Description of the thermodynamic properties and fluid-phase behavior of aqueous solutions of linear, branched, and cyclic amines

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Abstract
The SAFT-\(\gamma\) Mie group-contribution equation of state is used to represent the fluid-phase behavior 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 (NH\(_2\), NH, N), cyclic secondary and tertiary amine groups (cNH, cN), and cyclic methine-amine groups (cCHNH, cCHN) with water (H\(_2\)O). 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 behavior of mixtures of molecules comprising those groups over broad ranges of temperature, pressure, and composition. A number 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 are reproduced here with the SAFT-\(\gamma\) 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 vapor–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 behavior.

KEYWORDS
associating fluids, equations of state, fluid-phase equilibria, perturbation theories, statistical thermodynamics

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, that only contain hydrogen or alkyl (branched or cyclic) substituents, and cyclic amines where the nitrogen atom is bonded to or included in the 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 markedly affected by the presence of hydrogen bonds donors on the NH₂ 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 are subject to 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 the 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 applications such as in dyes, pesticides, varnishes, ion-exchange resins, surfactants, and perfumes.⁴⁻⁶ 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 cosmetics¹² 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 sulfide (H₂S) and carbon dioxide (CO₂), and a wide variety of aliphatic amines have been used as gas sweeteners and CO₂ 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 to 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 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 thermodynamic behavior of many 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 complex molecular detail that needs to be accounted for. In spite of the paucity of studies on modeling the phase behavior of aqueous solutions of amines, an important example worthy of mention is the work of Hartono et al.²⁰ who modeled the vapor–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 allows for the prediction of the VLE of aqueous solutions of AMP and PZ. These models provide a good description of the binary VLE data and the interaction parameters were then used to predict the phase behavior of the ternary system AMP + PZ + H₂O. The UNIQUAC approach was seen to provide the best representation of the experimental data. The electrolyte non-random two-liquid (enRTL) 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 eNRTL parameters from VLE and excess enthalpy data for N-methylpiperazine (MPZ) + H₂O system, allowing for a good representation of the fluid-phase behavior though the average relative deviation of the mole fraction of MPZ in the vapor phase is found to be higher than 10%.

Even though these approaches have been shown to give a good representation of the VLE of aqueous solutions of amines, the activity-coefficient models are not suited to deal with the effect of pressure, are restricted to a limited domain of thermodynamic conditions, 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 system such as the presence of an LCST.

In order to provide a good understanding of the link between the macroscopic behavior of aqueous solutions of amines and the specific molecular interactions relevant in these mixtures, approaches such as molecular-simulation methods²²,²³ or molecular-based equations of state (EOSs) are better suited to the task. In these approaches, one can account for highly polarizable functional groups to consider the physical interactions (such as hydrogen bonding), that markedly influence 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),²₄,²₅ can be used to provide a versatile platform for the accurate description of the phase behavior of aqueous solutions of amines. The SAFT family of EOSs is well known for its suitability to model complex mixtures of associating fluids and has been used in a number of studies to describe the fluid-phase behavior 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 allowing for a description of the LLE seen in aqueous solutions of n-hexylamine. The amines were modeled 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 behavior of aqueous mixtures of multifunctional alkanolamines.²₉ and
later similar systems were studied with a reformulation of SAFT as a group-contribution (GC) approach. In this case, the SAFT-γ SW group-contribution approach was used to describe the interactions between the various functional groups characterizing 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 low molecular-weight alkanolamines. In the same fashion, the group-contribution SAFT-VR EOS (GC-SAFT-VR) which is based on an underlying square-well potential has been applied to study the phase behavior of primary and secondary amines and their mixtures with alcohols and hydrocarbons. A group-contribution version of the polar PC-SAFT, namely the GC-PPC-SAFT approach, has been applied to represent thermodynamic properties of primary, secondary, and tertiary amines, and their mixtures with n-alkanes, primary, and secondary alcohols.

In our current article, we implement the SAFT-γ Mie group-contribution 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 modeled 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 unsaturated bonds, the molecular volume, and the shape of the variety of functional groups present in these 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 of, and reliability in, the experimental data; 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 behavior 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 small and large molecular structures, which feature strong intermolecular interactions that give rise to complex hydrogen-bonded aggregates. Several of the molecules considered and their SAFT-γ Mie representation are shown in Figure 1.

In the SAFT-γ Mie approach, 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 $\nu_k$ identical segments). Segments $k$ and $l$ are assumed to interact through a Mie potential of variable attractive and repulsive ranges,

$$
\phi_{\text{Mie}} = C_{\text{Mie}} \left[ \frac{\sigma_{kl}}{r_{kl}^{\nu_k \nu_l}} \right],
$$

where $r_{kl}$ represents the distance between the centers of the segments, $\sigma_{kl}$ is the segment diameter, $-\sigma_{kl}$ is the minimum in the potential energy of interaction between segments, and $\lambda_{kl}$ and $\lambda_{lk}$ represent the repulsive and attractive exponents of the inter-segment interactions, respectively. The prefactor $C_{\text{Mie}}$ is a function of these exponents and is defined as
\[
C_{kl} = \frac{\lambda_{kl}}{\lambda_{kl} - \lambda_{kl}^{*}} \left( \frac{\sigma_{kl}^{*}}{\sigma_{kl}} \right)^{\kappa_{kl}}.
\] (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 number \(N_a\) of different site types \(a\), the number \(n_{kl,a}\) of sites of a given type \(a\), the energy \(\varepsilon_{kl,ab}\) and the range (in the form of the bonding volume) \(K_{kl,ab}\) of the association between site \(a\) on group \(k\) and site \(b\) on group \(l\) have to be determined. The bonding-volume parameter \(K_{kl,ab}\) can take a wide range of values for the hydrogen-bonding interactions between the various chemical groups. The site geometry (position from the center of the segment and range) employed to determine the contribution due to association in the SAFT-VR Mie and SAFT-\(\gamma\) Mie approaches was fixed to simplify the development of the theory.\(^{40,41}\) In the current version of the theory this would correspond to a dimensionless bonding-volume parameter of \(K_{kl,ab} = 1\). Deviations from a value of 1 suggest different site geometries to the one used in References 40 and 41, and the bonding-volume parameter can therefore be used empirically to represent different site geometries. 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 nitrogen 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 terms:

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

where \(A^{\text{IDEAL}}\) is the ideal free energy of the mixture, \(A^{\text{MONO}}\) is the contribution to the free energy due to the interaction between the monomer Mie segments, \(A^{\text{CHAIN}}\) is the contribution due to fusing the segments to form chain molecules, and \(A^{\text{ASSOC}}\) is the term describing the contribution to the free energy due to intermolecular hydrogen-bonding association. For a complete description of the theory and the detailed expressions for each of the contributions, we direct the reader to the original SAFT-\(\gamma\) Mie publications.\(^{39-42}\)

### 2.1 Combining rules

In order to fully specify the expressions for the Helmholtz free energy presented in Equation (3) a number of like and unlike group interaction parameters need to be characterized. All of the like parameters are determined by minimization of an objective function including experimental data, while the unlike parameters are initially determined using combining rules (CRs) and then estimated from experimental data when necessary. The unlike segment diameter \(\sigma_{kl}\) is obtained using the Lorentz arithmetic mean of the like diameters\(^{43}:\)

\[
\sigma_{kl} = \frac{\sigma_{kl} + \sigma_{kl}^{*}}{2}.
\] (4)

The unlike dispersion energy \(\varepsilon_{kl}\) is obtained by applying an augmented geometric mean (Berthelot-like rule), which also accounts for asymmetries in size\(^{44}:\)

\[
\varepsilon_{kl} = \sqrt[3]{\frac{\sigma_{kl}^{*} \sigma_{kl}}{\sigma_{kl}^{3}}} \sqrt{\varepsilon_{kl}^{*} \varepsilon_{kl}}.
\] (5)

The exponents of the unlike segment–segment interaction \(\lambda_{kl}\) and \(\lambda_{kl}^{*}\) are obtained as

\[
\lambda_{kl} = 3 + \sqrt{(\lambda_{kl} - 3)(\lambda_{kl}^{*} - 3)},
\] (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 \(\lambda_{kl}^{*}\). The bonding volume \(K_{kl,ab}^{HB}\) and association energy parameter \(e_{kl}^{HB}\) between unlike sites can also be approximated following arithmetic and geometric averages as

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

and

\[
e_{kl}^{HB} = \left( e_{kl,ab}^{HB,aa} + e_{kl,ab}^{HB,bb} \right)^{\frac{1}{2}}.
\] (8)

These combining rules provide a 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 and association 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 include the vapor 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 fluid-phase equilibria and excess enthalpy 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 characterized the cyclic methine cCH and methylene cCH\(_2\) groups by considering pure-component data for cyclic hydrocarbons, the parameters of these groups are transferred to model other chemical families such as cyclic...
amines, allowing for the estimation of the set of parameters for the amines groups.

The objective function used in the parameter estimation procedure is

\[
\min_{\Theta} f_{\text{obj}} = \frac{1}{N_{\exp}} \sum_{s=1}^{N} \sum_{p=1}^{N_p} \sum_{i=1}^{N_{s,p}} W_{s,p,i} \left( \frac{X_{s,p,i}^{\exp} - X_{s,p,i}^{\text{calc}}(\Theta)}{X_{s,p,i}^{\exp}} \right)^2 \tag{9}
\]

where \( \Theta \) is the vector of model parameters, \( N_{\exp} \) is the total number of experimental points considered in the parameter estimation, \( N^s \) is the number of systems (pure compounds/mixtures) used in the estimation, \( N^p_s \) is the number of property types for system \( s \), \( N^p_i \) is the number of experimental data for system \( s \) and property \( p \), \( W_{s,p,i} \) is a weight that controls the relative importance of data point \( i \) for property \( p \) of system \( s \). We consider here the same weight for each point (i.e., \( w_{s,p,i} = 1 \) for all points), \( X_{s,p,i}^{\exp} \) is the \( i \)th measured value of property \( p \) of system \( s \), and \( X_{s,p,i}^{\text{calc}}(\Theta) \) is the corresponding value calculated with \( \gamma \) Mie and the parameters \( \Theta \). The estimation of the group parameters is carried out using the numerical solvers of the commercial software package gPROMS.45 In order to assess the quality of the description, the percentage absolute average deviation (%AAD) of a property \( p \) for a given system \( s \) is determined as follows:

\[
%\text{AAD}[p] = \frac{1}{N_{s,p}} \sum_{i=1}^{N_{s,p}} \left| \frac{X_{s,p,i}^{\exp} - X_{s,p,i}^{\text{calc}}}{X_{s,p,i}^{\exp}} \right| \times 100 \tag{10}
\]

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 characterized. We start our investigation by focusing on the fluid-phase equilibria of pure cyclic amines in order to obtain the optimal values of the group interaction parameters for the cNH and cN groups, which represent the secondary and tertiary cyclic amine groups, respectively. The NH2, NH, and N groups that represent primary, secondary, and tertiary alkyl amine groups, respectively, are considered next. We then discuss the case of the larger cCHNH and cCHN groups, which are developed to model the secondary and tertiary cyclic methine-amine groups, respectively.

4.1 | Parameter tables

The SAFT-\( \gamma \) Mie groups developed here to model the primary, secondary, and tertiary amines, and their aqueous solutions are summarized in Table 1. The corresponding like and unlike group parameters are presented in Tables 2–4.

4.2 | Pure compounds

As is usual practice in developing SAFT-\( \gamma \) Mie group-interaction models, pure compound vapor-pressure and 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 the current work.

| TABLE 1 | Group-interaction matrix of SAFT-\( \gamma \) Mie 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 42 and 46. The gray shading indicates that the group interactions are derived from the expressions for the combining rules given in Equations (4)–(8) [Color table can be viewed at wileyonlinelibrary.com] |
| --- | --- |
| 1 | cCH2 | 2 | cCH3 | 4 | cNH | 5 | cN | 6 | N | 7 | NH | 8 | NH2 | 9 | cCHNH | 10 | cCHN | 11 | H2O | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
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 contained in Molecules I, II, and III of Figure 1. The cNH group is modeled as an associating group featuring one association site of type H and 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 shown 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,⁴⁷ pyrrolidine,⁴⁸ and piperidine⁴⁹) are used to estimate the parameters of this group and its interactions with other alkyl groups (methyl CH₃ and methylene CH₂) using experimental data for pure cyclic amines.

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, dimethylocyclohexylamine, and N-methylpiperidine (see Molecules I, V, and VII, respectively, in Figure 1) and related compounds belong to this class of amine. Alkyl derivatives of these compounds all feature a substituted chemical cyclic methine group cCH. Here, we estimate the parameters of this group and its interactions with other alkyl groups (methyl CH₃ and methylene CH₂) using experimental data for pure substituted cyclic alkanes,⁵³ namely ethylcyclohexane, ethylcyclopentane, and n-propylcyclopentane; specific details of the number of 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 Figure 2c,d, the parameters obtained in this way for the cCH chemical group interactions (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 and cyclic alkanes, and allows 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.

### TABLE 3

| k   | l   | Group k | Group l | $\epsilon_{kl}$ (K) | $\lambda_{ijkl}$ | Ref. | k   | l   | Group k | Group l | $\epsilon_{kl}$ (K) | $\lambda_{ijkl}$ | Ref. |
|-----|-----|---------|---------|----------------------|-----------------|------|-----|-----|---------|---------|----------------------|-----------------|------|
| 1   | 1   | cCH₂   | cCH₂    | 477.36               | 20.386          | 42   | 4   | 10  | CH₃    | cCHNH  | 406.97               | CR              | †    |
| 1   | 2   | cCH₂   | cCH     | 321.71               | CR              | †    | 4   | 11  | CH₃    | cCHN   | 761.79               | CR              | †    |
| 1   | 3   | cCH₂   | CH₂     | 469.67               | CR              | †    | 4   | 12  | CH₃    | H₂O    | 358.18               | 100.00          | 46   |
| 1   | 4   | cCH₂   | CH₃     | 355.95               | CR              | †    | 5   | 5   | cNH    | cNH    | 631.92               | 19.491          | †    |
| 1   | 5   | cCH₂   | cNH     | 605.45               | CR              | †    | 5   | 6   | cNH    | cN     | 812.26               | CR              | †    |
| 1   | 6   | cCH₂   | cN      | 536.66               | CR              | †    | 5   | 7   | cNH    | N      | CR                  | CR              | †    |
| 1   | 7   | cCH₂   | N       | 650.24               | CR              | †    | 5   | 8   | cNH    | NH     | CR                  | CR              | †    |
| 1   | 8   | cCH₂   | NH      | 549.43               | CR              | †    | 5   | 9   | cNH    | NH₂    | CR                  | CR              | †    |
| 1   | 9   | cCH₂   | NH₂     | 332.15               | CR              | †    | 5   | 10  | cNH    | cCHNH  | CR                  | CR              | †    |
| 1   | 10  | cCH₂   | cCHNH   | 486.88               | CR              | †    | 5   | 11  | cCHN   | cCH    | CR                  | CR              | †    |
| 1   | 11  | cCH₂   | cCHN    | 750.06               | CR              | †    | 5   | 12  | cNH    | H₂O    | 523.83               | 8.4243          | †    |
| 1   | 12  | cCH₂   | H₂O     | 350.99               | 28.000          | †    | 6   | 6   | cN     | cN     | 174.04               | 7.0024          | †    |
| 2   | 2   | cCH    | cCH     | 699.92               | 8.0000          | †    | 6   | 7   | cN     | N      | CR                  | CR              | †    |
| 2   | 3   | cCH    | CH₂     | 522.57               | CR              | †    | 6   | 8   | cN     | NH     | CR                  | CR              | †    |
| 2   | 4   | cCH    | CH₃     | 690.17               | CR              | †    | 6   | 9   | cN     | NH₂    | CR                  | CR              | †    |
| 2   | 5   | cCH    | cNH     | 332.15               | CR              | †    | 6   | 10  | cN     | cCHNH  | CR                  | CR              | †    |
| 2   | 6   | cCH    | cN      | CR                  | CR              | †    | 6   | 11  | cN     | cCHN   | CR                  | CR              | †    |
| 2   | 7   | cCH    | N       | CR                  | CR              | †    | 6   | 12  | cN     | H₂O    | 2,990.0             | 66.109          | †    |
| 2   | 8   | cCH    | NH      | CR                  | CR              | †    | 7   | 7   | N     | N      | 62.971               | 8.8971          | †    |
| 2   | 9   | cCH    | NH₂     | CR                  | CR              | †    | 7   | 8   | N     | NH     | CR                  | CR              | †    |
| 2   | 10  | cCH    | cCHNH   | CR                  | CR              | †    | 7   | 9   | N     | NH₂    | CR                  | CR              | †    |
| 2   | 11  | cCH    | cCHN    | CR                  | CR              | †    | 7   | 10  | N     | cCHNH  | CR                  | CR              | †    |
| 2   | 12  | cCH    | H₂O     | 377.16               | 22.265          | †    | 7   | 11  | N     | cCHN   | CR                  | CR              | †    |
| 3   | 3   | CH₂    | CH₂     | 473.39               | 19.871          | 42   | 7   | 12  | N     | H₂O    | 1,481.3             | 21.217          | †    |
| 3   | 4   | CH₂    | CH₃     | 350.77               | CR              | †    | 8   | 8   | NH    | NH     | 100.00               | 19.999          | †    |
| 3   | 5   | CH₂    | cNH     | 429.49               | CR              | †    | 8   | 9   | NH    | NH₂    | 381.98               | CR              | †    |
| 3   | 6   | CH₂    | cN      | 508.54               | CR              | †    | 8   | 10  | NH    | cCHNH  | CR                  | CR              | †    |
| 3   | 7   | CH₂    | N       | 348.30               | CR              | †    | 8   | 11  | NH    | cCHN   | CR                  | CR              | †    |
| 3   | 8   | CH₂    | NH      | 394.58               | CR              | †    | 8   | 12  | NH    | H₂O    | 646.10               | 13.195          | †    |
| 3   | 9   | CH₂    | NH₂     | 348.39               | CR              | †    | 9   | 9   | NH₂    | NH₂    | 284.78               | 10.254          | †    |
| 3   | 10  | CH₂    | cCHNH   | 309.95               | CR              | †    | 9   | 10  | NH₂    | cCHNH  | 101.61               | CR              | †    |
| 3   | 11  | CH₂    | cCHN    | 893.50               | CR              | †    | 9   | 11  | NH₂    | cCHN   | CR                  | CR              | †    |
| 3   | 12  | CH₂    | H₂O     | 423.63               | 100.00          | 46   | 9   | 12  | NH₂    | H₂O    | 358.55               | CR              | †    |
| 4   | 4   | CH₃    | CH₃     | 256.77               | 15.050          | 42   | 10  | 10  | cCHNH  | cCHN   | 691.56               | 9.2374          | †    |
| 4   | 5   | CH₃    | cNH     | 583.72               | CR              | †    | 10  | 11  | cCHNH  | cCHN   | CR                  | CR              | †    |
| 4   | 6   | CH₃    | cN      | 710.00               | CR              | †    | 10  | 12  | cCHNH  | H₂O    | 855.01               | 32.132          | †    |
| 4   | 7   | CH₃    | N       | 462.18               | CR              | †    | 11  | 11  | cCHNH  | cCHN   | 709.98               | 8.0016          | †    |
| 4   | 8   | CH₃    | NH      | 530.87               | CR              | †    | 11  | 12  | cCHNH  | H₂O    | 1,067.9             | 8.0010          | †    |
| 4   | 9   | CH₃    | NH₂     | 244.15               | CR              | †    | 12  | 12  | H₂O    | H₂O    | 266.68               | 17.020          | 42   |

### 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: NH$_2$ for primary n-alkylamines; NH for secondary alkylamines; and N for tertiary alkylamines. The interaction parameters with the methyl CH$_3$ and methylene CH$_2$ groups are taken from previous work.$^{42,62}$ The procedure followed to estimate the values of the N, NH, and NH$_2$ group parameters, as well as those relating to their interactions with the CH$_2$ and CH$_3$ groups, is similar to that presented in the previous section. The NH$_2$ group is modeled 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; 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 NH$_2$ group. The parameters of the NH$_2$ group and its interactions with the CH$_3$ and CH$_2$ groups are estimated using target experimental data for the fluid-phase equilibria of pure primary n-alkylamines, specifically ethylamine,$^{63}$ n-propylamine,$^{64}$ n-butylamine,$^{56}$ n-pentylamine,$^{61}$ n-hexylamine, n-heptylamine,$^{53}$ and n-octylamine.$^{56}$ The adequacy of the theoretical description of the fluid-phase equilibria for each one of these compounds is apparent from Figure 3a,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 modeled 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; only sites of different type interact. The like NH–NH and unlike NH–CH$_3$, NH–CH$_2$ group interactions are obtained using pure-component experimental vapor-pressure and saturated-liquid density data for four secondary alkylamines: diethylamine, dibutylamine, dihexylamine, and dioctylamine.$^{57,58}$ Furthermore, in order to obtain reliable estimates of the interaction between the amine and alkyl groups, experimental data for the isobaric VLE of binary mixtures of secondary alkylamines and linear alkanes are also considered.$^{59,60}$ Specifically, experimental data for diethylamine + n-hexane,$^{59}$ diethylamine + n-heptane,$^{59}$ and dipropylamine + n-hexane$^{60}$ are included in the parameter estimation procedure. The optimal values estimated for the NH group interactions are reported in Tables 2–4.

### 4.2.4 | Cyclohexylamines: cCHNH and cCHN groups

Having determined 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 alkyl groups in cyclohexylamines confer unique properties to their mixtures with water. We find that, while the smaller cCH and NH (or N) groups can be used to accurately

### Table 4

| k | l | Group k | Site a of group k | Group l | Site b of group l | \( \frac{\varepsilon_{HB}}{K} \) | \( K_{slab}/A^3 \) | Ref. |
|---|---|---------|------------------|---------|------------------|----------------|----------------|-----|
| 5 | 5 | cNH | e | cNH | H | 1,511.6 | 87.651 | † |
| 5 | 6 | cNH | H | cN | e | 901.35 | 1.1555 | † |
| 5 | 12 | cNH | e | H$_2$O | H | 2,838.4 | 37.395 | † |
| 5 | 12 | cNH | H | H$_2$O | e | 1,701.0 | 1.6177 | † |
| 6 | 12 | cN | e | H$_2$O | H | 5,203.7 | 0.037400 | † |
| 7 | 12 | N | e | H$_2$O | H | 2,783.7 | 15.536 | † |
| 8 | 8 | NH | e | NH | H | 1,370.3 | 10.062 | † |
| 8 | 9 | NH | e | NH$_2$ | H | 1,639.9 | 37.900 | † |
| 8 | 9 | NH | H | NH$_2$ | e | 1,682.1 | 0.58200 | † |
| 8 | 12 | NH | e | H$_2$O | H | 1,799.8 | 125.45 | † |
| 8 | 12 | NH | H | H$_2$O | e | 1,064.5 | 400.82 | † |
| 9 | 9 | NH$_2$ | e | NH$_2$ | H | 1,070.8 | 95.225 | † |
| 9 | 12 | NH$_2$ | e | H$_2$O | H | 1,460.0 | 179.60 | † |
| 9 | 12 | NH$_2$ | H | H$_2$O | e | 1,988.3 | 55.824 | † |
| 10 | 10 | cCHNH | e | cCHNH | H | 1,293.5 | 438.49 | † |
| 10 | 12 | cCHNH | e | H$_2$O | H | 5,903.8 | 0.0020750 | † |
| 10 | 12 | cCHNH | H | H$_2$O | e | 5,477.7 | 0.0095820 | † |
| 11 | 12 | cCHN | e | H$_2$O | H | 4,115.4 | 0.23070 | † |
| 12 | 12 | H$_2$O | H | H$_2$O | e | 1,985.4 | 101.69 | 42 |
represent the properties of the pure cyclohexylamines, in order to capture the complex phase behavior of the aqueous solutions of these cyclohexylamines requires the introduction of new, larger, groups: specifically the cCHNH and cCHN groups for monoalkylcyclohexylamines and dialkyl-cyclohexylamines, respectively, are developed here for this family of systems. The phase behavior 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. The tertiary cCHN amine group is modeled with just one association site of type e corresponding to the electron lone pair on the nitrogen atom.

Experimental data for pure cyclohexylamines, \(^{65}\) namely, MCA, N-ethylcyclohexylamine (ECA), and DMCA is used. The target experimental properties considered are the vapor 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 2–4. As can be seen in Figure 3c,d, the theoretical description of the fluid-phase equilibria obtained with the SAFT-\(\gamma\) 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.) because the cCHNH group incorporates one donor and one acceptor association site. This type of self-association scheme is not considered for tertiary cyclohexylamines (i.e., DMCA, DECA, etc.) where only one electron lone pair is present on the nitrogen atom.

It is well known that second-derivative thermodynamic properties are challenging to represent for any thermodynamic model and therefore, in order to validate the reliability of the group interaction parameters developed in our present work for cyclic amines (cCH,cN) and alkyamines (NH2, NH, and N) we assess our models by predicting the vapour pressure, \(P_{\text{vap}}\), and the saturated-liquid density \(\rho_{\text{sat}}\) obtained with the SAFT-\(\gamma\) Mie group-contribution approach for the pure compounds of interest. \(N_p\) and \(N_r\) are the numbers of data points of \(P_{\text{vap}}\) and \(\rho_{\text{sat}}\), respectively. The temperature range of the data and references to the experimental data are denoted in each case.

### Table 5

| Compound                  | \(T / K\) | \(N_p\) | \% AAD \(P_{\text{vap}}\) | Ref. | \(T / K\) | \(N_p\) | \% AAD \(\rho_{\text{sat}}\) | Ref. |
|---------------------------|-----------|---------|---------------------------|-----|-----------|---------|---------------------------|-----|
| Cyclic amines             |           |         |                           |     |           |         |                           |     |
| Pyrrolidine (PY)          | 293–510   | 50      | 2.12                      | 52  | 275–508   | 10      | 0.55                      | 52  |
| Piperidine (PD)           | 273–416   | 37      | 1.06                      | 53  | 296–519   | 12      | 0.12                      | 53  |
| Piperazine (PZ)           | 379–625   | 20      | 0.36                      | 51  | 384–620   | 24      | 0.02                      | 51  |
| N-methyldipiperidine (MPD)| 273–354   | 11      | 0.03                      | 53  | 288–338   | 6       | 0.76                      | 53  |
| N-ethylpiperidine (EPD)   | 274–313   | 9       | 0.57                      | 53  | 293.15    | 1       | 0.01                      | 53  |
| N-methyldipiperazine (MPZ)| 355–410   | 9       | 0.02                      | 53  | -         | 0       | -                         |     |
| N-ethylpiperazine (EPZ)   | 365–429   | 15      | 0.01                      | 53  | -         | 0       | -                         |     |
| Cyclic alkanes            |           |         |                           |     |           |         |                           |     |
| Ethylcyclohexane          | 243–403   | 17      | 0.09                      | 54  | 223–548   | 14      | 1.98                      | 54  |
| Ethylcyclopentane         | 301–378   | 20      | 0.11                      | 54  | 249–511   | 15      | 0.70                      | 54  |
| Methylcyclopentane        | 293–344   | 20      | 0.05                      | 54  | 200–474   | 14      | 1.93                      | 54  |
| \(n\)-propylcyclohexane   | 345–431   | 20      | 0.17                      | 54  | 264–575   | 17      | 1.90                      | 54  |
| Alkyamines                |           |         |                           |     |           |         |                           |     |
| Ethylamine                | 288–456   | 11      | 1.76                      | 55  | 223–293   | 12      | 0.99                      | 55  |
| \(n\)-propylamine         | 283–343   | 13      | 0.65                      | 56  | 243–293   | 12      | 0.16                      | 56  |
| \(n\)-butylamine          | 292–515   | 40      | 6.68                      | 57  | 233–293   | 12      | 0.35                      | 57  |
| \(n\)-pentylamine         | 322–378   | 13      | 1.84                      | 57  | 213–453   | 13      | 0.74                      | 58  |
| \(n\)-hexylamine          | 321–406   | 6       | 5.70                      | 59  | 253–493   | 13      | 1.03                      | 59  |
| \(n\)-heptylamine         | 327–430   | 7       | 3.57                      | 59  | 288–353   | 14      | 0.13                      | 59  |
| \(n\)-octylamine          | 344–495   | 23      | 1.43                      | 60  | 298–328   | 7       | 0.11                      | 60  |
| Alkyl cyclohexylamines    |           |         |                           |     |           |         |                           |     |
| \(N\)-methylcyclohexylamine (MCA) | 275–314 | 14 | 0.03 | 61 | 274–552 | 16 | 0.80 | 61 |
| \(N\)-ethylcyclohexylamine (ECA) | 274–552 | 16 | 0.00 | 61 | 350–626 | 17 | 0.82 | 61 |
| \(N,N\)-dimethylcyclohexylamine (DMCA) | 275–314 | 14 | 0.34 | 61 | 276–557 | 14 | 3.55 | 61 |
Figure 4, we present the prediction of these properties for a variety of pure amines selected based on the availability of the experimental measurements. When the parameters presented in Tables 2–4 are used within the SAFT-\(\gamma\)Mie group-contribution approach one is able to represent the experimental data, exhibiting good agreement and validating the transferability of the group parameters as one of the main features of our approach. It is worth noting that by using limited vapor–liquid thermodynamic properties for pure amines (or related chemical families) we are able to extend the predictive capability to caloric properties.

Moreover, by using the same set of parameters developed for pure amines, the SAFT-\(\gamma\)Mie group-contribution approach allows one to represent the behavior of mixtures between compounds formed of the chemical moieties considered in the parameter estimation procedure. As an illustration the results for selected binary amine–alkane mixtures are presented in Figure 5. The prediction of the excess enthalpies for the systems: primary \(n\)-butylamine + \(n\)-hexane and tertiary \(N,N\)-Diethylethanamine (TEA) + \(n\)-octane at varying conditions are presented in Figure 5a,b, respectively. The predictions are found to be in good agreement with experiment.

4.3 Aqueous mixtures of cycloalkanes: \(c\text{CH}_2\text{H}_2\text{O}\) and \(c\text{CH}\text{H}_2\text{O}\) interactions

In systems such as aqueous mixtures of cycloalkanes the hydrophobic effect plays an important role in determining the solubility and fluid-phase behavior. In our work the unlike interactions between the cyclic \(c\text{CH}_2\) and \(c\text{CH}\) groups and the \(\text{H}_2\text{O}\) group are characterized by estimating both the energy \(\epsilon_{ij}\) and repulsive-range \(\lambda_{ij}\) parameters from target experimental data. These group interactions allow one to extend the capability of the SAFT-\(\gamma\) group-contribution approach to the description of the aqueous solubility of aromatic hydrocarbons\(^{42}\) and \(n\)-alkanes\(^{46}\) developed in previous work. The appropriate determination of these
interactions is a crucial step for an accurate description of the fluid-phase behavior of aqueous solutions of both cyclic amines and cyclohexylamines.

In order to describe correctly the unlike interactions between the cCH and cCH$_2$ groups and H$_2$O, the parameters are estimated from mutual solubility data for the H$_2$O-rich and cycloalkane-rich liquid phase at the orthobaric conditions of three-phase equilibria using the experimental data for binary systems.$^{75}$ More specifically, the unlike interactions between the cCH and H$_2$O groups and between the cCH$_2$ and H$_2$O 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.

The values for the unlike interaction parameters between the CH$_3$ and H$_2$O groups and between the CH$_2$ and H$_2$O groups are taken from Reference 46 as these are able to accurately represent 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-$\gamma$ Mie group-contribution approach is shown in Figure 6. As can be seen the model developed here can be used to accurately describe the solubilities of cycloalkanes over a wide temperature range. We are not able to reproduce the experimentally observed solubility minima of aqueous solutions of cyclohexane in the water-rich phase with the SAFT-$\gamma$ Mie group-contribution approach. This inadequacy is most likely due to the inability of the theory to reproduce the anomalous density behavior of pure water close to freezing.

4.4 | Aqueous solutions of secondary cyclic amines: cNH–H$_2$O interaction

As the cNH group incorporates one association site of type H and one site of type e, the parameters describing the energy and bonding volume of association between these sites and those of
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 VLE data for aqueous solutions of piperazine are used. The resulting parameters are presented in Tables 3 and 4, and isothermal pressure-composition VLE phase boundaries of PZ + water at three temperatures calculated with the SAFT-$\gamma$ Mie group-contribution approach are compared to experimental data in Figure 7a.

4.5 Aqueous solutions of tertiary cyclic amines: cN–$H_2O$ interactions

An important feature of the molecular interactions in aqueous solution of tertiary 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 incorporated in the cN and $H_2O$ groups. One site of type e corresponding to the electron lone pair on the nitrogen atom is included 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 $H_2O$ groups, we find that the repulsive exponent $\xi_{cN,H_2O}$, the unlike dispersion energy $\varepsilon_{cN,H_2O}$, the unlike association energy between sites $\varepsilon_{cN,H_2O}$, and the unlike bonding volume $K_{cN,H_2O}$ 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\textsuperscript{52} and N-ethylpiperazine (EPZ) + water\textsuperscript{77} binary mixtures at \( P = 0.1 \) MPa. The optimized values of the set of parameters describing the interactions between the cN and H\(_2\)O groups are presented in Tables 3 and 4. The description of the isobaric VLE for MPZ + water with our group-contribution approach is presented in Figure 7b and the corresponding results for EPZ + water in Figure 7c. As can be seen the description obtained using SAFT-\( \gamma \), Mie accurately represents the experimental data.

It is important to point out that the results presented in Figure 7 are obtained using the parameters between the cN and H\(_2\)O groups optimized using the data presented in the figures as well as transferring the parameters corresponding to the unlike interactions between the H\(_2\)O and CH\(_2\) groups and between the H\(_2\)O and CH\(_2\) groups\textsuperscript{46} developed in previous work for aqueous solutions of \( n \)-alkanes. The 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–H\(_2\)O, NH\(_2\)–H\(_2\)O, and N–H\(_2\)O interactions

The unlike association interactions between the water and alkylamine groups (NH and NH\(_2\)) are assumed to be asymmetric \[ \varepsilon^{\text{HB}}_{\text{NH}H,\text{e}} \neq \varepsilon^{\text{HB}}_{\text{NH}H,\text{H}} \] \textsuperscript{78} 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 NH\(_2\) and NH, respectively (group l), featuring association sites of both types e and H. For NH\(_2\) two sites of type H and one site of type e are used, whereas for 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 \( \varepsilon^{\text{HD}}_{\text{H,O}} \), the unlike repulsive exponent \( \lambda^{\text{RD}}_{\text{H,O}} \) of the inter-segment interaction, the unlike energy
and bonding volume $K_{H_2O,l}$ of association between sites of type H of water and e of the amine group l, and the energy $\varepsilon_{H_2O,l,H,e}$ and bonding volume $K_{H_2O,l,H}$ of association between sites of type e of water and H of the primary or secondary amine group l. 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 one electron lone pair association site of type e.

These parameters are estimated using experimental data relating to binary aqueous mixtures of n-alkylamines: specifically VLE data for aqueous mixtures of ethylamine, n-propylamine, and n-butylamine are used for the unlike interactions NH$_2$–H$_2$O; data of aqueous solutions of diethylamine, and dipropylamine for the NH–H$_2$O unlike interactions; and data of solutions of methyl diethylamine, and triethylamine for the N–H$_2$O unlike interactions. The interaction parameters determined in this way for the alkylamine chemical groups are reported in Tables 3 and 4, and a comparison of the SAFT-$\gamma$ Mie group-contribution approach [Color figure can be viewed at wileyonlinelibrary.com]
description with the experimental VLE data of some of the primary \(n\)-alkylamines used in the parameter estimation procedure is shown in Figure 8. The adequacy of the approach for compounds of both low and high molecular weight can be gleaned from the figure. Furthermore, as is apparent from Figure 9, the predictions of the excess enthalpy of mixing for aqueous solutions of \(n\)-propylamine (Figure 9a) and of piperidine (Figure 9b) with the parameters estimated from the VLE data are in good agreement with the experimental values.

**FIGURE 9** Isothermal–isobaric excess molar enthalpy of mixing \(H^E\) for selected aqueous solutions of amines with varying mole fraction \(x\). The symbols represent the experimental data and the continuous curves the description with the SAFT-\(\gamma\) Mie group-contribution approach: (a) \(n\)-propylamine (1) + water (2) at \(T = 298.15\) K and \(P = 0.1\) MPa (black circles\(^{84}\)), \(T = 323.15\) K and \(P = 0.5\) MPa (blue squares\(^{84}\)), \(T = 373.15\) K and \(P = 3.0\) MPa (red triangles\(^{84}\)), \(T = 373.15\) K and \(P = 3.0\) MPa (red triangles\(^{84}\)), and \(T = 403.15\) K and \(P = 5.0\) MPa (magenta crosses\(^{84}\)); (b) Piperidine (1) + water (2) at \(T = 298.15\) K and \(P = 0.1\) MPa (black circles,\(^{85}\) blue squares\(^{85}\)). [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 10** Isobaric temperature-composition (\(T\)-\(x\)) slices of the vapor–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\(^{57}\)); (b) \(N\)-ethylcyclohexyl (ECA) + water (black triangles,\(^{18}\) black circles\(^{57}\)). The symbols represent the experimental data and the continuous curves the calculations with the SAFT-\(\gamma\) Mie group-contribution approach [Color figure can be viewed at wileyonlinelibrary.com]

### 4.7 Aqueous mixtures of cyclohexyl amines: \(c\text{CHNH–H}_2\text{O}\) and \(c\text{CHN–H}_2\text{O}\) interactions

A key feature of the fluid-phase behavior of aqueous solutions of cyclic amines is their low solubility in water.\(^{18}\) Several aqueous solutions of alkylcyclohexylamines have been studied experimentally by Stephenson,\(^{18}\) 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 for MCA and DMCA in order to estimate the interactions between \(c\text{CHNH}\) and \(c\text{CHN}\) groups developed in previous sections and the \(\text{H}_2\text{O}\) group. The unlike interactions between the \(c\text{CHNH}\) and \(\text{H}_2\text{O}\) are estimated using LLE data.
for aqueous mixtures of MCA, and the unlike interactions between the cCHN and H2O are estimated using the LLE data for aqueous 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 DMCA + water and ECA + water are shown in Figure 10. It is very encouraging to see that the SAFT-\(\gamma\) Mie group-contribution approach provides an accurate representation of the LCST behavior, which is typically very challenging to describe, particularly in the case of ECA + water which are predictive calculations.

At this point we highlight the predictive capability of the SAFT-\(\gamma\) Mie group-contribution approach in describing the complex fluid-phase behavior of aqueous solutions of amines. This is demonstrated from the results presented in Figure 11. The binary mixtures methylpiperidine (MPD) + water and triethylamine (TEA) + 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 \(T = 41.85^\circ C\) (at 0.101 MPa). The mixture TEA + water also presents a liquid–liquid demixing, with a trend of increasing solubility of the two components as the temperature is lowered; an LCST has however not been reported experimentally.

Although these types of systems are notoriously difficult to treat, the liquid–liquid coexistence predicted with the SAFT-\(\gamma\) Mie group-contribution approach, offers a very reliable description of the phase behavior, as exemplified by the results presented in Figure 11. Indeed for both types of amines considered (cyclic and branched alkyamines), although only VLE experimental data used in the parameter estimation (cf. Figures 7 and 8), one is able to describe the complex LLE phase equilibria using the same set of parameters. We can therefore conclude that the SAFT-\(\gamma\) Mie group-contribution approach provides a predictive platform for the fluid-phase behavior (including both VLE and LLE) of aqueous solutions of amines with broadly varying chemistries, over wide ranges of pressures and temperatures.

5 | CONCLUSIONS

We have employed the SAFT-\(\gamma\) 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, and cyclohexyl amines) as well as the vapor–liquid, liquid–liquid, and vapor–liquid–liquid equilibria of aqueous mixtures of the amines 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 associate. The reliability and transferability of the modeling is demonstrated by the prediction of regions of liquid–liquid immiscibility bounded by LCSTs 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 the approach as a tool to describe and understand the complex fluid-phase behavior of amine systems, which have a broad of application in the chemical, pharmaceutical, and biotechnology industries.

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