and cyclic amines alongside the SAFT- γ model: I) piperazine (PZ); II) pyrrolidine (PY); III) piperidine (PD); IV) trimethylamine (TMA); V) N,N-dimethylcyclohexylamine (DMCA); VI) *n*-butylamine; and VII) N-methylpiperidine (MPD);

In the SAFT- γ Mie approach [33, 34, 35] molecules are subdivided into distinct functional groups selected to represent their various chemical moieties. Each group k is represented as a fused spherical segment (or v_k^* identical segments). Segments k and l are assumed to interact through Mie potentials of variable attractive and repulsive ranges,

$$\Phi_{kl}^{\text{Mie}} = C_{kl} \epsilon_{kl} \left[\left(\frac{\sigma_{kl}}{r_{kl}} \right)^{\lambda_{kl}^r} - \left(\frac{\sigma_{kl}}{r_{kl}} \right)^{\lambda_{kl}^a} \right] \quad (1)$$

where r_{kl} represents the distance between the centres of the segments, σ_{kl} is the segment diameter, $-\epsilon_{kl}$ is the minimum in the potential energy of interaction between segments, and λ_{kk}^r and λ_{kk}^a represent the repulsive and attractive exponents of the inter-segment interactions, respectively. The prefactor C_{kl} is a function of these exponents and is defined as

$$C_{kl} = \frac{\lambda_{kl}^r}{\lambda_{kl}^r - \lambda_{kl}^a} \left(\frac{\lambda_{kl}^r}{\lambda_{kl}^a} \right)^{\frac{\lambda_{kl}^a}{\lambda_{kl}^r - \lambda_{kl}^a}}. \quad (2)$$

Hydrogen bonding is mediated by embedding short-range square-well sites of specified types on a given group of type k , and as a consequence, in the case of associating groups the different site types a , the number $n_{k,a}$ of sites of a given type a , the energy $\epsilon_{kl,ab}^{HB}$ and the range (in the form of the bonding volume) $K_{kl,ab}$ of the association between sites have to be determined.

In the case of amine groups, sites of types H and e are typically specified, where e represents the lone pair of electrons on the N atom, and one H site is included per hydrogen atom.

Once the relevant parameters are specified, the total Helmholtz free energy A of a mixture of associating heterogroup chain molecules formed from Mie segments of different type can be obtained from the appropriate contributions of the different groups to four separate contributions:

$$A = A^{\text{IDEAL}} + A^{\text{MONO}} + A^{\text{CHAIN}} + A^{\text{ASSOC}}, \quad (3)$$

where, A^{IDEAL} is the ideal free energy of the mixture, A^{MONO} is the residual free energy due to the interaction between the monomer Mie segments, A^{CHAIN} is the contribution due to fusing the segments to form chain molecules, and A^{ASSOC} is the term describing the contribution to the free energy due to intermolecular hydrogen-bonding association. For a complete description of the theory and full expressions for each of the contributions we direct the reader to the original SAFT- γ Mie publications [33, 34, 35, 36].

2.1 | Combining Rules

In order to specify fully the expressions for the Helmholtz free energy presented in Equation (3) a number of like and unlike group interaction parameters need to be characterised. All of the like parameters are determined by minimisation of an objective function including experimental data, while the unlike parameters are initially determined using combining rules and then estimated from experimental data when necessary. The unlike segment diameter σ_{kl} is obtained using the Lorentz arithmetic mean of the like diameters [37]:

$$\sigma_{kl} = \frac{\sigma_{kk} + \sigma_{ll}}{2}. \quad (4)$$

The unlike dispersion energy ϵ_{kl} is obtained by applying an augmented geometric mean (Berthelot-like rule), which also accounts for asymmetries in size [38]:

$$\epsilon_{kl} = \frac{\sqrt{\sigma_{kk}^3 \sigma_{ll}^3}}{\sigma_{kl}^3} \sqrt{\epsilon_{kk} \epsilon_{ll}}. \quad (5)$$

The exponents of the unlike segment-segment interaction λ_{kl}^r and λ_{kl}^a are obtained as

$$\lambda_{kl} = 3 + \sqrt{(\lambda_{kk} - 3)(\lambda_{ll} - 3)} \quad (6)$$

which results from the imposition of the geometric mean of the integrated van der Waals energy (Berthelot rule) for a Sutherland fluid of range λ_{kl} [33]. The bonding volume $K_{kl,ab}^{HB}$ and association energy parameter $\epsilon_{kl,ab}^{HB}$ between unlike

sites can also be approximated following arithmetic and geometric averages as

$$K_{kl,ab}^{HB} = \left(\frac{\sqrt[3]{K_{kk,aa}^{HB}} + \sqrt[3]{K_{ll,bb}^{HB}}}{2} \right)^3 \quad (7)$$

and

$$\epsilon_{kl,ab}^{HB} = \left(\epsilon_{kk,aa}^{HB} \epsilon_{ll,bb}^{HB} \right)^{\frac{1}{2}} \quad (8)$$

These combining rules provide a good first estimate of the values of the required unlike group parameters; however, it is best to use experimental data when available to estimate these parameters, especially in the case of the unlike attractive interactions (dispersion energies). An advantage of the heteronuclear model used in our approach is that the use of pure component data is sufficient in many cases to obtain an accurate estimate of the values of these unlike energetic parameters.

3 | PARAMETER ESTIMATION

The interaction parameters between groups of the same or different type are estimated from appropriate single-phase thermodynamic and fluid-phase equilibrium data; pure component as well as selected mixture data are used in the parameter estimation. For pure compounds the selected experimental properties vapour pressure and saturated-liquid density data, from the triple point to 90% of the critical temperature, when available. When additional data are needed to increase the statistical significance of the parameters, single-phase density and mixture vapour-liquid equilibria data are also typically considered. We follow a sequential procedure to determine the parameters required to represent the systems of interest (cf. Figure 1). For example, once we have characterised the cyclic methine cCH and methylene cCH₂ groups by considering pure-component cyclic alkane data, the parameters of these groups are transferred to model other chemical families such as cyclic amines, allowing for the estimation of the set of group parameters for the amines groups.

The objective function used in the parameter estimation procedure is

$$\min_{\Theta} f_{obj} = \sum_{I=1}^{N_I} w_I \sum_{i=1}^{N_{p,I}} \left(\frac{X_{i,I}^{\text{exp}} - X_{i,I}^{\text{calc}}}{X_{i,I}^{\text{exp}}} \right)^2 \quad (9)$$

Θ denotes the vector of the parameters to be estimated, N_I is the number of properties considered, the index i allows for sums over the experimental (exp) points for each property, $X_{i,I}^{\text{exp}}$, denoted as $N_{p,I}$. The desired level of accuracy for each calculated (calc) property, $X_{i,I}^{\text{calc}}$, can be adjusted by employing the weighting factors w_I . The estimation of the group parameters is carried out using the numerical solvers of the commercial software package gPROMS [39]. In order to assess the quality of the description, the percentage average absolute deviation (%AAD) is determined in each case as follows:

$$\%AAD = \frac{100}{N_{Z,i,p}} \sum_{j=1}^{np} \left| \frac{Z_{i,j}^{\text{exp}} - Z_{i,j}^{\text{calc}}}{Z_{i,j}^{\text{exp}}} \right| \quad (10)$$

where $Z_{i,j}$ denotes the selected property of compound i , including the vapour pressure, saturated-liquid density, single-phase density or mixture vapour-liquid equilibria compositions, and $N_{Z_{i,p}}$ is the number of experimental points being considered.

4 | RESULTS

The compounds studied in our current work cover a broad spectrum of amine chemical families: primary, secondary, and tertiary; linear, branched and cyclic and cyclohexyl amines. Additionally, aqueous solutions of amines are also considered and the relevant amine-water unlike group interactions parameters are characterised. We start our investigation focusing on the fluid-phase equilibria of pure amines in order to obtain the optimal value of the group interaction parameters for the cNH and cN groups, which represent the secondary and ternary cyclic amine groups, respectively. The NH₂, NH and N groups which represent primary, secondary, and ternary alkyl amine groups, respectively studied next. We then discuss the case of the larger cCHNH and cCHN groups, which are developed to model the secondary and ternary cyclohexyl amine groups, respectively.

4.1 | Parameter tables

The SAFT- γ Mie groups that are developed here to model the primary, secondary, and ternary amines, and their aqueous solutions are summarized in Table 1. All of the corresponding like and unlike group parameters are presented in Tables 2 – 4.

TABLE 1 Group interaction matrix of SAFT- γ functional groups for the aqueous amine solutions considered. The blue shading indicates that the group interaction parameters are estimated in the current work. The green shading indicates that the group parameters have been previously determined and can be taken directly from references [36, 40]. The gray shading indicates that the group interactions are derived from the expressions for the combining rules given in equations (4)-(8).

		1											
1	cCH ₂		2										
2	cCH			3									
3	CH ₂				4								
4	CH ₃					5							
5	cNH						6						
6	cN							7					
7	N								8				
8	NH									9			
9	NH ₂										10		
10	cCHNH											11	
11	cCHN												12
12	H ₂ O												

TABLE 2 Like group parameters for use within the SAFT- γ Mie group-contribution approach relevant to linear, branched, and cyclic amines: v_k^* , S_k and σ_{kk} are the number of segments constituting group k , the shape factor, and the segment diameter of group k , respectively; λ_{kk}^r and λ_{kk}^a are the repulsive and attractive exponents, and ϵ_{kk} is the dispersion energy of the Mie potential characterizing the interaction of two k groups; $N_{ST,k}$ represents the number of association site types on group k , with $n_{k,H}$ and $n_{k,e}$ denoting the number of association sites of type H and e respectively. The symbol † indicates that the parameters are developed in the current work

k	Group k	v_k^*	S_k	λ_{kk}^r	λ_{kk}^a	$\sigma_{kk}/\text{\AA}$	$\left(\frac{\epsilon_{kk}}{k_B}\right)/K$	$N_{ST,k}$	$n_{k,H}$	$n_{k,e}$	Ref.
1	cCH ₂	1	0.24751	20.386	6.0000	4.7852	477.36	-	-	-	[36]
2	cCH	1	0.096095	8.0000	6.0000	5.4116	699.92	-	-	-	†
3	CH ₂	1	0.22932	19.871	6.0000	4.8801	473.39	-	-	-	[36]
4	CH ₃	1	0.57255	15.050	6.0000	4.0773	256.77	-	-	-	[36]
5	cNH	1	0.16529	19.491	6.0000	4.9810	631.92	2	1	1	†
6	cN	1	0.071900	7.0024	6.0000	4.6120	174.04	1	0	1	†
7	N	1	0.15069	8.8970	6.0000	3.0755	62.971	1	0	1	†
8	NH	1	0.36589	19.999	6.0000	3.2568	100.00	2	1	1	†
9	NH ₂	1	0.79675	10.254	6.0000	3.2477	284.78	2	2	1	†
10	cCHNH	1	0.15346	9.2374	6.0000	5.5000	691.56	2	1	1	†
11	cCHN	1	0.10264	8.0016	6.0000	4.4454	709.98	1	0	1	†
12	H ₂ O	1	1.0000	17.020	6.0000	3.0063	266.68	2	2	2	[36]

TABLE 3 Group-group dispersion interaction energies ε_{kl} and repulsive exponent λ_{kl}^r relevant to aqueous solutions of linear, branched, and cyclic amines for use within the SAFT- γ Mie approach. CR indicates that the unlike repulsive exponent λ_{kk}^r is obtained from the combining rule given by Equation 6 and the unlike dispersion energy ε_{kl} is obtained with Equation 5. The symbol † indicates that the parameters are developed in the current work.

k	l	group k	group l	$\left(\frac{\varepsilon_{kl}}{k_B}\right)/K$	λ_{kl}^r	Ref.	k	l	group k	group l	$\left(\frac{\varepsilon_{kl}}{k_B}\right)/K$	λ_{kl}^r	Ref.
1	1	cCH ₂	cCH ₂	477.36	20.386	[36]	4	10	CH ₃	cCHNH	406.97	CR	†
1	2	cCH ₂	cCH	321.71	CR	†	4	11	CH ₃	cCHN	761.79	CR	†
1	3	cCH ₂	CH ₂	469.67	CR	[36]	4	12	CH ₃	H ₂ O	358.18	100.00	[40]
1	4	cCH ₂	CH ₃	355.95	CR	[36]	5	5	cNH	cNH	631.92	19.490	†
1	5	cCH ₂	cNH	605.45	CR	†	5	6	cNH	cN	812.26	CR	†
1	6	cCH ₂	cN	536.66	CR	†	5	7	cNH	N	CR	CR	†
1	7	cCH ₂	N	650.24	CR	†	5	8	cNH	NH	CR	CR	†
1	8	cCH ₂	NH	549.43	CR	†	5	9	cNH	NH ₂	CR	CR	†
1	9	cCH ₂	NH ₂	332.15	CR	†	5	10	cNH	cCHNH	CR	CR	†
1	10	cCH ₂	cCHNH	486.88	CR	†	5	11	cNH	cCHN	CR	CR	†
1	11	cCH ₂	cCHN	750.06	CR	†	5	12	cNH	H ₂ O	523.83	8.4243	†
1	12	cCH ₂	H ₂ O	350.99	28.497	†	6	6	cN	cN	174.04	7.0000	†
2	2	cCH	cCH	699.92	8.0000	†	6	7	cN	N	CR	CR	†
2	3	cCH	CH ₂	522.57	CR	†	6	8	cN	NH	CR	CR	†
2	4	cCH	CH ₃	690.17	CR	†	6	9	cN	NH ₂	CR	CR	†
2	5	cCH	cNH	CR	CR	†	6	10	cN	cCHNH	CR	CR	†
2	6	cCH	cN	CR	CR	†	6	11	cN	cCHN	CR	CR	†
2	7	cCH	N	781.41	CR	†	6	12	cN	H ₂ O	2990.0	66.109	†
2	8	cCH	NH	731.36	CR	†	7	7	N	N	62.971	8.8971	†
2	9	cCH	NH ₂	CR	CR	†	7	8	N	NH	CR	CR	†
2	10	cCH	cCHNH	CR	CR	†	7	9	N	NH ₂	CR	CR	†
2	11	cCH	cCHN	CR	CR	†	7	10	N	cCHNH	CR	CR	†
2	12	cCH	H ₂ O	377.16	22.266	†	7	11	N	cCHN	CR	CR	†
3	3	CH ₂	CH ₂	473.39	19.871	[36]	7	12	N	H ₂ O	1481.3	21.217	†
3	4	CH ₂	CH ₃	350.77	CR	[36]	8	8	NH	NH	100.00	19.999	†
3	5	CH ₂	cNH	429.49	CR	†	8	9	NH	NH ₂	381.98	CR	†
3	6	CH ₂	cN	508.54	CR	†	8	10	NH	cCHNH	CR	CR	†
3	7	CH ₂	N	348.30	CR	†	8	11	NH	cCHN	CR	CR	†
3	8	CH ₂	NH	394.58	CR	†	8	12	NH	H ₂ O	646.10	13.195	†
3	9	CH ₂	NH ₂	348.39	CR	†	9	9	NH ₂	NH ₂	284.78	10.254	†
3	10	CH ₂	cCHNH	309.95	CR	†	9	10	NH ₂	cCHNH	CR	CR	†
3	11	CH ₂	cCHN	893.49	CR	†	9	11	NH ₂	cCHN	CR	CR	†
3	12	CH ₂	H ₂ O	423.63	100.00	[40]	9	12	NH ₂	H ₂ O	358.55	CR	†
4	4	CH ₃	CH ₃	256.77	15.050	[36]	10	10	cCHNH	cCHNH	691.56	9.2374	†
4	5	CH ₃	cNH	583.72	CR	†	10	11	cCHNH	cCHN	CR	CR	†
4	6	CH ₃	cN	710.00	CR	†	10	12	cCHNH	H ₂ O	949.96	37.405	†
4	7	CH ₃	N	462.18	CR	†	11	11	cCHN	cCHN	709.98	8.0016	†
4	8	CH ₃	NH	530.87	CR	†	11	12	cCHN	H ₂ O	1067.9	8.0008	†
4	9	CH ₃	NH ₂	244.15	CR	†	12	12	H ₂ O	H ₂ O	266.68	17.020	[36]

TABLE 4 Group-group association energies $\epsilon_{kl,ab}^{HB}$ and bonding volume $K_{kl,ab}$ parameters relevant to aqueous solutions of linear, branched, and cyclic amines for use within the SAFT- γ Mie approach. The symbol † indicates that the parameters are developed in the current work.

k	l	group k	site a of group k	group l	site b of group l	$\epsilon_{kl,ab}^{HB}/K$	$K_{kl,ab}/\text{\AA}$	Ref.
5	5	cNH	e	cNH	H	1511.6	87.651	†
5	6	cNH	H	cN	e	901.35	1.1555	†
5	12	cNH	e	H ₂ O	H	2838.4	37.395	†
5	12	cNH	H	H ₂ O	e	1700.9	1.6177	†
6	12	cN	e	H ₂ O	H	5203.7	0.037423	†
7	12	N	e	H ₂ O	H	3846.2	0.56178	†
8	8	NH	e	NH	H	1370.3	10.062	†
8	9	NH	e	NH ₂	H	1639.9	37.900	†
8	9	NH	H	NH ₂	e	1682.1	0.5820	†
8	12	NH	e	H ₂ O	H	1799.8	125.45	†
8	12	NH	H	H ₂ O	e	1064.5	400.82	†
9	9	NH ₂	e	NH ₂	H	1070.8	95.225	†
9	12	NH ₂	e	H ₂ O	H	1460.0	179.60	†
9	12	NH ₂	H	H ₂ O	e	1988.3	55.824	†
10	10	cCHNH	e	cCHNH	H	1293.5	438.49	†
10	12	cCHNH	e	H ₂ O	H	5588.7	0.00010007	†
10	12	cCHNH	H	H ₂ O	e	4143.6	0.77966	†
11	12	cCHN	e	H ₂ O	H	4115.4	0.23069	†
12	12	H ₂ O	H	H ₂ O	e	1985.4	101.69	[36]

4.2 | Pure compounds

As is usual practice in developing SAFT- γ Mie group-interaction models, pure compound vapour pressure and the saturated-liquid density data are used to estimate the molecular group parameters in the first instance. If available, the temperature range considered spans from the triple point to 90% of the critical temperature. In the following subsections we discuss in turn each of the chemical families studied and the new group interactions that are developed in this work.

4.2.1 | Secondary and Tertiary Cyclic Amines: cNH and cN groups

In order to model the chemical family of cyclic amines we define two new chemical groups: the secondary cyclic amine group cNH, and the tertiary cyclic amine group cN as in molecules I, II, and III of Figure 1. The cNH group is modelled as an associating group featuring one association site of type H and one association site of type e, whereas the cN group only features one association site of type e. The presence of the e sites in both groups plays an important role in the

description of fluid-phase equilibria in aqueous solutions of cyclic amines, as will be seen later. The like parameters of these cyclic groups as well as the unlike interaction parameters with other cyclic (cCH, cCH₂) and alkyl (CH₂, CH₃) groups are estimated by using experimental data for cyclic amines. The selection of the specific cyclic amine experimental data used is based on availability. Data for three unsubstituted cyclic amines (piperazine [41], pyrrolidine [42], and piperidine [43]) are used to estimate the parameters of the secondary cyclic amine group cNH, and the experimental data of four substituted cyclic amines (the methyl and ethyl substituted piperidine/piperazine: N-methylpiperidine (MPD), (see VII in Figure 1); N-methylpiperazine (MPZ); N-ethylpiperidine (EPD); and N-ethylpiperazine (EPZ) are used to estimate the parameters of the ternary cyclic amine group cN. Detailed information about the specific experimental data used and the degree of the agreement in the representation obtained with the SAFT- γ Mie approach is presented in Table 5. The calculated vapour pressures compared with the available data [42, 43, 41, 44, 45, 46] are presented in Figure 2 (a); in order to visualize better the low-temperature region, the vapour-pressure is depicted in a Clausius-Clapeyron representation. A comparison of the vapour-liquid temperature-density coexistence curves is presented in Figure 2 (b). Very good agreement between theory and experiment is apparent in all the cases. The group-interaction parameters estimated with the SAFT- γ Mie approach can then be used directly for the prediction of thermodynamic properties of a variety of cyclic amines without any further experimental information.

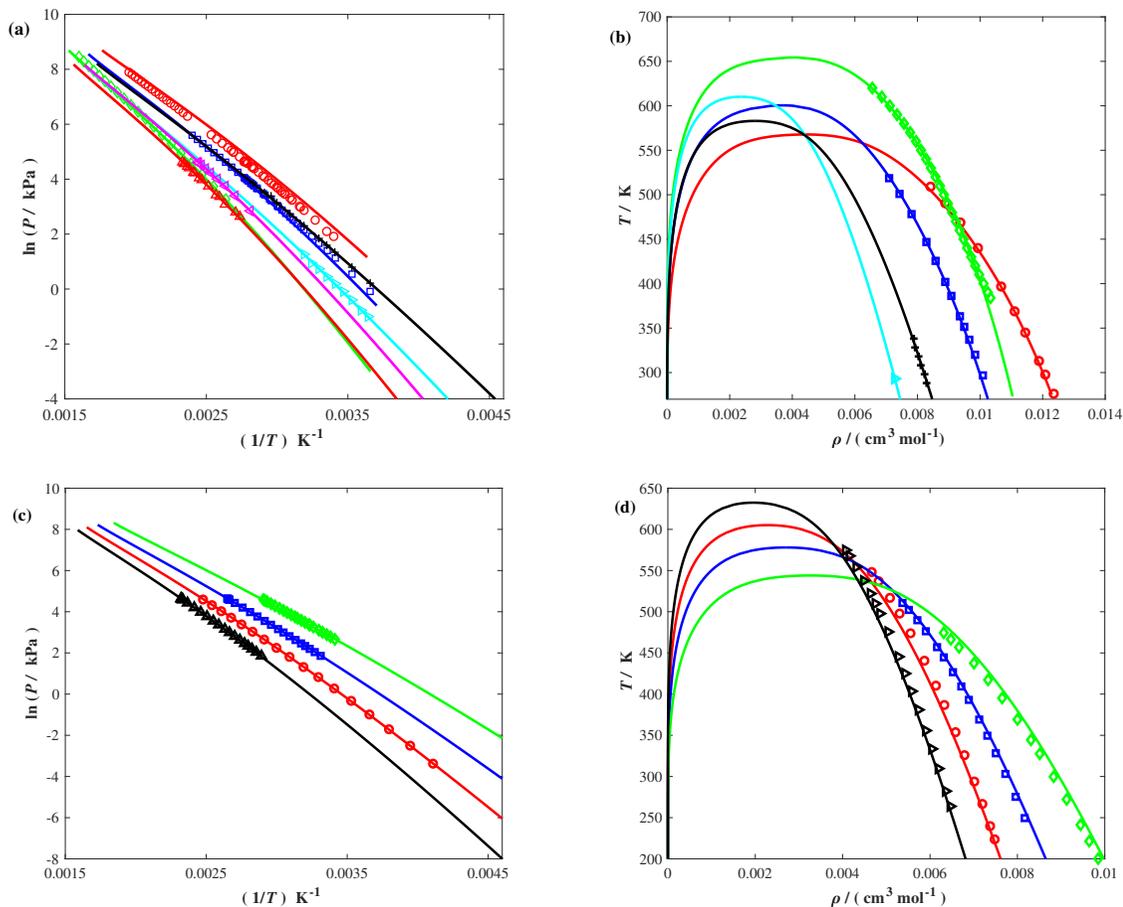


FIGURE 2 (a) The vapour pressure P (Clausius-Clapeyron representation), and (b) coexisting vapour-liquid densities ρ as a function of temperature T for pyrrolidine (PY, red circles [42]), piperidine (PD, blue squares [43]), piperazine (PZ, green diamonds [41]), N-ethylpiperazine (EPZ, red triangles [44]), N-ethylpiperidine (EPD, cyan triangles [45]), N-methylpiperazine (MPZ, magenta triangles [44]), and N-methylpiperidine (MPD, black crosses [46]). (c) The vapour pressure P (Clausius-Clapeyron representation), and (d) coexisting vapour-liquid densities ρ as a function of temperature T for ethylcyclohexane (red circles [47]), ethylcyclopentane (blue squares [47]), methylcyclopentane (green diamonds [47]), propylcyclohexane (black triangles). The symbols correspond to experimental data and continuous curves to the calculations with the SAFT- γ Mie group-contribution approach.

TABLE 5 Percentage average absolute deviation %AAD of the experimental data for the vapour pressure $P_{vap}(T)$ and the saturated liquid density $\rho_{sat}(T)$ obtained with the SAFT- γ Mie group-contribution approach for pure compounds of interest here. N_p and N_ρ are the numbers of data points of P_{vap} and ρ_{sat} respectively. The references of the experimental data are denoted in each case

Compound	T / K	N_p	%AAD P_{vap}	Ref.	T / K	N_ρ	%AAD ρ_{sat}	Ref.
Cyclic amines								
pyrrolidine (PY)	293 – 510	50	2.12	46	275 – 508	10	0.55	46
piperidine (PD)	273 – 416	37	1.06	47	296 – 519	12	0.12	47
piperazine (PZ)	379 – 625	20	0.36	45	384 – 620	24	0.02	45
N-methylpiperidine (MPD)	273 – 354	11	0.03	47	288 – 338	6	0.76	47
N-ethylpiperidine (EPD)	274 – 313	9	0.57	47	293.15	1	0.01	47
N-methylpiperazine (MPZ)	355 – 410	9	0.02	47	-	0	-	
N-ethylpiperazine (EPZ)	365 – 429	15	0.01	47	-	0	-	
Cyclic alkanes								
ethylcyclohexane	243 – 403	17	0.09	51	223 – 548	14	1.98	51
ethylcyclopentane	301 – 378	20	0.11	51	249 – 511	15	0.70	51
methylcyclopentane	293 – 344	20	0.05	51	200 – 474	14	1.93	51
n-propylcyclohexane	345 – 431	20	0.17	51	264 – 575	17	1.90	51
Alkylamines								
ethylamine	288 – 456	11	1.76	53	223 – 293	12	0.99	53
n-propylamine	283 – 343	13	0.65	54	243 – 293	12	0.16	54
n-butylamine	292 – 515	40	6.68	55	233 – 293	12	0.35	55
n-pentylamine	322 – 378	13	1.84	56	213 – 453	13	0.74	56
n-hexylamine	321 – 406	6	5.70	57	253 – 493	13	1.03	57
n-heptylamine	327 – 430	7	3.57	57	288 – 353	14	0.13	57
n-octylamine	344 – 495	23	1.43	58	298 – 328	7	0.11	58
Alkyl cyclohexylamines								
N-methylcyclohexylamine (MCA)	275 – 314	14	0.03	63	274 – 552	16	0.80	63
N-ethylcyclohexylamine (ECA)	274 – 552	16	0.00	63	350 – 626	17	0.82	63
N,N-dimethylcyclohexylamine (DMCA)	275 – 314	14	0.34	63	276 – 557	14	3.55	63

4.2.2 | Substituted cyclic alkanes: cCH group

Among the amines selected in our current study there are several important types which are currently being assessed in the context of CO₂ capture as they exhibit partial miscibility with water at relatively low temperatures, piperazine, dimethylcyclohexylamine, and 1-methylpiperidine (see molecules I, V, and VII respectively in Figure 1) belong to the class of amine. As can be seen in their chemical structure these compounds all feature a substituted chemical cyclic group cCH. Here, we estimate the parameters of this group and its interactions with other alkyl groups (cCH-CH₂ and cCH-CH₃) using experimental data for pure substituted cyclic alkanes [47], namely ethylcyclohexane, ethylcyclopentane,

and *n*-propylcyclopentane; specific details of the number data points, thermodynamic conditions, and deviations of the SAFT- γ Mie description from the experimental value are provided in Table 5. The corresponding group-group interactions estimated are reported in Tables 2 and 3. As can be seen from Figures 2 (c) and (d) the parameters obtained in this way for the cCH chemical group (namely, cCH-cCH, cCH-CH₂, and cCH-CH₃) allow for an accurate description of the fluid-phase equilibria of pure cycloalkanes with the SAFT- γ Mie approach. The characterization of the parameters of cyclic substituted compounds is important not only for the description of cyclic amines but also relevant to linear alkanes [36] and cyclic alkanes, and allows also for a description of the properties of mixtures of hydrocarbons and amines. Having developed the parameters for the cyclic chemical groups (cNH, cN and cCH). We proceed to determine the parameters for linear amines in a similar fashion.

4.2.3 | Primary, secondary, and tertiary alkylamines: NH₂, NH, and N groups

In order to develop a SAFT- γ Mie model for the chemical family of the primary, secondary, and tertiary alkylamines we define the following aliphatic alkylamine groups: NH₂ for primary *n*-alkylamines; NH for secondary alkylamines; and N for tertiary alkylamines. The interaction parameters with the methyl CH₃ and methylene CH₂ groups are taken from previous work [36, 48]. The procedure undertaken to estimate the values of the N, NH, and NH₂ group parameters, as well as those relating to their interactions with the CH₂ and CH₃ groups, is similar to that presented in the previous section. The NH₂ group is modelled as an associating group with two association sites of type H corresponding to the hydrogen atoms and one association site of type e corresponding to the electron lone pair on the nitrogen atom, where only sites of different type interact; i.e., only e-H site-site interactions are allowed. As will be shown in the following sections, the description of the fluid-phase equilibria of *n*-alkylamines is very sensitive to the values of the interaction parameters for the NH₂ group. The parameters of the NH₂ group and its interactions within CH₃ and CH₂ are estimated using target experimental data for the fluid-phase equilibria of pure primary *n*-alkylamines, specifically ethylamine [49], *n*-propylamine [50], *n*-butylamine [51], *n*-pentylamine [52], *n*-hexylamine, *n*-heptylamine [53], and *n*-octylamine [54]. The adequacy of the theoretical description of the phase equilibria for each one of these compounds is apparent from Figures 3 (a) and (b) and Table 5.

The description of the chemical family of the secondary *n*-alkylamines is carried out by specifying the secondary amine NH group, which is also modelled as an associating group, but in this case it features only one association site of type e to represent the electron lone pair on the nitrogen atom and one hydrogen site of type H; as before only sites of different type interact. Like NH-NH and unlike NH-CH₃, NH-CH₂ group interactions are obtained using pure-component experimental vapour-pressure and saturated-liquid density data for four secondary alkylamines: diethylamine, dibutylamine, dihexylamine, and dioctylamine [55, 56].

Furthermore, in order to obtain reliable estimates of the interaction between amine and alkyl groups, experimental data for the isobaric vapour-liquid equilibria of binary mixtures of secondary alkylamines and alkanes are also considered [57, 58]. Specifically, experimental data for diethylamine + hexane [57], diethylamine + heptane [57], and dipropylamine + hexane [58] are included in the parameter estimation procedure. The optimal values estimated for the NH group interactions are given in Tables 2, 3 and 4.

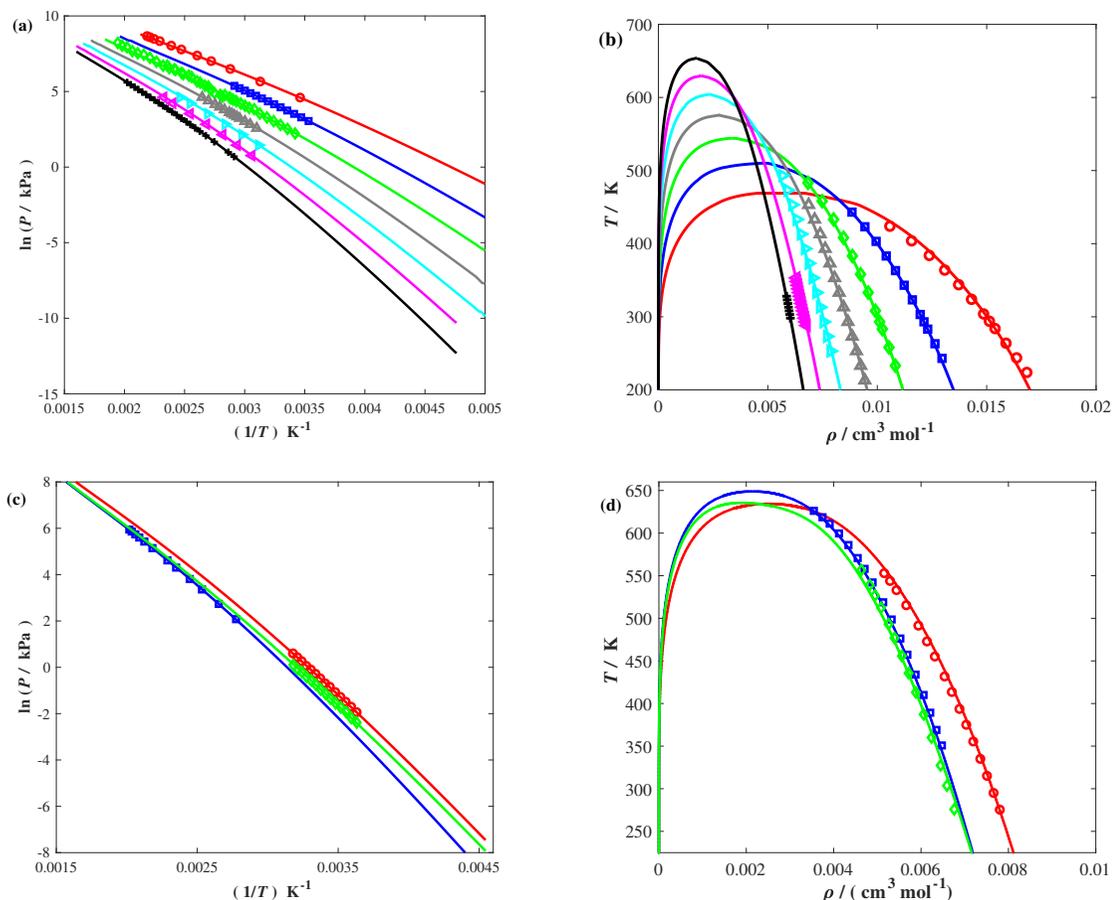


FIGURE 3 (a) The vapour pressure P (Clausius-Clapeyron representation), and (b) coexisting vapour-liquid densities ρ as a function of temperature T for ethylamine (red circles [49]), *n*-propylamine (blue squares [50]), *n*-butylamine (green diamonds [51]), *n*-pentylamine (grey triangles [52]), *n*-hexylamine (cyan triangles [53]), *n*-heptylamine (magenta triangles [53]), *n*-octylamine (black crosses [54]). (c) The vapour pressure P (Clausius-Clapeyron representation), and (d) coexisting vapour-liquid densities ρ as a function of temperature T for N-methylcyclohexylamine (MCA, red circles [59]), N-ethylcyclohexylamine (ECA, blue squares [59]) and N,N-dimethylcyclohexylamine (DMCA, green diamonds [59]). The symbols correspond to experimental data and continuous curves to the calculations with the SAFT- γ Mie group-contribution approach.

4.2.4 | Cyclohexylamines: cCHNH and cCHN groups

Having determined all the interaction parameters for the groups that represent the chemical family of cycloalkanes as well as those which describe the alkyl amines, it is possible to use these to predict the properties of the family of cyclohexylamines which feature both cyclohexyl and alkyl substituents. In particular N-methylcyclohexylamine (MCA) and N,N-dimethylcyclohexylamine (DMCA) (cf. Figure 1) are of interest here. As shown in the following sections the presence of the alkyl groups in cyclohexylamines confers unique properties to their mixtures with water. We find that,

while the smaller cCH and NH (or N) groups can be used to deliver accurate properties of the pure cyclohexylamines, in order to capture the complex phase behaviour of the aqueous solutions of these cyclohexylamines the introduction of new, larger, groups is required; specifically the cCHNH and cCHN groups for monoalkyl-cyclohexylamines and dialkyl-cyclohexylamines, respectively are developed here for this family of systems. The phase behaviour of these molecules in aqueous solution is presented later in section 4.7. The secondary cCHNH amine group is treated as an associating group and presents the same association features as the NH group: one site of type e corresponding to the electron lone pair on the nitrogen atom, and one site of type H corresponding to the hydrogen atom. The ternary cCHN amine group is modelled with just one association site of type e corresponding to the electron lone pair on the nitrogen atom. The parameters of the cCHNH and cCHN groups as well as those relating to the interactions with the aliphatic CH₂ and CH₃ groups, and with the cyclic cCH₂ are estimated using the same procedure as for the others types of amines.

Experimental data for pure cyclohexylamines [59], namely MCA, N-ethylcyclohexylamine (ECA), and DMCA is used. The target experimental properties considered are the vapour pressure and saturated-liquid density. In each case the average absolute deviation (%AAD) of the theory in comparison to the experimental data is determined in order to assess the quality of the description (see Table 5). The parameters pertaining to the cCHNH and cCHN groups are included in Tables 2, 3 and 4. As can be seen in Figures 3 (c) and (d), the theoretical description of the fluid-phase equilibria obtained with the SAFT- γ Mie approach and the new groups developed is in very close agreement with experimental data.

It is important to note that, as is apparent from the parameters in Table 4, our model allows for self association between secondary cyclohexylamines (i.e., MCA, ECA, etc.) as the group cCHNH incorporates one donor and one acceptor association site. This type of self association scheme is not considered for ternary cyclohexylamines (i.e., DMCA, DECA, etc.) where only one electron lone pair is present on the nitrogen atom.

4.3 | Aqueous mixtures of cycloalkanes: cCH₂-H₂O and cCH-H₂O interactions

In systems such as aqueous mixtures of cycloalkanes the hydrophobic effect plays an important role in the solubility and fluid-phase behaviour. In our work the unlike interactions between the cyclic cCH₂ and cCH groups and H₂O are characterized by estimating both energy ϵ_{kl} and repulsive-range λ_{kk}^r parameters from target experimental data. These group interactions allow one to extend the capability of the SAFT- γ group-contribution approach the description for the aqueous solubility of aromatic hydrocarbons [36] and *n*-alkanes [60] developed in previous work to treat saturated and substituted cyclic alkanes. The appropriate determination of these interactions is a crucial step for the accurate description of the fluid-phase behaviour of aqueous solutions of both cyclic amines and cyclohexylamines.

In order to describe correctly the unlike interactions between the cCH and cCH₂ groups and H₂O, the parameters are estimated from mutual solubility data for the H₂O-rich and cycloalkane-rich liquid phase at orthobaric conditions of three-phase equilibria using the experimental data for binary systems [61]. More specifically, the unlike interactions between the cCH and H₂O groups and between the cCH₂ and H₂O groups are obtained by considering the mutual solubility of cyclohexane, cyclopentane, ethylcyclohexane and methylcyclohexane in water. The interaction parameters estimated in this fashion are reported in Table 3.

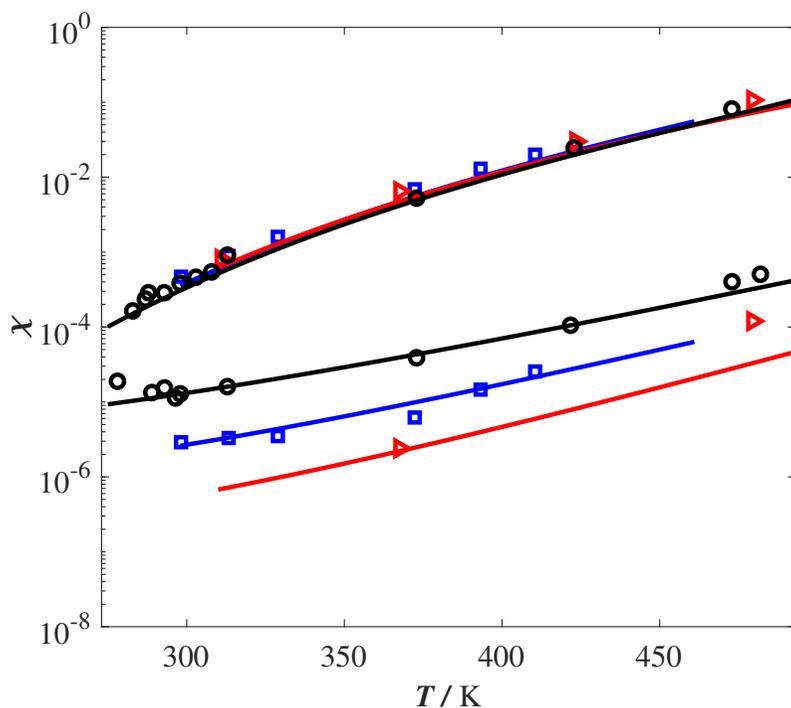


FIGURE 4 Mutual solubilities (mol fraction) of water in the cycloalkane-rich liquid phase (top) and cycloalkanes in the water-rich liquid phase (bottom) for cyclohexane (black circles), methylcyclohexane (blue squares), ethylcyclohexane (red circles). The symbols correspond to experimental data at conditions of three-phase equilibria [61], and the continuous curves to the calculations with the SAFT- γ Mie group-contribution approach.

The values for the unlike interaction parameters between the CH_3 and H_2O groups and between the CH_2 and H_2O groups are taken from Reference [40] as these are able to accurately predict the solubility of n -alkanes in the water-rich phase. The fluid-phase equilibria of methylcyclohexane and ethylcyclohexane along the orthobaric three-phase coexistence (vapor-liquid-liquid equilibria) calculated with the SAFT- γ Mie group-contribution approach is shown in Figure 4. As can be seen the model developed here can be used to accurately describe the solubilities of cycloalkanes over a wide temperature range.

4.4 | Aqueous solutions of secondary cyclic amines: cNH – H_2O interaction

As the cNH group incorporates one association site of type H and one site of type e, the parameters describing energy and bonding volume association between these associating sites and those of type e and H present on the H_2O group have to be specified, in addition to the unlike dispersion energy. To determine these unlike interaction parameters isothermal vapour-liquid equilibrium data for aqueous solutions of piperazine are used. The resulting optimised parameters are presented in tables 3 and 4 and isothermal pressure-composition vapour-liquid equilibrium phase boundaries of this system at three temperatures calculated with the SAFT- γ Mie group-contribution approach, compared to experimental data are shown in Figure 5 (a).

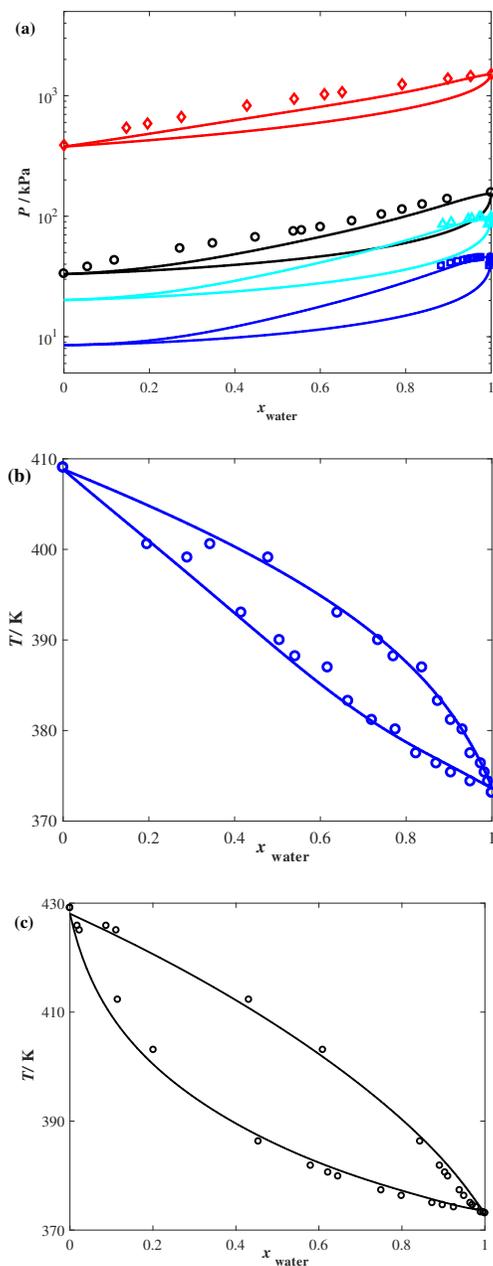


FIGURE 5 Vapour-liquid equilibria of aqueous solutions of: (a) piperazine (PZ) at $T=471.15$ K (red diamonds [62]), $T=386.15$ K (black circles [62]), $T=373.15$ K (cyan triangles [62]), and $T=353.15$ K (blue squares [62]); (b) N-methylpiperazine (MPZ) at a pressure of $P= 101.325$ kPa (blue circles [63]); (c) N-ethylpiperazine (EPZ) at a pressure of $P= 101.325$ kPa (black circles[64]). The continuous curves represent the calculations with the SAFT- γ Mie group-contribution approach.

4.5 | Aqueous solutions of tertiary cyclic amines: cN – H₂O interactions

An important feature of the molecular interactions in aqueous solution of ternary cyclic amines involves the interaction between the cyclic group cN and the polar water molecules. The presence of donor electron lone pairs on the tertiary amine group and the acceptor hydrogen atoms on water allows for the formation of strong hydrogen bonds. These molecular interactions can be accurately described by means of the association sites present in the cN and H₂O groups. One site of type e corresponding to the electron lone pair on the nitrogen atom used in the cN group, which can bond with the two associating sites of type H corresponding to the hydrogen atoms of the water molecule.

In order to completely describe the interactions between the cN and H₂O groups, we find that the repulsive exponent of the unlike segment-segment interaction, λ_{cN,H_2O}^r , as well as the unlike dispersion energy, ε_{cN,H_2O} , the unlike association energy between sites, $\varepsilon_{cN,H_2O,e,H}^{HB}$, and the unlike bonding volume, $K_{cN,H_2O,e,H}$ need to be determined by comparison to experimental mixture data. The parameter estimation for these unlike interactions is carried out using experimental data for the isobaric VLE of the N-methylpiperazine (MPZ) + water [63] and N-ethylpiperazine (EPZ) + water [64] binary mixtures at $P = 0.1$ MPa. The optimised values of the set of parameters describing the interactions between the cN and H₂O groups are presented in Tables 3 and 4. The description of the isobaric VLE for MPZ + water with our group-contribution approach can be seen in Figure 5 (b) and the corresponding results for the isobaric temperature-composition slices of the VLE for aqueous mixtures of EPZ are presented in Figure 5 (c). As can be seen the description obtained using SAFT- γ Mie accurately represents the experimental data.

It is important to point out that the results presented in Figure 5 are obtained using the parameters between the cN and H₂O groups optimised using the data presented in the figures as well as transferring the parameters corresponding to the unlike interactions between the H₂O and CH₂ groups, and between the H₂O and CH₃ groups [40] developed in previous works for aqueous solutions of n-alkanes. Transferability of group interaction parameters is one of the main features and a great advantage of the implementation of a group-contribution approach.

4.6 | Aqueous solutions of alkylamines : NH – H₂O, NH₂ – H₂O, and N – H₂O interactions

The unlike association interactions between water and alkylamine groups (NH and NH₂) are assumed to be asymmetric ($\varepsilon_{k,l,H,e}^{HB} \neq \varepsilon_{k,l,e,H}^{HB}$) and therefore a certain number of parameters have to be specified to represent the respective solution depending on which type of amine is being considered. Primary and secondary alkylamines comprise the groups NH₂ and NH respectively (group *l*), featuring associating sites of both types e and H. (In modelling NH₂ two sites of type H and one site of type e are used, whereas in NH one site of type H and one site of type e are included.) As a result a total of six parameters have to be specified to represent their interaction with water, namely, the unlike dispersion energy ($\varepsilon_{H_2O,l}$), the unlike repulsive exponent of inter-segment interaction ($\lambda_{H_2O,l}^r$), the unlike energy and bonding volume of association between sites of type H of water and e of the amine group, l ($\varepsilon_{H_2O,l,H,e}^{HB}$ and $K_{H_2O,l,H,e}$) and the energy and bonding volume association between sites of type e of water and H of primary or secondary amine group l ($\varepsilon_{H_2O,l,e,H}^{HB}$ and $K_{H_2O,l,e,H}$). In the case of tertiary alkylamines four adjustable parameters have to be specified to represent their aqueous solutions as the tertiary amine group N features only with one electron lone pair association site of type e.

These parameters are estimated using experimental data relating to binary aqueous mixtures of alkylamines, specifically VLE data for aqueous mixtures of ethylamine, *n*-propylamine, and *n*-butylamine are used for the unlike interactions

$\text{NH}_2\text{-H}_2\text{O}$ [65, 66]; data of aqueous solutions of diethylamine, and dipropylamine [67, 68, 69] for the unlike interactions $\text{NH-H}_2\text{O}$; and data of solutions of methyl diethylamine, and triethylamine [68, 70] for the unlike interactions $\text{N-H}_2\text{O}$. The interaction parameters determined in this way for the alkylamine chemical groups are reported in Tables 2 and 3 and a comparison of the SAFT- γ Mie description with the experimental VLE data of some of the primary *n*-alkylamines used in the parameter estimation procedure is shown in Figure 6. The adequacy of the approach for compounds of both low and high molecular weight can be gleaned from the figure.

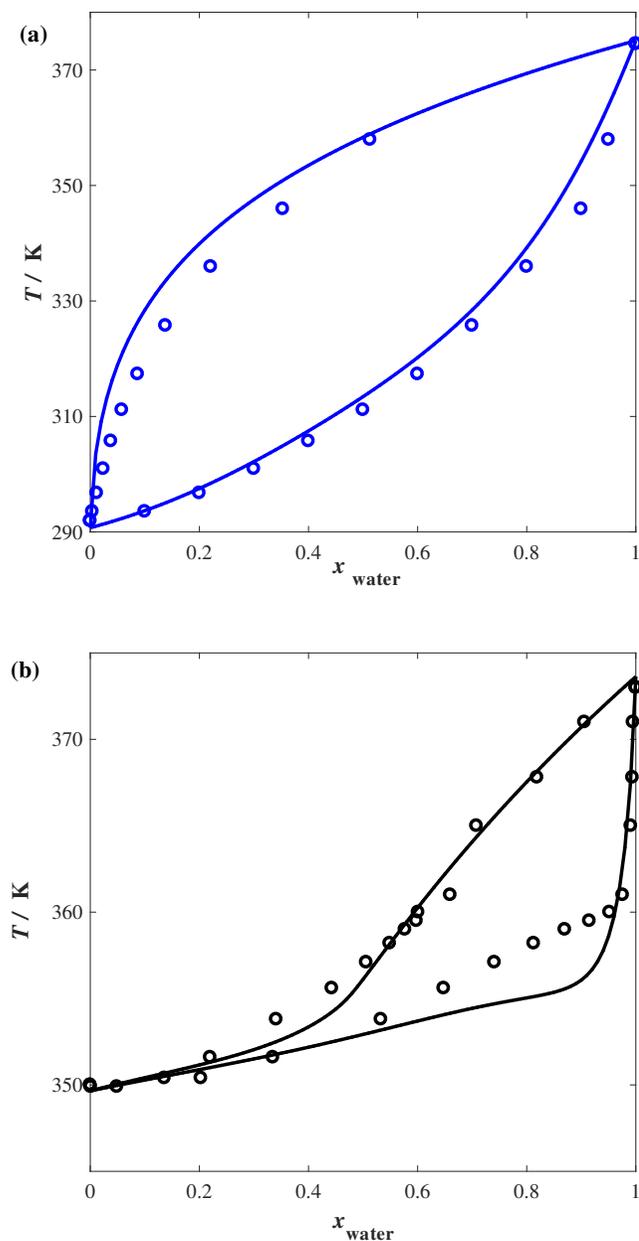


FIGURE 6 Isobaric temperature-composition (T - x) slices of the vapour-liquid equilibria of aqueous solutions of alkyl amines at $P = 101.325$ kPa: (a) ethylamine + water (blue circles[65]); (b) n -butylamine + water (black circles [66]). The symbols represent the experimental data and the continuous curves the calculations with the SAFT- γ Mie group-contribution approach.

4.7 | Aqueous mixtures of cyclohexyl amines: cCHNH – H₂O and cCHN – H₂O interactions

A key feature of the fluid-phase behaviour of aqueous solutions of cyclic amines is their low solubility in water [18]. Several aqueous solutions of alkylcyclohexylamines were measured by Stephenson, and MCA, DMCA, and ECA were found to exhibit LCSTs in the range between 0 and 90° C. In this section, we use these experimental LLE data in order to estimate the interactions between cCHNH and cCHNH groups developed in previous sections and the H₂O group. Specifically unlike interactions between the cCHNH group and H₂O are estimated using LLE data for aqueous mixtures of MCA and of ECA, and the unlike interactions between the cCHN group and H₂O are estimated using the LLE data for mixtures of DMCA. The corresponding interaction parameters are included in Tables 3 and 4 and the fluid-phase equilibria (VLE and LLE) for the mixtures ECA + H₂O and DMCA + H₂O are shown in Figure 7. As can be seen from the figure the theoretical description is in good agreement with the experimental measurements of Stephenson [18]; it is very encouraging to see that the SAFT- γ Mie group-contribution approach provides an accurate representation of the LCST behaviour, which is typically very challenging to describe.

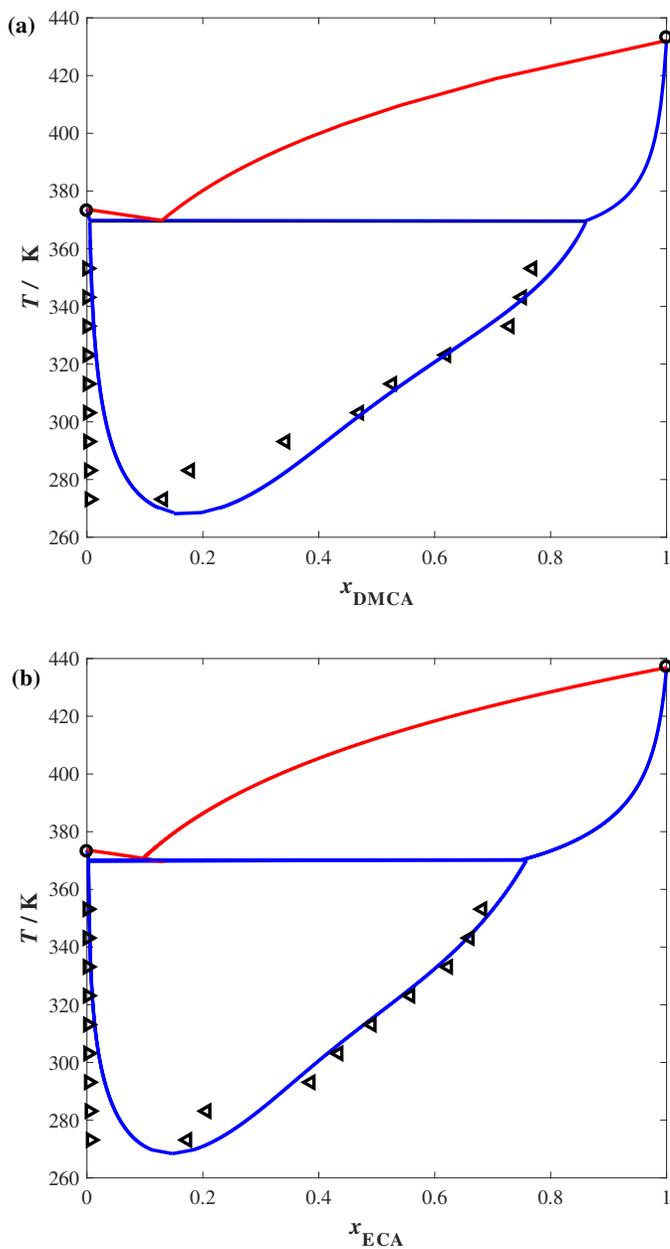


FIGURE 7 Isobaric temperature-composition (T - x) slices of the vapour-liquid-liquid equilibria of aqueous solutions of alkyl cyclohexylamines at $P=101.325$ kPa: (a) N,N-dimethylcyclohexylamine (DMCA) + water (black triangles[18], black circles [55]); (b) N-ethylcyclohexyl (ECA) + water (black triangles[18], black circles [55]). The symbols represent the experimental data and the continuous lines the calculations with the SAFT- γ Mie group-contribution approach.

At this point we highlight the predictive capability of the SAFT- γ Mie group-contribution approach in describing the complex fluid-phase behaviour of aqueous solutions of amines. This is demonstrated from the results presented in Figure 8. The binary mixtures methylpiperidine (MPD) + water and trimethylamine (TMA) + water are challenging case studies as both systems exhibit complex regions of liquid-liquid immiscibility. In the case of aqueous solutions of MPD, the mixture is seen to exhibit phase separation into two liquid phases bounded by an LCST at $T = 41.85^\circ\text{C}$ (at 0.101 MPa pressure). The mixture TMA + water also presents a liquid-liquid demixing, with a trend of increasing solubility of the two components for the lower temperatures; an LCST has however not been reported from experiment.

Although these types of systems are notoriously difficult to treat, the liquid-liquid coexistence predicted with the SAFT- γ Mie group-contribution approach, offers a very reliable description of the phase behaviour, as exemplified by the results presented in Figure 8. Indeed for both types of amines presented (cyclic and branched alkylamines), although the experimental data used in the parameter estimation corresponded only to VLE (cf. Figures 5 and 6), the model is able to describe the complex LLE phase equilibria using the same set of parameters. We can therefore conclude that the SAFT- γ Mie group-contribution approach provides a predictive platform for the fluid-phase behaviour (including both VLE and LLE) for aqueous solutions of amines with broadly varying chemistries, over wide ranges of pressures and temperatures.

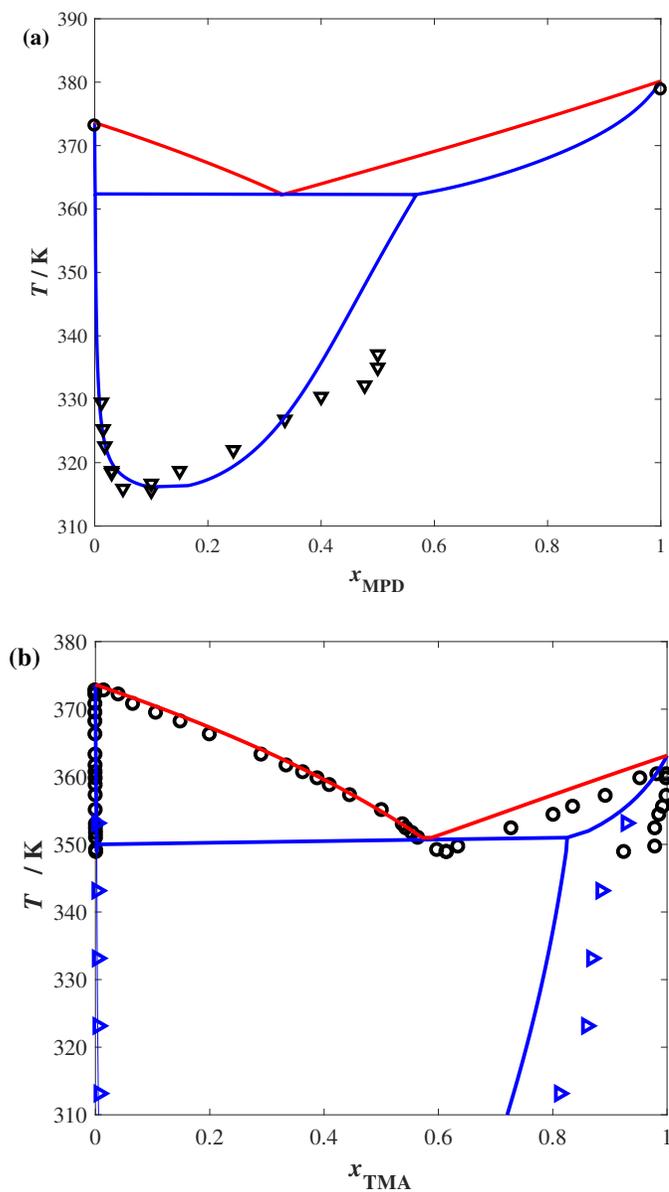


FIGURE 8 (a) Isobaric temperature-composition (T - x) slices of the fluid-phase equilibria at $P=0.101$ MPa of (a) N-methylpiperidine (MPD) + water (blue circles [19], black circles [55]) and (b) trimethylamine (TMA) + water (black circles correspond to experimental data for VLE and the blue triangles for LLE [18]). In both figures the continuous curves represent predictions with the SAFT- γ Mie group-contribution approach.

5 | CONCLUSIONS

We have employed the SAFT- γ Mie group-contribution approach to describe the fluid-phase equilibria of aqueous solutions of amines which feature a complex balance of molecular interactions between both species and have extended the matrix of group interactions to include groups relevant to these systems. The methodology can be applied to predict accurately the thermodynamic properties of a variety of pure amines (including alkyl, cyclic, cyclohexyl amines) as well as the vapour-liquid, liquid-liquid, and vapour-liquid-liquid equilibria of mixtures of the amines and water using a selected set of functional groups that enable one to take into account the hydrogen-bonding interactions and the influence of the surrounded alkyl substituents which can modify the ability of the nitrogen atom to hydrogen bond. The reliability and transferability of the modelling is demonstrated by the prediction of regions of liquid-liquid immiscibility bounded by lower critical solution temperatures for different type of amines solutions, using the same set of group interaction parameters estimated from experimental data of pure amines and some representative binary systems. The findings presented here validate this approach as a tool to describe and understand the complex fluid-phase behaviour of amine systems which have a broad of application in the chemical, pharmaceutical, and biotechnology industries.

REFERENCES

- [1] Lawrence SA. Amines: synthesis, properties and applications. Cambridge University Press; 2004.
- [2] Jesus AL, Redinha J. Molecular insight into the amine-water interaction: A combined vibrational, energetic and NBO/NEDA study. *Computational and Theoretical Chemistry* 2013;1023:74–82.
- [3] Idrissi A, Jedlovsky P. Thermodynamics of Mixing Primary Alkanolamines with Water. *The Journal of Physical Chemistry B* 2018;122:6251–6259.
- [4] Smith EL, Page J. The acid-binding properties of long-chain aliphatic amines. *Journal of the Society of Chemical Industry* 1948;67:48–51.
- [5] Schnell S, Bak F, Pfennig N. Anaerobic degradation of aniline and dihydroxybenzenes by newly isolated sulfate-reducing bacteria and description of *Desulfobacterium anilini*. *Archives of microbiology* 1989;152:556–563.
- [6] Essington ME. Adsorption of aniline and toluidines on montmorillonite. *Soil science* 1994;158:181–188.
- [7] Eyal AM, Bressler E, Bloch R, Hazan B. Extraction of metal salts by mixtures of water-immiscible amines and organic acids (acid-base couple extractants). 1. A review of distribution and spectroscopic data and of proposed extraction mechanisms. *Industrial & engineering chemistry research* 1994;33:1067–1075.
- [8] Eyal AM, Kogan L, Bressler E. Extraction of metal salts by mixtures of water-immiscible amines and organic acids (acid-base couple extractants). 2. Theoretical treatment and analysis. *Industrial & engineering chemistry research* 1994;33:1076–1085.
- [9] Tamada JA, King CJ. Extraction of carboxylic acids with amine extractants. 2. Chemical interactions and interpretation of data. *Industrial & engineering chemistry research* 1990;29:1327–1333.
- [10] Hong YK, Hong WH. Equilibrium studies on reactive extraction of succinic acid from aqueous solutions with tertiary amines. *Bioprocess Engineering* 2000;22:477–481.
- [11] Roundhill DM. Transition metal and enzyme catalyzed reactions involving reactions with ammonia and amines. *Chemical reviews* 1992;92:1–27.
- [12] Brenecker KD, Natonski J, Eachus A. The role of primary alkanolamines in cosmetic formulation. *International journal of cosmetic science* 1991;13:235–247.

- [13] Fang L, Numajiri S, Kobayashi D, Morimoto Y. The use of complexation with alkanolamines to facilitate skin permeation of mefenamic acid. *International journal of pharmaceutics* 2003;262:13–22.
- [14] Zhang J, Misch R, Tan Y, Agar DW. Novel Thermomorphic Biphasic Amine Solvents for CO₂ Absorption and Low-Temperature Extractive Regeneration. *Chemical engineering & technology* 2011;34:1481–1489.
- [15] Dugas RE, Rochelle GT. CO₂ absorption rate into concentrated aqueous monoethanolamine and piperazine. *Journal of Chemical & Engineering Data* 2011;56:2187–2195.
- [16] Zhong J, Wang P, Zhang Y, Yan Y, Hu S, Zhang J. Adsorption mechanism of oil components on water-wet mineral surface: A molecular dynamics simulation study. *Energy* 2013;59:295–300.
- [17] Asinari P, Chiavazzo E. The notion of energy through multiple scales: From a molecular level to fluid flows and beyond. *Energy* 2014;68:870–876.
- [18] Stephenson RM. Mutual solubility of water and aliphatic amines. *Journal of Chemical & Engineering Data* 1993;38:625–629.
- [19] Coulier Y, Ballerat-Busserolles K, Rodier L, Coxam JY. Temperatures of liquid–liquid separation and excess molar volumes of {N-methylpiperidine–water} and {2-methylpiperidine–water} systems. *Fluid Phase Equilibria* 2010;296:206–212.
- [20] Hartono A, Saeed M, Ciftja AF, Svendsen HF. Binary and ternary VLE of the 2-amino-2-methyl-1-propanol (AMP)/piperazine (Pz)/water system. *Chemical Engineering Science* 2013;91:151–161.
- [21] Li H, Le Moullec Y, Lu J, Chen J, Marcos JCV, Chen G, et al. CO₂ solubility measurement and thermodynamic modeling for 1-methylpiperazine/water/CO₂. *Fluid Phase Equilibria* 2015;394:118–128.
- [22] Börjesson U, Hünenberger PH. Explicit-solvent molecular dynamics simulation at constant p H: Methodology and application to small amines. *The Journal of chemical physics* 2001;114:9706–9719.
- [23] Chapman WG, Jackson G, Gubbins KE. Phase equilibria of associating fluids: chain molecules with multiple bonding sites. *Molecular Physics* 1988;65:1057–1079.
- [24] Jackson G, Chapman WG, Gubbins KE. Phase equilibria of associating fluids: Spherical molecules with multiple bonding sites. *Molecular Physics* 1988;65:1–31.
- [25] Chapman WG, Gubbins KE, Jackson G, Radosz M. SAFT: Equation-of-state solution model for associating fluids. *Fluid Phase Equilibria* 1989;52:31–38.
- [26] Gil-Villegas A, Galindo A, Whitehead PJ, Mills SJ, Jackson G, Burgess AN. Statistical associating fluid theory for chain molecules with attractive potentials of variable range. *The Journal of Chemical Physics* 1997;106:4168–4186.
- [27] Galindo A, Davies L, Gil-Villegas A, Jackson G. The thermodynamics of mixtures and the corresponding mixing rules in the SAFT-VR approach for potentials of variable range. *Molecular Physics* 1998;93:241–252.
- [28] Mac Dowell N, Pereira F, Llovel F, Blas F, Adjiman C, Jackson G, et al. Transferable SAFT-VR models for the calculation of the fluid phase equilibria in reactive mixtures of carbon dioxide, water, and n-alkylamines in the context of carbon capture. *The Journal of Physical Chemistry B* 2011;115:8155–8168.
- [29] Rodriguez J, Mac Dowell N, Llovel F, Adjiman C, Jackson G, Galindo A. Modelling the fluid phase behaviour of aqueous mixtures of multifunctional alkanolamines and carbon dioxide using transferable parameters with the SAFT-VR approach. *Molecular Physics* 2012;110:1325–1348.
- [30] Chremos A, Forte E, Papaioannou V, Galindo A, Jackson G, Adjiman CS. Modelling the phase and chemical equilibria of aqueous solutions of alkanolamines and carbon dioxide using the SAFT- γ SW group contribution approach. *Fluid Phase Equilibria* 2016;407:280–297.

- [31] Lymperiadis A, Adjiman CS, Galindo A, Jackson G. A group contribution method for associating chain molecules based on the statistical associating fluid theory (SAFT- γ). *The Journal of chemical physics* 2007;127:234903.
- [32] Lymperiadis A, Adjiman CS, Jackson G, Galindo A. A generalisation of the SAFT- γ group contribution method for groups comprising multiple spherical segments. *Fluid Phase Equilibria* 2008;274:85–104.
- [33] Papaioannou V, Lafitte T, Avendano C, Adjiman CS, Jackson G, Müller EA, et al. Group contribution methodology based on the statistical associating fluid theory for heteronuclear molecules formed from Mie segments. *The Journal of chemical physics* 2014;140:054107.
- [34] Dufal S, Lafitte T, Haslam AJ, Galindo A, Clark GNI, Vega C, et al. The A in SAFT: developing the contribution of association to the Helmholtz free energy within a Wertheim TPT1 treatment of generic Mie fluids. *Molecular Physics* 2015;113:948–984.
- [35] Jackson G, Dufal S, Lafitte T, Haslam A, Galindo A, Clark G, et al. Corrigendum: The A in SAFT: developing the contribution of association to the Helmholtz free energy within a Wertheim TPT1 treatment of generic Mie fluids. *Molecular Physics* 2018;116:283–285.
- [36] Dufal S, Papaioannou V, Sadeqzadeh M, Pogiatzis T, Chremos A, Adjiman CS, et al. Prediction of thermodynamic properties and phase behavior of fluids and mixtures with the SAFT- γ Mie group-contribution equation of state. *Journal of Chemical & Engineering Data* 2014;59:3272–3288.
- [37] Rowlinson JS, Swinton F. *Liquids and Liquid Mixtures*. Butterworths: London; 1982.
- [38] Haslam AJ, Galindo A, Jackson G. Prediction of binary intermolecular potential parameters for use in modelling fluid mixtures. *Fluid Phase Equilibria* 2008;266:105–128.
- [39] gPROMS v. 3.4.0; PSE Ltd.: London, 2011;. <http://www.psenterprise.com>.
- [40] Hutcharoen P, Dufal S, Papaioannou V, Shanker RM, Adjiman CS, Jackson G, et al. Predicting the Solvation of Organic Compounds in Aqueous Environments: From Alkanes and Alcohols to Pharmaceuticals. *Industrial & Engineering Chemistry Research* 2017;56:10856–10876.
- [41] Steele WV, Chirico RD, Knipmeyer SE, Nguyen A, Smith NK. Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Dicyclohexyl Sulfide, Diethylenetriamine, Di-n-octyl Sulfide, Dimethyl Carbonate, Piperazine, Hexachloroprop-1-ene, Tetrakis(dimethylamino)ethylene, N,N'-Bis-(2-hydroxyethyl)ethylenediamine, and 1,2,4-Triazolo[1,5-a]pyrimidine. *Journal of Chemical & Engineering Data* 1997;42:1037–1052.
- [42] Wu HS, Locke III WE, Sandler SI. Isothermal vapor-liquid equilibrium of binary mixtures containing pyrrolidine. *Journal of Chemical & Engineering Data* 1990;35:169–172.
- [43] Osborn AG, Douslin DR. Vapor pressure relations of 13 nitrogen compounds related to petroleum. *Journal of chemical & Engineering Data* 1968;13:534–537.
- [44] Gu F. Study of vapor-liquid equilibrium on piperazine - N-ethylpiperazine and water - N-ethylpiperazine binary system. *Journal of Chemical Engineering of Chinese Universities* 2000;14:281–284.
- [45] Verevkin SP. Thermochemistry of Amines: Experimental Standard Molar Enthalpies of Formation of N-Alkylated Piperidines. *Structural Chemistry* 1998;9:113–119.
- [46] Chen S, Fang W, Yao J, Zong H. Density and Refractive Index at 298.15 K and VaporLiquid Equilibria at 101.3 kPa for Binary Mixtures of Ethanol + N-Methylpiperazine. *Journal of Chemical & Engineering Data* 2001;46:596–600.
- [47] Mokbel I, Rauzy E, Loiseleur H, Berro C, Jose J. Vapor pressures of 12 alkylcyclohexanes, cyclopentane, butylcyclopentane and trans-decahydronaphthalene down to 0.5 Pa. Experimental results, correlation and prediction by an equation of state. *Fluid Phase Equilibria* 1995;108:103 – 120.

- [48] Papaioannou V, Calado F, Lafitte T, Dufal S, Sadeqzadeh M, Jackson G, et al. Application of the SAFT- Mie group contribution equation of state to fluids of relevance to the oil and gas industry. *Fluid Phase Equilibria* 2016;416:104 – 119.
- [49] Berthoud A. Determinations of Critical Temperatures and Pressures of Amines and Alkyl Chlorides 1917;15:3–29.
- [50] Wolff H, Shadiakhy A. The vapour-pressure behaviour and the association of isomeric propylamines and n-deuteriopropylamines in mixtures with n-hexane. *Fluid Phase Equilibria* 1983;11:267–287.
- [51] Daubert JWW, Thomas E, Goren V. Vapor pressure of 22 pure industrial chemicals. *AIChE Symp* 1987;83:128–156.
- [52] Antosik M, Gałka M, Malanowski SK. VaporLiquid Equilibrium for Acetonitrile + Propanenitrile and 1-Pentanamine + 1-Methoxy-2-propanol. *Journal of Chemical & Engineering Data* 2004;49:11–17.
- [53] Ralston A, Selby W, Pool W, Potts R. Boiling Points of n-Alkyl Primary Amines. *Industrial & Engineering Chemistry* 1940;32:1093–1094.
- [54] Steele WV, Chirico RD, Knipmeyer SE, Nguyen A, Smith NK, Tasker IR. Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Cyclohexene, Phthalan (2,5-Dihydrobenzo-3,4-furan), Isoxazole, Octylamine, Dioctylamine, Trioctylamine, Phenyl Isocyanate, and 1,4,5,6-Tetrahydropyrimidine. *Journal of Chemical & Engineering Data* 1996;41:1269–1284.
- [55] Linstrom P. NIST Standard Reference Database Number 69. NIST Standard Reference Simulation Website 2003;69.
- [56] Navia P, Bessières D, Plantier F. Heat capacity of 1-pentylamine and 1-hexylamine: Experimental determination and modeling through a two-state association model (TSAM). *The Journal of Chemical Thermodynamics* 2013;57:367 – 371.
- [57] Bayles JW, Letcher TM. Thermodynamics of some binary liquid mixtures containing aliphatic amines. *Journal of Chemical & Engineering Data* 1971;16:266–271.
- [58] Humphrey JL, Van Winkle M. Vapor-liquid equilibrium at 60 ° C. for n-hexane-alkyl amines and 1-hexene-alkyl amines. *Journal of Chemical & Engineering Data* 1967;12:526–531.
- [59] Verevkin SP, Emelyanenko VN. Thermodynamic properties of cyclohexanamines: Experimental and theoretical study. *Thermochemica Acta* 2015;608:40 – 48.
- [60] Hutcharoen P, Dufal S, Papaioannou V, Shanker RM, Adjiman CS, Jackson G, et al. Predicting the Solvation of Organic Compounds in Aqueous Environments: From Alkanes and Alcohols to Pharmaceuticals. *Industrial & Engineering Chemistry Research* 2017;56:10856–10876.
- [61] Maczyński A, Wiśniewska-Gocłowska B, Góral M. Recommended Liquid–Liquid Equilibrium Data. Part 1. Binary Alkane–Water Systems. *Journal of Physical and Chemical Reference Data* 2004;33:549–577.
- [62] Wilson HL, Wilding WV. Vapor liquid and liquid-liquid equilibrium measurements on twenty two binary mixtures. Experimental results for DIPPR 1990;91:63–115.
- [63] Chen S, Fang W, Yao J, Zong H. Density and Refractive Index at 298.15 K and VaporLiquid Equilibria at 101.3 kPa for Binary Mixtures of Ethanol + N-Methylpiperazine. *Journal of Chemical & Engineering Data* 2001;46:596–600.
- [64] Gu F, Fang W. Density and Refractive Index at 298.15 K and VaporLiquid Equilibria at 101.3 kPa for Binary Mixtures of Water + N-Ethylpiperazine. *Journal of Chemical & Engineering Data* 2000;45:288–291.
- [65] Bittrich HJ. Isobaric vapour–liquid equilibrium measurements on the system monoethylamine–water, *Wiss. Z Tech Hochsch Chem Leuna-Merseburg* 1963;5:21–24.
- [66] Komarov VM, Krichevstov BK. Liquid–vapour equilibria in binary systems of n-butylamines with water. II. *J Appl Chem USSR* 1966;39:2655–2658.

-
- [67] Davison R. Vapor-liquid equilibriums of water-diisopropylamine and water-di-n-propylamine. *Journal of Chemical & Engineering Data* 1968;13:348-351.
- [68] Copp J. Thermodynamics of binary systems containing amines. Part 2. *Transactions of the Faraday Society* 1955;51:1056-1061.
- [69] Frangieh M, Bougrine A, Tenu R, Dhenain A, Counioux J, Goutaudier C. Evolution of the liquid-vapor equilibrium properties of several unsymmetrical amines: determination of their binary isobaric diagrams and applications to the distillation. *Journal of Chemical & Engineering Data* 2013;58:576-582.
- [70] Chun K, Clinkscates T, Davison R. Vapor-liquid equilibrium of triethylamine-water and methyldiethylamine-water. *Journal of Chemical & Engineering Data* 1971;16:443-446.