The development of asymmetric unlike induced association-site models to study the phase behaviour of aqueous mixtures comprising acetone, alkanes and alkyl carboxylic acids with the SAFT- γ Mie group contribution methodology

*Majid Sadeqzadeh, Vasileios Papaioannou, Simon Dufal, Claire S. Adjiman, George Jackson, and Amparo Galindo**

Department of Chemical Engineering, Centre for Process Systems Engineering,
Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

Abstract

Providing accurate predictions of the thermodynamic properties of highly polar and hydrogen bonding compounds and their mixtures is challenging from a theoretical perspective. The combination of an equation of state (EoS) based on the statistical associating fluid theory (SAFT) with a group contribution (GC) methodology offers both accuracy and predictive capability for the thermodynamic properties of mixtures. In our current work, the SAFT- γ Mie equation of state is used to capture the underlying complexity of systems in which specific interactions (e.g., hydrogen bonding, dipolar interactions, chemical association) play an important role, by incorporating highly versatile association-site schemes to model mixtures in which unlike induced association interactions occur; this is done by assigning to the functional groups a number of association sites that are inactive in the pure fluid, but become active in certain mixtures. We refer to this type of association mechanism as “unlike induced” association and to the sites involved in this interaction as “unlike induced” association sites. The concept of unlike induced association sites is applied here to develop reliable SAFT- γ Mie group contribution models to describe the properties of acetone, alkyl carboxylic acids, and their mixtures with water and *n*-alkanes. The parameter table of available SAFT- γ Mie models is expanded to incorporate the corresponding group interaction parameters for acetone, which is treated as a molecular group, the carboxyl group COOH, and their unlike interaction group parameters with water, and the methyl CH₃, methanediyl CH₂, and methanetriyl CH alkyl groups. In particular, one unlike induced site is used with the acetone model to mediate hydrogen-bonding of the acetone oxygen in mixtures containing hydrogen-bond donors, and two pairs of unlike induced sites are included on the COOH group to mediate hydrogen-bond formation in mixtures of carboxylic acids and hydrogen-bond donors. The models developed allow for the successful description of the complex fluid-phase behaviour of the relevant binary and ternary mixtures, including accurate predictions of systems which have not been used to determine the model parameters.

Keywords:

SAFT- γ Mie; Group contribution; Unlike induced association sites; Acetone; Carboxylic acid; Water; *n*-alkane

1 Introduction

Water, acetone and carboxylic acids are commonly used solvents due to their ease of availability and ability to solubilize a large number of substances. In addition to their use as pure solvents, mixtures of these components with other common solvents such as the alkanes are often used in the pharmaceutical industry [1], for example, in Counter-Current Chromatography (CCC) [2], as well as in solvent extraction and solution crystallization [3]. The formulation of mixtures provides a continuous range of solvents with properties that can be easily tailored to specific applications solely by varying the composition, since changes in composition can result in changes of polarity of the solvent mixture which can be tuned for a particular solute. For example the solubility of paracetamol in the water + acetone mixture at 303 K exhibits a maximum at a composition of approximately 30% mass percent of water, at which point the solubility is over 4 times that in pure acetone and over 30 times that in pure water [4]. In order to develop an effective processing medium, it is important for any phase separation that occurs when the solvent components are mixed to be known. The prediction of the thermodynamic properties of multicomponent mixtures remains challenging, especially when highly polar and hydrogen-bonding molecules are present. The formation of hydrogen bonds between water molecules has been recognized since the advent of the concept of hydrogen bond itself [5, 6]. Molecular-scale observations, such as the broadening of the infrared (IR) O-H absorption band [7] (see Reference [8] for a detailed discussion on the IR spectra of hydrogen-bonded species), and the proton NMR chemical shift of water, which changes with concentration and temperature corresponding to the extent of hydrogen-bond formation [7, 8], confirm the presence of these interactions. Furthermore, a quantitative analysis of the proportion of water molecules that are hydrogen bonded can be determined by overtone IR [9] or neutron scattering [10] techniques. In the liquid phase the frequency and magnitude of the extinction coefficient of free (non-hydrogen-bonded) OH groups can also be

obtained from the spectrum of water in a non-hydrogen-bonding solvent, by comparison with the spectrum of pure water, to calculate the ratio of free and hydrogen-bonded OH groups. Similarly, the hydrogen-bonding behaviour of carboxylic acids was also recognized early on [11], with IR spectroscopy indicating the formation of dimers, both in the liquid [12, 13] and vapour [14] phases of the pure fluids through analysis of different absorption bands. The existence of hydrogen bonds in water and in carboxylic acids has also been investigated from an *ab initio* perspective, with the results confirmed by comparison to spectroscopic data (a review of these early works can be found in reference [15]). Hydrogen bonding interactions in these systems have been extensively studied by *ab initio* (see for example refs. [16, 17] and references therein) and classical (e.g., the reviews of refs. [18, 19], and references therein) molecular simulation.

The formation of hydrogen bonds in systems containing carboxylic acids and/or water influences dramatically their bulk thermodynamic properties. Pure water exhibits an abnormally high boiling temperature of 373 K [8, 20] and a maximum in density around 277 K [8, 20] at ambient pressure due to the formation of a three-dimensional network of bonds [8]. Similarly, the boiling points of the alkyl carboxylic acids (e.g., 436 K for butanoic acid [20]) are higher than those of the isomeric esters (e.g., 350 K for ethyl acetate [20]) due to the formation of hydrogen-bonded dimers in the liquid phase. Aqueous mixtures of short-chain carboxylic acids are fully miscible under ambient conditions, although they exhibit low-boiling azeotropes from acetic to butanoic acid [21] (a reflection of the presence of strongly hydrophobic alkyl groups). Indeed mixtures of pentanoic acid and longer carboxylic acids with water exhibit liquid-liquid immiscibility at ambient conditions [22]. This type of phase behaviour is similar to that of aqueous mixtures of 1-alkanols, although the liquid-liquid immiscibility at ambient conditions first appears for butan-1-ol [23], with its shorter alkyl chain. The difference in the behaviour of the acid and the alcohol series suggests that the

number of hydrogen bonds between the acid molecules and water is greater than that between the alcohol and water. It is also interesting to note the difference with the phase behaviour of aqueous solutions of *n*-alkanes, which are characterized by extreme liquid-liquid demixing, due to the very weak attractive interaction between the two species, and especially to the lack of unlike hydrogen bonding interaction between them.

On the other hand, acetone is a highly polar but aprotic compound, with a dipole moment of 2.88 D in the vapour phase [24]. It is a liquid at ambient conditions and exhibits a comparatively high boiling point of 329 K. Coupled with its polarity, the hydrophobic character of the methyl groups makes acetone a good solvent for a wide range of organic components, and as a consequence acetone is one of the most common solvents in the chemical industry. Although acetone does not form hydrogen bonds in its pure form as it does not possess a suitable hydrogen atom, it can form hydrogen bonds when mixed with substances that possess polarised hydrogen atoms, such as chloroform. Binary mixtures of acetone and chloroform exhibit high-boiling azeotropes, reflecting the strong interaction between the two components (see, e.g., refs. [25, 26]). The formation of hydrogen bonds between water and acetone has been confirmed by *ab initio* simulation [27], and is observed experimentally in the ultraviolet (UV) absorption spectra of acetone in water [28]. Acetone and water are fully miscible at all temperatures in the liquid phase. The phase diagram at high temperatures, however, exhibits a low-boiling azeotrope [29], instead of the high-boiling azeotrope that would be expected if a strong unlike interaction were present between the two components.

From a theoretical perspective the development of molecular models suitable for studies of the properties of mixtures containing strongly polar molecules and at least one hydrogen-bond donor, requires a detailed understanding of the molecular properties, of the association interactions, and of the detailed balance between the strongly polar interactions

and any hydrophobic interactions between the alkyl groups in water. The chemical theory of solutions developed by Dolezalek [30] led to the first successful description of associating fluids where distinct molecular species are assumed to exist in the solution at chemical equilibrium, in order to characterize the hydrogen-bonding interactions present in the system. The main drawback of chemical approaches is the necessity of describing all of the chemical reactions that may occur in solution, the resulting products, as well as the corresponding equilibrium constants. While this is feasible in simple dimerizing fluids, the products that occur in fluids characterised by the formation of long linear-chain aggregates, branched and three-dimensional networks formed, e.g., in aqueous systems cannot be as easily described [31]. The predictive power of chemical approaches is therefore somewhat limited and these methods cannot be extended reliably to conditions far from those considered at the model development stage. The physical approach of van Laar [32, 33] on the other hand neglects any chemically reacted molecular species and attributes the mixture properties to the strong physical intermolecular interactions between the unassociated species. It is now recognized that the use of a physical approach is reasonable as long as no species are formed that are very different chemically from the initial ‘reactants’ [34].

The physical approach most commonly used nowadays is rooted in the framework initially developed by Hill [35, 36], who generated two parallel methods, one based on expansions of the free energy in terms of cluster densities [37-43] and the other based on incorporating an intermolecular potential model explicitly to account for association interactions within integral equation theories [44-57]. Of particular relevance to our work is the thermodynamic perturbation theory (TPT) of Wertheim [58-61], which is cast both as an integral equation and as a highly convergent cluster expansion.

In TPT, strong short-range directional attractive interactions (represented as short-ranged attractive sites) are considered to be responsible for the formation of associated

clusters as a perturbation of the properties of a non-associating monomeric fluid. Wertheim's theory is mostly formulated in its simplest first-order form (TPT1 [58-61]), in which double bonding is neglected and bonding at different sites is treated independently; in addition the reference potential is assumed to be repulsive enough such that two molecules may not bond simultaneously to a third via the same sites. This approach results in an expression for the contribution to the Helmholtz free energy due to the formation of different associated aggregates which depends only on the geometrical properties of the association site and the two-body radial distribution function of the non-associating (monomer) system. The distribution of aggregate species is obtained as a result of the choice of intermolecular potential model and the accompanying theory, rather than specified *a priori* as in the chemical approach. It was shown early on that in the limit of complete association the theory provides an accurate description of the thermodynamic properties of fully bonded molecular chain [62].

The theory of Wertheim is the principal basis for the development of the statistical associating fluid theory (SAFT [63, 64]) family of equations of state (EoSs). In the SAFT framework the molecules of the fluid are modelled as chains of bonded spherical segments, often referred to as monomers, with short-range (square-well) association sites mediating hydrogen bonding and other strong attractive directional forces. Different SAFT EoSs have been developed by considering different potential models (e.g., Lennard-Jones [65], square-well [66], Mie [67]) to treat the reference monomer system or by adding different contributions to account for other phenomena, such as multipoles or ions (see references [31, 68-70] for detailed reviews of the different SAFT-type approaches).

Within the SAFT family of EoSs, our focus is on the SAFT- γ Mie [71, 72] framework, a group-contribution (GC) reformulation of the SAFT-VR Mie EoS [67] for heteronuclear molecules composed of fused segments. This approach enables the treatment of fluids

composed of spheres interacting through a Mie (generalized Lennard-Jones) potential. It provides a description of variable attractive and repulsive interactions, which leads to an improved description of the phase behaviour and thermodynamic properties of complex fluids, including second-derivative properties such as the speed of sound, compressibility, and heat capacity. The use of a group contribution concept in the SAFT- γ Mie EoS, with the assumption that the property of any given compound can be obtained from the individual contributions of different chemically distinct functional groups present in the compound leads to a highly predictive and accurate EoS that can be used to obtain the properties of complex mixtures from group models. Importantly, the group parameters are characterized based on appropriate thermophysical data for simple systems (often pure component data alone is enough) but can be used for multifunctional molecules [72].

A particular strength of SAFT-based approaches is the versatility of the association schemes that can be developed to describe the specific interactions that exist within mixtures containing hydrogen-bond donors and acceptors. For instance, a limiting form of ‘asymmetric’ association models, in which association sites are active only in a mixture but not in the pure component was employed early on by Chapman et al. [73], who investigated model binary liquid mixtures with unlike dimerization (association) but no like dimerization. The association sites mediating the unlike dimerization do not have any impact on the properties of the pure fluid. The idea of using association sites of this type, which we refer to as ‘induced unlike sites’, to mediate only selected types of unlike hydrogen-bonding interactions was also used to treat aqueous mixtures of alkyl polyoxyethylene (C_iE_j) surfactants [74, 75] which were studied using the SAFT-HS (hard sphere) equation of state, with only two sites (one H and one e sites) situated on the hydroxyl group active in the pure C_iE_j molecules, with three association sites per ether unit active only in the presence of water to interact with the hydrogen sites of water, as well as the three sites corresponding to the terminal hydroxyl

group. The use of these unlike induced association sites leads to a very good description of the highly non-ideal behaviour of these mixtures, which exhibit liquid-liquid closed-loop immiscibility. The perturbed-chain SAFT (PC-SAFT) and perturbed-chain polar-SAFT (PCP-SAFT) [76, 77] have also been used to study the fluid-phase behaviour of binary mixtures containing a polar component that does not self-associate and water or an alcohol, using unlike induced association sites to model the interactions of the polar substance. Induced association sites were also used with the simplified PC-SAFT and Nonrandom Hydrogen Bonding [78, 79] and applied to a number of different mixtures, comprising acetone and carboxylic acids. Models with and without induced association were compared, and it was found that the incorporation of induced association sites significantly improves the description of the fluid-phase behaviour of the mixtures considering. A summary of the modelling of carboxylic acids with different SAFT-based methods can be found in the paper by Breil *et al.* [80].

In our current work we develop sophisticated group-group pair potential models that provide an accurate description of the thermodynamic properties of complex mixtures containing water, carboxylic acids, and acetone. These models are also applied to predict the fluid-phase behaviour of mixtures of these substances with *n*-alkanes to ensure that they are appropriate for the simultaneous treatment of non-polar (and hence non hydrogen-bonding) and polar substances. In order to obtain high-fidelity models for these mixtures the concept of unlike induced association sites is introduced in the heteronuclear group SAFT- γ Mie methodology.

We first present a brief overview of the SAFT- γ methodology and underlying heteronuclear model followed by an introduction to the generic association schemes used in our work. The unlike induced association-site concept is then introduced along with the parameter estimation procedure. This is followed by calculations of the fluid-phase behaviour

of pure compounds as well as the properties of mixtures of compounds of different polarity and association capability.

2 SAFT- γ Mie theory and molecular models

2.1 Brief overview of the SAFT- γ Mie group contribution EoS

The SAFT- γ Mie [71] EoS is based on the group-contribution concept where one assumes that the properties of a mixture (in this case thermodynamic properties) can be calculated from appropriate contributions of the different chemical functional groups composing the molecules in the system. In the SAFT- γ Mie formalism the molecules are modelled as associating heteronuclear chains formed from fused spherical segments, with each functional group k comprising a number v_k^* of spherical segments. The interaction between two segments k and l is modelled via a Mie potential of variable range [67]:

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

where σ_{kl} is the segment diameter, r_{kl} is the distance between the centers of the two segments, ε_{kl} is the depth of potential well, and λ_{kl}^r and λ_{kl}^a are the repulsive and attractive exponent of segment–segment interactions, respectively. The pre-factor C_{kl} is used to ensure that the minimum value of the interaction corresponds to $-\varepsilon_{kl}$:

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

Segments are characterized by further attributes. The shape factor S_k determines the extent to which the segments of group k contribute to the overall thermodynamic properties. Hydrogen bonding or strongly polar interactions are mediated by the addition of a number of short-range off-centre square-well association sites that can be positioned on any functional

group; the number of different association site types on segment k is denoted $N_{ST,k}$, while the numbers of sites for each type are denoted $n_{k,a}, n_{k,b}, \dots, n_{k,N_{ST,k}}$, for sites of type $a, b, \dots$. The association interaction between two square-well association sites of type a in segment k and b in segment l is calculated from:

$$\Phi_{kl,ab}^{\text{HB}}(r_{kl,ab}) = \begin{cases} -\varepsilon_{kl,ab}^{\text{HB}} & \text{if } r_{kl,ab} \leq r_{kl,ab}^c, \\ 0 & \text{if } r_{kl,ab} > r_{kl,ab}^c, \end{cases} \quad (3)$$

where $r_{kl,ab}$ corresponds to the distance between the centers of two association sites (a site of type a on segment k and a site of type j on segment l), $\varepsilon_{kl,ab}^{\text{HB}}$ to the depth of the association potential, and $r_{kl,ab}^c$ to the cutoff distance of the interaction between the two association sites.

The distance from the centre of the segment is also described by $r_{kk,aa}^d$ for a site type a placed on segment k . The bonding geometry can be described equivalently with the bonding volume $K_{kl,ab}$ [81].

In summary, every functional group k in the SAFT- γ Mie methodology is characterized by its constituent number of identical spherical segments (V_k^*), the shape factor of each segment (S_k), the diameter (σ_{kk}), the interaction energy (ε_{kk}), and the exponents (λ_{kk}^r and λ_{kk}^a) of the Mie potential. In the case of associating groups, a number of additional parameters are required to describe the site-site association interactions: the number of different association site types ($N_{ST,k}$), the number of sites for each type ($n_{k,a}, n_{k,b}, \dots, n_{k,N_{ST,k}}$), as well as the energy ($\varepsilon_{kk,ab}^{\text{HB}}$) and the bonding volume parameter ($K_{kk,ab}$) for the association interaction between sites a and b . Both $r_{kk,ab}^c$ and $r_{kk,aa}^d$ are fixed at $0.4\sigma_{kk}$ in the current version of the theory [82]. The interactions between functional groups k and l are also described by the corresponding unlike parameters for interactions between groups of type k and l : $\sigma_{kl}, \varepsilon_{kl}$,

λ_{kl}^r , λ_{kl}^a , $\varepsilon_{kl,ab}^{HB}$ and $K_{kl,ab}$. Examples of the SAFT- γ Mie representation for propanoic acid and acetone are given in Figure 1.

Figure 1

Once a complete set of relevant molecular parameters is determined, the total Helmholtz free energy of a given pure fluid or mixture of associating heteronuclear chains of fused segments interacting via Mie potentials is calculated from the various contributions to the SAFT- γ Mie Helmholtz free energy terms as

$$A = A^{\text{IDEAL}} + A^{\text{MONO}} + A^{\text{CHAIN}} + A^{\text{ASSOC}} , \quad (4)$$

where the term A^{IDEAL} refers to the free energy of an ideal gas mixture of corresponding molecules, and A^{MONO} , A^{CHAIN} , and A^{ASSOC} are residual contributions to the free energy due to the repulsive and attractive (dispersion) interactions between monomeric segments, to the formation of chain molecules from Mie segments, and to site–site intermolecular association, respectively. The Helmholtz free energy of a fluid mixture is thus determined from the appropriate contributions of its constituent chemical functional groups; a brief summary of the expressions for the individual terms is given in the following paragraphs. The reader is referred to the original SAFT- γ Mie paper [71] and corresponding treatment of the association term [85] for the detailed expressions.

Ideal Term: The free energy of any ideal mixture of molecules is given by [83]

$$\frac{A^{\text{IDEAL}}}{Nk_B T} = \left(\sum_{i=1}^{N_C} x_i \ln(\rho_i \Lambda_i^3) \right) - 1 , \quad (5)$$

where x_i and ρ_i are the mole fraction and the number density of component i in a mixture of N_C components, respectively, N is the total number of molecules, k_B is the Boltzmann constant, and T is the absolute temperature. The summation is over all of the components N_C in the mixture, and the thermal de Broglie volume represented by Λ_i^3 is used to implicitly include the translational, vibrational, and rotational contributions to the ideal free energy.

Monomer Term: The contribution of the repulsive and attractive interactions between monomeric segments interacting via Mie pair potentials is obtained following a Barker-Henderson [84, 85] high-temperature perturbation expansion up to the third order [67]:

$$\frac{A^{\text{MONO}}}{Nk_B T} = \frac{A^{\text{HS}}}{Nk_B T} + \frac{A_1}{Nk_B T} + \frac{A_2}{Nk_B T} + \frac{A_3}{Nk_B T} , \quad (6)$$

where A^{HS} represents the free energy of a hard-sphere reference system of diameter d_{kk} , which is temperature dependent [84]. The remaining terms correspond to the mean-attractive energy, which is calculated from a knowledge of the contact radial distribution function of the reference hard-sphere fluid at an effective density; the fluctuation term, calculated following the improved macroscopic compressibility approximation proposed by Zhang [86] and a correction of the type proposed by Paricaud [87]; and the third-order term which is represented with an empirical expression based on simulation phase-coexistence data for representative pure Mie fluids. Detailed information about the development of the each if these terms can be found in the original paper [71] and is summarised in reference [72].

Chain Term: In the SAFT- γ Mie approach the contribution to the free energy due to the formation of a model molecule i from its constituent functional groups and segments is calculated using effective molecular parameters ($\bar{\sigma}_{ii}$, $\bar{d}_{ii}$, $\bar{\varepsilon}_{ii}$, and $\bar{\lambda}_{ii}$) [71, 88, 89] obtained using the molecular fraction $z_{k,i}$ of a given group k in molecule i , defined as

$$z_{k,i} = \frac{v_{k,i} v_k^* S_k}{\sum_{j=1}^{N_G} v_{j,i} v_j^* S_j} , \quad (7)$$

where $v_{k,i}$ are the number of occurrences of group k in molecule i , and N_G corresponds to the number of types of groups present in the system.

The effective molecular segment diameter $\bar{\sigma}_{ii}$, reference hard-sphere diameter $\bar{d}_{ii}$, interaction energy $\bar{\varepsilon}_{ii}$, and exponents that characterize the range of the Mie potential $\bar{\lambda}_{ii}$ are defined as [71, 88, 89]

$$\bar{\sigma}_{ii}^3 = \sum_{k=1}^{N_G} \sum_{l=1}^{N_G} z_{k,i} z_{l,i} \sigma_{kl}^3, \quad (8)$$

$$\bar{d}_{ii}^3 = \sum_{k=1}^{N_G} \sum_{l=1}^{N_G} z_{k,i} z_{l,i} d_{kl}^3, \quad (9)$$

$$\bar{\varepsilon}_{ii} = \sum_{k=1}^{N_G} \sum_{l=1}^{N_G} z_{k,i} z_{l,i} \varepsilon_{kl}, \quad (10)$$

$$\bar{\lambda}_{ii} = \sum_{k=1}^{N_G} \sum_{l=1}^{N_G} z_{k,i} z_{l,i} \lambda_{kl}, \quad (11)$$

respectively. The chain-term contribution to the free energy is then given as

$$\frac{A^{\text{CHAIN}}}{Nk_B T} = - \sum_{i=1}^{N_C} x_i \left(\sum_{k=1}^{N_G} v_{k,i} v_k^* S_k - 1 \right) \ln g_{ii}^{\text{Mie}}(\bar{\sigma}_{ii}; \zeta_x), \quad (12)$$

where $g_{ii}^{\text{Mie}}(\bar{\sigma}_{ii}; \zeta_x)$ is the radial distribution function (RDF) evaluated at a distance $\bar{\sigma}_{ii}$ in a hypothetical fluid of packing fraction $\zeta_x = (\pi/6)\rho_s \sum_{k=1}^{N_G} \sum_{l=1}^{N_G} x_{s,k} x_{s,l} d_{kl}^3$ [71]. It is relevant to mention here that a different expression is used by Peng et al. [90, 91] in the GC-SAFT-VR theory. They propose a chain term summing the contributions from the different segments in each group and each contact between groups, thereby preserving the connectivity present in the molecule. It has been shown previously [71] that the two approaches perform similarly in the description of model systems but that the SAFT- γ approach is generally more accurate for the treatment of real substances.

Association Term: The change in the Helmholtz free energy due to the formation of associated species is obtained following the original TPT1 expressions of Wertheim [58-61, 81] as

$$\frac{A^{\text{ASSOC}}}{Nk_B T} = \sum_{i=1}^{N_C} x_i \sum_{k=1}^{N_G} v_{k,i} \sum_{a=1}^{N_{sf,k}} n_{k,a} \left(\ln X_{i,k,a} + \frac{1 - X_{i,k,a}}{2} \right), \quad (13)$$

where $n_{k,a}$ is the number of sites of type a on functional group k , and $X_{i,k,a}$ is the fraction of molecules of component i that are not bonded at a site of type a on group k [71]. The fractions $X_{i,k,a}$ are obtained by solving the mass action equations [71, 81]:

$$X_{i,k,a} = \left[1 + \rho \sum_{j=1}^{N_C} x_j \sum_{l=1}^{N_G} v_{l,j} \sum_{b=1}^{N_{ST,l}} n_{l,b} X_{j,l,b} \Delta_{ij,kl,ab} \right]^{-1}, \quad (14)$$

where the integral $\Delta_{ij,kl,ab}$ specifies the association strength between a site of type a on group type k in component i and a site of type b on a group of type l in component j . The corresponding integral is approximated as [82]

$$\Delta_{ij,kl,ab} = F_{kl,ab} K_{kl,ab} I_{ij,kl,ab}, \quad (15)$$

where $F_{kl,ab} = \exp(\varepsilon_{kl,ab}^{HB} / k_B T) - 1$ and $K_{kl,ab}$ is the bonding-volume parameter. The temperature-density polynomial correlation of the association integral $I_{ij,kl,ab}$ is calculated based on the reference Lennard-Jones RDF and is given by

$$I_{ij,kl,ab} = \sum_{p=0}^{10} \sum_{q=0}^{10-p} c_{pq} (\rho \sigma_x^3)^p \left(\frac{k_B T}{\bar{\varepsilon}_{ij}} \right)^q, \quad (16)$$

with the coefficients c_{pq} of the LJ-based association kernel given in Table A1 of reference [82]. The size parameter σ_x^3 is calculated as

$$\sigma_x^3 = \sum_{k=1}^{N_C} \sum_{l=1}^{N_G} x_{s,k} x_{s,l} \sigma_{kl}^3, \quad (17)$$

the energy parameter $\bar{\varepsilon}_{ij}$ as

$$\bar{\varepsilon}_{ij} = \frac{\sqrt{\bar{\sigma}_{ii}^3 \bar{\sigma}_{jj}^3}}{\bar{\sigma}_{ij}^3} \sqrt{\bar{\varepsilon}_{ii}^3 \bar{\varepsilon}_{jj}^3}, \quad (18)$$

where $\bar{\sigma}_{ii}$ and $\bar{\sigma}_{jj}$ are calculated from equation 8 and $\bar{\sigma}_{ij}$ is obtained from

$$\bar{\sigma}_{ij} = \frac{\bar{\sigma}_{ii} + \bar{\sigma}_{jj}}{2}, \quad (19)$$

and $\bar{\varepsilon}_{ii}$ and $\bar{\varepsilon}_{jj}$ are given by equation 10.

Combining Rules: In addition the evaluation of the Helmholtz free energy contributions given in the previous section require a set of unlike group parameters that define the interactions between the various species. As in previous work [71, 72] combining rules are used to

determine the values of a number of these parameters, and further refinements are carried out using target experimental data if required.

The Lorentz-like arithmetic mean of the like diameters [92] is used to define the unlike segment diameter σ_{ij} :

$$\sigma_{kl} = \frac{\sigma_{kk} + \sigma_{ll}}{2} . \quad (20)$$

The unlike reference hard-sphere diameter d_{ij} is represented in the same way as

$$d_{kl} = \frac{d_{kk} + d_{ll}}{2} . \quad (21)$$

The unlike dispersion energy ε_{ij} between groups k and l is determined using an augmented Berthelot-like geometric mean, which also includes the asymmetry of the segment sizes [93]:

$$\varepsilon_{kl} = \frac{\sqrt{\sigma_{kk}^3 \sigma_{ll}^3}}{\sigma_{kl}^3} \sqrt{\varepsilon_{kk} \varepsilon_{ll}} . \quad (22)$$

Both the repulsive and attractive exponents of the unlike segment-segment interaction

λ_{kl}^r and λ_{kl}^a are given by [67]

$$\lambda_{kl} = 3 + \sqrt{(\lambda_{kk} - 3)(\lambda_{ll} - 3)} . \quad (23)$$

In associating mixtures, the unlike association energy $\varepsilon_{kl,ab}^{HB}$ is expressed in terms of a simple geometric mean [72]:

$$\varepsilon_{kl,ab}^{HB} = \sqrt{\varepsilon_{kk,aa}^{HB} \varepsilon_{ll,bb}^{HB}} , \quad (24)$$

and the unlike bonding volume is obtained as [72]

$$K_{kl,ab} = \left(\frac{\sqrt[3]{K_{kk,aa}} + \sqrt[3]{K_{ll,bb}}}{2} \right)^3 . \quad (25)$$

Although equations 20-25 provide a first estimate of the unlike group parameters, the use of experimental data when available is often the best way to estimate the value of the

unlike parameters more accurately, especially in the case of the unlike dispersion and association energies.

The thermodynamic properties of a given compound/mixture are easily derived once the complete functional form of the Helmholtz free energy is established by then using standard thermodynamic relationships [94]. In particular, the fluid phase equilibria are determined from relations for the pressure $P = (-\partial A / \partial V)_{T,N}$ and chemical potential $\mu_i = (-\partial A / \partial N_i)_{T,V,N_j}$ of each species i , with the total Gibbs free energy $G = A + PV = \sum_i^{N_c} N_i \mu_i$ to ensure the minimum in the global free energy using the HELD algorithm [95]. The excess properties of mixing are defined as the differences between any given property of the mixture and that of each pure component at the same conditions of temperature and pressure weighted by the appropriate mole fraction, i.e.,

$$Z^E(T, P, x_1, x_2, \dots, x_n) = Z^M(T, P, x_1, x_2, \dots, x_n) - \sum_{i=1}^n x_i Z_i(T, P, x_i = 1) , \quad (26)$$

where Z^E represent the excess property of mixing for a mixture of n components, Z^M the total property of the mixture, and Z_i the property of pure component i , respectively.

2.2 SAFT- γ Mie models for water, acetone, carboxylic acids, n -alkanes and their mixtures

In order to treat mixtures where the presence of a second component may result in the formation of hydrogen bonding interactions not present in one or both of the pure fluids, we propose models with “unlike induced” sites. A given group is characterized by a number of association sites of different type as described in the previous section, but the case arises that the sites may be inactive in the pure fluid (the site-site hydrogen bonding energy is zero), but active in the mixture. Wertheim’s TPT1 framework [58-61] offers a generic and accurate way to calculate the separate contribution to the Helmholtz free energy of each site-site interaction.

Following previous work [82, 96] water is modelled as a single Mie spherical segment with four association sites (2 H and 2 e_1 sites) that represent two hydrogen atoms and two electron lone pairs respectively, and are active both in pure water and mixtures. The alkyl groups CH_3 , CH_2 and CH are modelled as non-associating spherical Mie segments; details of these parameters can be found in previous publications [71, 72].

Acetone is treated as a molecular group composed of three spherical Mie segments with three site types (see Figure 1(a)). Two sites, one labelled as type H and one as type e_1 are used to mediate the strong dipolar interaction present in pure acetone where in this particular case there is of course no hydrogen atom only a strong head-to-tail dipolar intermolecular interaction; these sites are active in pure acetone and in all of its mixtures, regardless of the nature of the other components. The third site (labelled of type e_2) is active only in the presence of another associating species; it is added to mediate association on both of the electron lone-pairs of the acetone oxygen by other solvents. The choice of treating the dipolar interactions of acetone as associating and not as dispersive is in line with studies in which a linear alignment of molecules has been shown; it has the effect of maximizing the interaction between positive and negative partial charges (see for example reference [97]); such molecular arrangement can be represented with a two-site model in the treatment of Wertheim TPT [58-61] and in SAFT [59].

In the case of a binary mixture of acetone (labelled as group 5 in component 1; cf. Table 1 for the group numbering) and water (group 4 and component 2) the model of the mixture includes five site types (and seven sites in total). For clarity, the contribution to the Helmholtz free energy due to association in such a system follows from equations 13 and 14 as:

$$\frac{A^{\text{ASSOC}}}{Nk_B T} = x_1 \left[\left(\ln X_{1,5,H} - \frac{X_{1,5,H}}{2} \right) + \left(\ln X_{1,5,e_1} - \frac{X_{1,5,e_1}}{2} \right) + \left(\ln X_{1,5,e_2} - \frac{X_{1,5,e_2}}{2} \right) + \frac{3}{2} \right] \\ + x_2 \left[2 \left(\ln X_{2,4,H} - \frac{X_{2,4,H}}{2} \right) + 2 \left(\ln X_{2,4,e_1} - \frac{X_{2,4,e_1}}{2} \right) + \frac{4}{2} \right], \quad (27)$$

with the fractions of molecules not bonded at each site given by solving the appropriate mass action relations:

$$X_{1,5,H} = \frac{1}{1 + x_1 \rho X_{1,5,e_1} \Lambda_{11,55,H e_1} + 2x_2 \rho X_{2,4,e_1} \Lambda_{12,54,H e_1}}, \quad (28)$$

$$X_{1,5,e_1} = \frac{1}{1 + x_1 \rho X_{1,5,H} \Lambda_{11,55,e_1 H} + 2x_2 \rho X_{2,4,H} \Lambda_{12,54,e_1 H}}, \quad (29)$$

$$X_{1,5,e_2} = \frac{1}{1 + 2x_2 \rho X_{2,4,H} \Lambda_{12,54,e_2 H}}, \quad (30)$$

$$X_{2,4,H} = \frac{1}{1 + 2x_2 \rho X_{2,4,e_1} \Lambda_{22,44,e_1 H} + x_1 \rho X_{1,5,e_1} \Lambda_{12,54,e_1 H} + x_1 \rho X_{1,5,e_2} \Lambda_{12,54,e_2 H}}, \quad (31)$$

$$X_{2,4,e_1} = \frac{1}{1 + 2x_2 \rho X_{2,4,H} \Lambda_{22,44,e_1 H} + x_1 \rho X_{1,5,H} \Lambda_{12,54,H e_1}}. \quad (32)$$

A model of acetone including two CH₃ groups and one CO group was also considered, but it was found that it was not as accurate in representing the thermodynamic properties of mixtures as the model under current consideration. The strong polarization of the methyl groups due to the adjacent carbonyl group means that the inherent approximation of GC methods, namely on the independence of the behaviour of a given group on their position on a given molecule is inappropriate for acetone. It is worth noting that the fluid-phase behaviour of acetone deviates significantly from that of other ketones [98]. The use of molecular groups to treat the first members of homologous series of polar molecules is well established in group contribution methodologies (see e.g., methanol and acetonitrile in the modified UNIFAC approach [99]).

Let us consider now the family of alkyl carboxylic acids. As has already been mentioned, a number of alkyl groups have been considered in previous works [71, 72]; they are each modelled with one segment and no association. The COOH carboxyl group is, however, more complex. In order to model fluids (pure compounds or mixtures) containing carboxylic acids as the only associating compounds (e.g., pure carboxylic acids, mixtures of acids, or mixtures of acids with non-polar, non-associating species, such as alkanes), only one association site is employed to mimic the formation of dimers that is characteristic of these fluids [12-14, 89]. However, in aqueous solutions of carboxylic acids a large number of water molecules are expected to bond to (solvate) the carboxylic acid group [80]. In order to develop a model reflecting the formation of these associated clusters, a number of sites need to be incorporated to mediate this interaction. Our proposed model of the COOH group comprises a single spherical segment (whereas our previous SAFT- γ square-well model comprised three identical segments [89]) with five association sites: one site of type H corresponding to the hydrogen atom in this group, two sites of type e_1 corresponding to the lone pairs of one of the oxygen atoms, and two sites of type e_2 for the lone pairs of the other oxygen atom (cf. Figure 1(b)).

As an example, for clarity, in the case of a binary mixture of an acid (labelled as group 6 in component 1; cf. Table 1 for the group numbering) and water (group 4 and component 2) the model of the mixture includes five site-types (and nine sites in total). For clarity, we provide the contribution to the Helmholtz free energy due to association in such a system follows from equations 13 and 14:

$$\begin{aligned} \frac{A^{\text{ASSOC}}}{Nk_B T} = & x_1 \left[\left(\ln X_{1,6,H} - \frac{X_{1,6,H}}{2} \right) + 2 \left(\ln X_{1,6,e_1} - \frac{X_{1,6,e_1}}{2} \right) + 2 \left(\ln X_{1,6,e_2} - \frac{X_{1,6,e_2}}{2} \right) + \frac{5}{2} \right] \\ & + x_2 \left[2 \left(\ln X_{2,4,H} - \frac{X_{2,4,H}}{2} \right) + 2 \left(\ln X_{2,4,e_1} - \frac{X_{2,4,e_1}}{2} \right) + \frac{4}{2} \right], \end{aligned} \quad (33)$$

with the fractions of molecules not bonded at each site given by solving the following mass action equations

$$X_{1,6,H} = \frac{1}{1 + x_1 \rho X_{1,6,H} \Lambda_{11,66,HH} + 2x_2 \rho X_{2,4,e_1} \Lambda_{12,64,He_1}} , \quad (34)$$

$$X_{1,6,e_1} = \frac{1}{1 + 2x_2 \rho X_{2,4,H} \Lambda_{12,64,e_1H}} , \quad (35)$$

$$X_{1,6,e_2} = \frac{1}{1 + 2x_2 \rho X_{2,4,H} \Lambda_{12,64,e_2H}} , \quad (36)$$

$$X_{2,4,H} = \frac{1}{1 + 2x_2 \rho X_{2,4,e_1} \Lambda_{22,44,e_1H} + 2x_1 \rho X_{1,6,e_1} \Lambda_{12,64,e_1H} + 2x_1 \rho X_{1,6,e_2} \Lambda_{12,64,e_2H}} , \quad (37)$$

$$X_{2,4,e_1} = \frac{1}{1 + 2x_2 \rho X_{2,4,H} \Lambda_{22,44,e_1H} + x_1 \rho X_{1,6,H} \Lambda_{12,64,He_1}} . \quad (38)$$

A model of the COOH group with four association sites (one site of type H, two sites of type e_1 sites and one of type e_2) has also been developed for comparison (see section 3.4).

2.3 Parameter estimation of functional groups

The like and unlike group-group interaction parameters needed to model the systems of interest are estimated using the experimental data for the thermodynamic and fluid-phase equilibria of appropriate pure components and some mixtures. All fluid-phase equilibria calculations are carried out either using the HELD (P,T) flash algorithm [95, 100] or the numerical solvers available in the gPROMS[®] software [101]. The parameter estimation involves a minimization of a least-square objective function consisting of an appropriate sum of individual residuals.

The general form of the objective function F_{obj} is given by

$$F_{obj} = \sum_Z \frac{\omega_Z}{N_Z} \sum_{i=1}^{N_Z} \left[\frac{Z_i^{exp} - Z_i^{calc}}{Z_i^{exp}} \right]^2 , \quad (39)$$

where the first sum is over the different properties Z considered, N_Z is the number of data points of property Z , ω_Z the weight of each property, and Z_i^{exp} and Z_i^{calc} the experimental and calculated values of the property at each data point i , respectively. Here, a data point is defined as a specific combination of compound(s), temperature, pressure, and total composition where relevant. The properties considered vary for different estimations and can include the vapour pressure and saturated liquid density data of only the pure components, and additionally the vapour-liquid and liquid-liquid equilibrium data, and excess enthalpy and volume data of some binary mixtures. The properties used to estimate each of the interaction parameters are specified in Section 3. All of the experimental data are obtained either from the NIST [20] or the Detherm [102] databases.

The accuracy of the SAFT- γ Mie group contribution methodology for the description of pure component properties of the molecules of interest here is evaluated using a percentage average absolute deviation (%AAD) defined as

$$\%AAD_Z = \frac{1}{N_Z} \sum_{i=1}^{N_Z} \left| \frac{Z_i^{\text{exp}}(T_i) - Z_i^{\text{calc}}(T_i)}{Z_i^{\text{exp}}(T_i)} \right| \times 100 \quad , \quad (40)$$

for any property of interest Z_i (e.g., vapour pressure, saturated density etc). In the case of mixtures properties the quality of the theoretical description is assessed graphically in our current work.

3 Results and discussion

In this section, we first summarize the group interactions needed to model the systems of interest, and then assess the performance of the SAFT- γ Mie models in describing the properties of pure acetone and a number of alkyl carboxylic acids, since an accurate description of the pure-component properties is required to obtain a good description of the properties of mixtures. The description of the thermodynamic properties and fluid-phase

equilibria of the other pure components considered in this study (linear and branched alkanes, and water) as well as their mixtures can be found in previous publications [71, 72, 82]. The performance of the SAFT- γ Mie models incorporating induced unlike site-site interactions for the description of the fluid-phase equilibria acetone + alkanes, acetone + water, carboxylic acids + alkanes and finally carboxylic acids + water binary mixtures is then assessed. A ternary mixture of acetone + water + *n*-hexane is also investigated which provides an assessment of the models for aqueous mixtures of acetone with a non-polar molecule.

3.1 Group interaction parameter tables

A summary of the different group-group interactions that are needed to model the systems of current interest is presented in Table 1. We indicate in the table the group interactions that have been estimated in previous publications and those which are estimated in our current work.

Table 1.

The estimated like group parameters that describe acetone CH_3COCH_3 and the COOH functional group are given in Table 2 together with the previously obtained like group parameters for the CH_3 , CH_2 , CH and H_2O groups [71, 72]. The estimated values of the unlike group parameters for the Mie potential interactions are provided in Table 3, and the estimated association interaction parameters (site-site hydrogen bond energy and bonding volume) are given in Table 4.

Table 2.

Table 3.

Table 4.

3.2. Acetone

As mentioned previously, acetone is modelled as a molecular group comprising three identical segments with three association sites, but only two of these (one of type H and one of type e_1) are active in the representation of the pure-fluid properties

Experimental vapour pressures and saturated liquid density data of pure acetone have been considered in the range 180 – 460 K [20]. These were the only experimental data included in the regression of the parameters for acetone. Once the SAFT- γ Mie parameters for the CH_3COCH_3 group (see Tables 2 to 4) have been estimated, they can be used to calculate the vapour-liquid equilibrium of pure acetone as well as other thermodynamic equilibrium properties. As can be seen in Figure 2, the proposed SAFT- γ Mie model of acetone provides a very accurate description of its vapour-liquid equilibrium. The deviations (%AAD) from the experimental data are 0.19% for the vapour pressure and 0.25% for the saturated liquid density (see Table 5). A comparison with the performance of a non-associating model of acetone is also included in the figure in order to emphasize the improvement obtained by the incorporation of association sites to mimic the strong dipole-dipole interactions in acetone. The improvement is especially marked in the near-critical region, with the associating model of acetone providing a much smaller over-prediction of the critical point compared to the non-associating model. For completeness, SAFT- γ Mie group parameters for the non-associating model are $v_k^* = 3$, $S_k = 0.66275$, $\lambda_{kk}^r = 15.719$, $\lambda_{kk}^a = 6.0000$, $\sigma_{kk} = 3.7260 \text{ \AA}$, and $\varepsilon_{kk}/k_B = 356.277 \text{ K}$. The good description of the properties of acetone provided by the SAFT- γ Mie framework is also valid for second-derivative properties, as can be seen Figure 3, in which the experimental data [103-106] for the speed of sound and the isobaric heat capacity of pure acetone are compared with the SAFT- γ Mie predictions. As demonstrated previously [67, 71, 72], the incorporation of a variable softness in the repulsion

via the Mie potential leads to a much-improved description of the second-derivative properties.

Figure 2.

Figure 3.

3.3. Alkyl carboxylic acids

As discussed in section 2.2 our SAFT- γ Mie representation of the alkyl carboxylic acids consists of one COOH group and the relevant linear and branched alkyl groups for each of the molecules considered. As a consequence, the like COOH-COOH, as well as unlike COOH-CH₃ and COOH-CH₂ group interaction parameters need to be determined. We use pure component data of the family of linear carboxylic acids, as well as selected binary mixture data of mixtures of *n*-alkanes and acids. The COOH group is represented here as one spherical group with five association sites. In order to treat the pure-component fluids only one site is active; we use the H site in the model to mediate the dimerisation interaction. The remaining four sites (two of type e₁ and two of type e₂) are inactive in the pure alkyl carboxylic acids and in mixtures of acids with non-polar components, as no hydrogen bonding of the COOH group with the alkyl groups occurs.

The vapour pressures and saturated liquid densities of three linear carboxylic acids (butanoic, heptanoic, and decanoic acid) [50, 105, 107-112] and the excess enthalpies of mixing of the binary mixtures of *n*-heptane with hexanoic acid and with butanoic acid [113] are considered in the estimation of the COOH-COOH group parameters as well as the CH₃-COOH and CH₂-COOH cross-interaction parameters. We have observed that the consideration of mixture data in the estimation procedure leads to more reliable model parameters than when pure component data alone is used, while keeping the resulting models

fully predictive for the description of fluid-phase equilibria as the mixture data used correspond to single-phase properties. The estimated group parameters for the COOH group and the unlike interactions with the CH₃ and CH₂ groups are given in Tables 2 to 4, while the values of the %AAD of the properties calculated or predicted with SAFT- γ Mie from the experimental properties are provided in Table 5.

A comparison of the experimental and calculated coexistence densities and the vapour pressures of the pure carboxylic acids from butanoic to decanoic acid are also depicted in Figure 4. Note that only three of the compounds are used in the estimation of the group parameters, together with excess enthalpy data of selected mixtures. The vapour-liquid equilibria of the acids not included in the parameter estimation procedure (pentanoic, hexanoic, octanoic and nonanoic acids), as well as the enthalpies of vaporization for butanoic to octanoic acids [114-116] are hence predicted. The experimental data available for acids longer than propanoic is very limited as the majority of data in the literature relates to the vaporization enthalpy considering vapour phase containing only monomers, see the discussion in Verevkin [117]. Breil et al. [80] have highlighted the complexity of modelling the thermodynamic properties of acids, and suggest including enthalpy of vapourisation experimental data in the determination of model parameters in order to obtain a good accuracy in the description of this property. In this context, our SAFT- γ Mie description, while not perfect, can be considered as providing a very good prediction of this property.

Figure 4.

A summary of the %AAD values of the vapour pressure and saturated liquid density for acetone and the alkyl carboxylic acids assessed in our current work is presented in Table 5. We find that the models proposed provide an excellent description of the vapour-liquid equilibria of acetone and of the linear alkyl carboxylic acids over a wide temperature range. The derivative properties of the linear alkyl carboxylic acids are, as in the case of acetone,

well described, as can be seen for the speed of sound in Figure 6 (b) of Reference [72], while we find the %AAD for the isobaric heat capacity for butanoic to decanoic acid to be 11.25% in the temperature range 273-673 K [105, 118, 119].

Table 5.

3.4 Description of the fluid properties of mixtures

We now focus on the description of the phase equilibria of mixtures containing polar and non-polar components

3.4.1 Acetone + *n*-alkane binary mixtures

We first investigate the properties of binary mixtures of acetone with linear alkanes; these systems serve as a good assessment of the adequacy of the model of acetone presented in Section 3.2. for the calculation and prediction of properties of mixtures with simple non-polar molecules. The mixtures can exhibit liquid-liquid equilibrium at low temperatures, characteristic of type II phase behaviour in the classification of van Konynenburg and Scott [120], and the usual vapour-liquid equilibrium at higher temperatures for intermediate-length *n*-alkanes. The vapour-liquid equilibrium is found to exhibit a low-boiling azeotrope in the case of acetone + *n*-hexane and acetone + *n*-heptane (cf. Figures 5 (a) – (d)), but is zeotropic in the case of acetone + *n*-octane (cf. Figure 5 (e)). As the alkanes are non-polar non-associating molecules, the active association sites on the acetone group in these mixtures are the same as in pure acetone, i.e., one site of type H, and one of type e_1 . The unlike group-group dispersion energy and the unlike repulsive exponent between the acetone and alkane groups (CH_3 and CH_2) are estimated using experimental isothermal VLE data of mixtures of acetone + *n*-heptane at 273.15, 323.15, and 338.15 K [121, 122]. These parameters can then be used to predict the fluid-phase behaviour of acetone + *n*-heptane at different conditions as well the behaviour of other acetone + *n*-hexane and acetone + *n*-octane binary mixtures.

The performance of the SAFT- γ Mie group models presented here is illustrated in Figure 5 based on a comparison of the description of the experimental fluid-phase equilibria of three mixtures of acetone with *n*-alkanes systems [121-128]. Calculations of the same properties with the modified UNIFAC [99] group-contribution approach are also presented in the figure.

Figure 5.

As can be seen from Figure 5, a very accurate simultaneous prediction of both the liquid-liquid and vapour-liquid equilibria of the non-ideal mixtures of acetone + *n*-alkanes can be achieved using the SAFT- γ Mie methodology. It is interesting to note that the description provided by our approach of the region near the upper critical solution temperature captures with greater accuracy the very flat shape of the liquid-liquid boundary close to the upper critical solution temperature observed experimentally.

Furthermore, one of the strengths of the SAFT- γ Mie framework is that one is able to describe not only fluid-phase equilibrium but also other thermodynamic properties such as the excess properties of mixing. In Figure 6 the SAFT- γ Mie prediction of the excess enthalpy and excess volume for the mixture acetone + *n*-heptane are compared with available experimental data [129, 130]. Qualitative agreement for the excess volumes and quantitative agreement for the excess enthalpies are observed; these predictions serve to confirm the validity of the approach and of the parameters developed. Although not shown, we can confirm a similar level of agreement is found in comparison with the experimental data of Marino *et al.* [130] for the mixture of acetone + *n*-hexane.

Figure 6.

To conclude the study of the acetone + alkane mixtures, the model of acetone developed is used to describe phase envelopes of two binary mixtures of acetone + branched alkanes: acetone + 2-methylbutane [131] and acetone + 2-methylpropane [132, 133]. Comparisons of

the SAFT- γ Mie predictions of the vapour-liquid equilibria with the available experimental data are shown in Figure 7.

We have tested our calculations for the presence of liquid-liquid separation that it is often observed in mixtures which exhibit low-boiling azeotropes at high pressure. A liquid-liquid phase split is found using the SAFT- γ Mie model for the 2-methylbutane + acetone system with a corresponding upper critical solution temperature of 202.7 K. To the best of our knowledge no experimental liquid-liquid equilibrium data has been reported in these mixtures, although in the case of 2-methylbutane + acetone the solid-liquid equilibrium data of Sapgir [134] appears to indicate the presence of immiscibility as the reported melting temperature is almost constant for mixtures comprising between 97% and 23% mole percent acetone, very close to the calculated concentrations of the liquid-liquid split.

The CH_3COCH_3 -CH unlike dispersion energy (ϵ_{kl}) required to model these systems is estimated using the vapour-liquid equilibrium data for the mixture of acetone + 2-methylbutane at 101.3 kPa (see Table 3 and Figure 7(a)), with the unlike repulsive exponent (λ_{kl}^r) obtained using the combining rule of equation 23. The parameters can then be used to predict the vapour-liquid equilibrium of the acetone + 2-methylpropane mixture as shown in Figure 6(b). The very good agreement confirms the suitability of our group models in the study of the properties of these mixtures.

Figure 6.

3.4.2 Acetone + water binary mixture

A particular challenge is posed in the case of the binary mixture of acetone + water. The acetone model developed in our current work comprises three different association-site types, only two of which are active in pure acetone and in mixtures involving non-polar components, as described in the previous sections. These two sites (one of type H and one of type e1)

mimic the directional nature of the dipole-dipole interactions present in such fluids. In mixtures of acetone with polar protic molecules, and specifically in aqueous mixtures, a more complex type of association arises. Water and acetone can form a hydrogen bond involving one of the hydrogen atoms on water and either one of the electron lone pairs on the oxygen atom of acetone [27, 28], represented in our association scheme by the water H sites bonding to the e_1 and e_2 sites of acetone, or with the alignment of the dipoles of water and acetone (as in the acetone-acetone case), mediated in this association scheme by the e_1 sites of water bonding to the H site of acetone. The resulting association scheme incorporate the fundamental physics of the interactions in acetone + water mixtures by mimicking the competition between the like water-water and acetone-acetone association (both of which promote phase separation), and the unlike water-acetone association (which promotes mixing).

The SAFT- γ Mie description of the vapour-liquid equilibrium of the acetone + water system over a wide range of conditions, as well as the excess properties of mixing are compared with the relevant experimental data in Figure 8 [135-139]. As can be seen, this mixture exhibits non-ideal behaviour including low-boiling azeotropes. The $\text{CH}_3\text{COCH}_3\text{-H}_2\text{O}$ unlike dispersion energy (ϵ_{kl}) as well as the unlike association energies ($\epsilon_{kl,ab}^{\text{HB}}$) and bonding volumes ($K_{kl,ab}$) between the association sites on acetone and water are estimated using experimental vapour-liquid equilibrium data at 323.15 K and 293.15 K, and are subsequently used to predict the vapour-liquid equilibrium boundaries at other conditions as well as excess enthalpies and volumes of mixing for aqueous solutions of acetone. The use of asymmetric hydrogen bonding or site models to take into account the induced unlike association occurring in these mixtures is crucial to achieve good agreement between the theoretical predictions of the fluid-phase equilibria and the experiment.

Figure 8.

3.4.2 Alkyl carboxylic acid + *n*-alkane binary mixtures

Following the same approach as with the mixtures comprising acetone, we first consider binary mixtures containing alkyl carboxylic acids and *n*-alkanes. As in the case of acetone + *n*-alkane, the association scheme used to treat the COOH group in mixtures with the *n*-alkanes is identical to that of the pure carboxylic acids; no induced association is expected in these mixtures given the non-polar nature of the alkanes. Of the five sites included to treat the COOH group only one is active in these mixtures in order to mediate the formation of dimers of acid molecules. It is interesting to note, however, that whereas the treatment of the acetone + *n*-alkane mixtures involved the estimation of two unlike interaction group parameters for the description of the interactions of the acetone molecular group with the CH₃ and CH₂ alkyl groups, fully predictive calculations of the properties of the carboxylic acid + *n*-alkane mixtures can be carried out at this point, as the unlike COOH-CH₃ and COOH-CH₂ interaction parameters have already been determined using experimental vapour-liquid equilibrium data of the linear carboxylic acids (cf. section 3.3.). The implementation of a heteronuclear molecular model in our SAFT- γ Mie method provides this key advantage by which mixture properties can be predicted without the need for experimental data. We recall that in determining the group interaction parameters needed to model pure carboxylic acids only pure component data and a limited set of selected excess-enthalpy data for two binary mixtures are used. The predicted and experimental [140, 141] vapour-liquid equilibria of two mixtures of carboxylic acids + *n*-alkanes are compared in Figure 9. As is apparent the more symmetric mixture (pentanoic acid + *n*-heptane) exhibits an extensive vapour-liquid envelope without azeotropy, while in the case of the butanoic acid + *n*-octane an azeotrope is seen. In addition a comparison of the predicted excess enthalpies of mixing of different carboxylic acid + *n*-alkane mixtures with the available experimental data [113, 142] is presented in Figure 10. A comparison of our calculations of the excess enthalpy for mixtures of butanoic

acid + *n*-heptane and hexanoic acid + *n*-heptane (used to determine the group interaction parameters) is also shown in Figures 10 (b) and (e). As can be appreciated from the figures the description of the excess enthalpy provided by the SAFT- γ Mie approach is excellent, confirming the quality of the parameters developed and of the underlying theory.

Figure 9.

Figure 10.

3.4.3 Alkylcarboxylic acid + water binary mixtures

The versatility of the SAFT- γ approach and the use of unlike induced association sites are particularly relevant in modelling mixtures containing alkyl carboxylic acids and water. We assess the validity of the SAFT- γ Mie model developed earlier for the COOH group by studying a binary mixture of butanoic acid and water. As described in section 2.2, the COOH group comprises five association sites (one of type H, two of type e_1 and another two of type e_2), only one of which (the H site) is active in the absence of other associating groups; this site labelled H is used to mediate the formation of dimer species known to occur in pure acids. The other sites mediate the unlike association (solvation interactions) that occurs between the acids and water. The hydrogen bonding of the lone-pairs of electrons of the oxygens in the COOH group with the hydrogens of water, and of the hydrogen of the COOH group with the electron lone pairs of water are accounted for in our model. As in the case of the mixture of acetone + water the proposed association scheme resembles the competition between like interactions in the pure fluids, i.e., the dimerization of the acids and the hydrogen bonding between water molecules on the one hand, both of which promote phase separation, and the acid-water hydrogen bonding on the other that stabilizes a single liquid phase.

The experimental vapour-liquid equilibrium data of the butanoic acid + water system [21, 143] are compared with the description obtained with the SAFT- γ Mie approach in Figure 11.

In addition to the results obtained using the selected model of the COOH group with five association sites, the description obtained using a model with only four association sites is included for comparison. In this four site model the unlike induced association interaction is mediated by one site of type H site, two sites of type e1, and only one site of type e2. The SAFT- γ Mie group parameters for this four-site model are $\nu_k^* = 1$, $S_k = 0.55593$, $\lambda_{kk}^r = 8.0000$, $\lambda_{kk}^a = 6.0000$, $\sigma_{kk} = 4.3330 \text{ \AA}$, and $\varepsilon_{kk}/k_B = 405.78 \text{ K}$, $\varepsilon_{kl,ab}^{\text{HB}}/k_B = 6427.9 \text{ K}$, $K_{kl,ab} = 0.80620 \text{ \AA}^3$. As can be seen from Figure 11, it is apparent that the SAFT- γ Mie provides a very good description of the fluid-phase equilibria of the butanoic acid + water mixture; the model incorporating an unlike induced association interaction mediated by five sites in the acid group is found to be in better agreement with experiment than the corresponding model incorporating four sites for the unlike association.

Figure 11.

Although not shown in the figure we have also tested the COOH model proposed here to calculate the excess volume of mixing of butanoic acid + water at the conditions measured by Faucon [144] and find good agreement with the data. We note here however, that for the case of the phase behaviour of the shorter acids (acetic and propionic) the strong polarization of the proximal CH₃ and CH₂ groups mean that the phase behaviour is unfortunately not predicted accurately with the model proposed here for the COOH group. In future work we will introduce second-order group parameters to address the challenge of modelling the entire family of carboxylic-water mixtures. Thus, at this point, in order to validate our concept of the use of unlike induced association sites to treat complex aqueous mixtures we leave aside the treatment of aqueous mixtures containing acids and turn our attention to the study of a ternary mixture containing acetone.

3.4.5 Ternary mixtures containing acetone and water

As the various group-group interaction parameters have now been developed and their performance assessed for the description of the fluid-phase equilibrium and excess properties of representative pure components and binary mixtures, a more complex ternary mixture including polar and non-polar components can now be examined. As a prototypical example we select the mixtures of acetone + water + *n*-hexane and acetone + water + *n*-heptane, which have a direct application in CCC [2], as these systems exhibit liquid-liquid phase separation over a broad range of conditions. The phase separation in the acetone + water + *n*-alkane ternary mixture originates from the marked liquid-liquid immiscibility observed in the water + *n*-alkane mixtures, while acetone is fully soluble in water and in the *n*-alkanes. The SAFT- γ Mie predicted phase behaviour at 298 K and 0.1 MPa [145-149] is illustrated in Figure 12 (a) for acetone + water + *n*-hexane and compared to experimental data; in Figure 12 (b) the predicted phase behaviour for acetone + water + *n*-heptane is shown, also with corresponding experimental data. The fluid-phase behaviour of these systems is characterized by two-phase liquid-liquid immiscibility regions that are very wide at low acetone content, with the extent of phase separation decreasing as the amount of acetone increases, until both phases are fully miscible at so-called plait points (critical points). Here, the three sites of the SAFT- γ Mie acetone model are used to mediate the acetone-water induced unlike hydrogen interaction (solvation). Very good agreement of the theoretical prediction and the experimental data is observed, including the description of the tie lines in the case of acetone + water + *n*-hexane. The predicted tie-lines for the mixture of acetone + water + *n*-heptane are not in as good agreement with the reported experimental tie-lines, but it is encouraging to note that the phase boundary for this mixture is predicted with good accuracy.

The phase behaviour of mixtures including carboxylic acids is considered in Figure 13, where the experimental densities [150] for the acetone + water + butanoic acid system are

compared with the SAFT- γ Mie predictions. To the best of our knowledge these are the only experimental data available in the literature for mixtures of acetone + water + carboxylic acids of intermediate chain length (butanoic to decanoic). These data provide a good test of our unlike induced association-site models, as in these systems all the association sites are active.

The quality of the SAFT- γ Mie predictions for these three ternary systems underlines the ability and versatility of the theory in the treatment of induced unlike association interactions for systems comprising water, acetone, carboxylic acids, and alkanes.

Figure 12.

Figure 13.

4 Conclusion

The complexity of the interactions and specifically of the association behaviour observed in mixtures containing acetone and alkyl carboxylic acids in mixtures with water and with non-polar compounds requires an appropriate theoretical treatment to describe accurately the thermodynamic properties of these systems. We have presented new SAFT- γ Mie group models for acetone and the COOH carboxylic acid groups, and for a number of unlike group interactions involving these groups. In order to treat mixtures including water, unlike induced association sites are incorporated in the SAFT- γ Mie models proposed for acetone and for the COOH group to mediate the unlike association interactions. These sites are present in the groups, but are active only in some mixtures depending on the hydrogen bonding capability of the other groups and molecules in the system. The resulting association schemes effectively describe the competition of hydrogen-bond formation between the species in the mixtures. The resulting models are especially robust for the treatment of mixtures containing acetone and provide an excellent description of the fluid-phase behaviour (including both

vapour-liquid and liquid-liquid equilibrium) and the excess properties of the mixtures (excess enthalpy and volume of mixing), while retaining a high degree of transferability between thermodynamic conditions and systems, as well as the predictive capability that is a trademark of group-contribution models in general and of the SAFT- γ Mie framework in particular. For the case of the acid COOH group, we find the model developed to be suitable for the description and prediction of the phase equilibria and excess properties of alkylcarboxylic acids and of mixtures of acids and *n*-alkanes, but to be only of limited predictive ability in for aqueous solutions of acids. We have discussed here the results obtained for the binary mixture of butanoic acid + water, but leave for further work a more comprehensive study of the family of mixtures containing carboxylic acids and water. In our current paper we have employed the concept of induced unlike association within the SAFT- γ Mie framework to treat complex mixtures where the unlike association interactions are very different from those in one or both of the pure components. Given the overall accuracy of the description presented here, we plan in future to follow this route and extend the treatment to other groups and to the characterisation of further unlike interactions.

Author Information

Corresponding Author

*Email: a.galindo@imperial.ac.uk; Tel: +44 (0)20 75 94 56 06

Acknowledgement

We gratefully acknowledge the Technology Strategy Board (TSB) of the United Kingdom for providing financial support under the project CADSEP-101326 (grant EP/K504099). V.P. thanks the Engineering and Physical Sciences Research Council (EPSRC) of the UK for the award of a PhD studentship and a Doctoral Prize Fellowship 2013. C.S.A.

is thankful to the EPSRC for the award of a Leadership Fellowship (EP/J003840). The authors acknowledge additional funding to the Molecular Systems Engineering (MSE) Group from EPSRC (grants GR/T17595, GR/N35991, EP/E016340 and EP/J014958), the Joint Research Equipment Initiative (JREI) (grant GR/M94426), and the Royal Society-Wolfson Foundation refurbishment scheme (grant RSWF/SUC11/RND3/EEP).

5 References

- [1] J. Urilloyd, Solvents in pharmacy, *J. Am. Pharm. Assoc.*, 7 (1918) 137-149.
- [2] H. Guzek, Counter-current Chromatography for the Purification of High Value Natural Compounds: Performance Modelling and Solvent Selection., in, Imperial College London, London, UK, 2011.
- [3] Handbook of Industrial Crystallization 2nd ed., Butterworth-Heinemann, Woburn, 2002.
- [4] R.A. Granberg, A.C. Rasmuson, Solubility of Paracetamol in Binary and Ternary Mixtures of Water + Acetone + Toluene, *J. Chem. Eng. Data*, 45 (2000) 478-483.
- [5] L. Pauling, The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement, *J. Am. Chem. Soc.*, 57 (1935) 2680-2684.
- [6] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, NY, 1939.
- [7] G.A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, New York, 1997.
- [8] Y. Maréchal, The Hydrogen Bond and the Water Molecule, Elsevier, 2007.
- [9] W.A.P. Luck, A Model of Hydrogen - Bonded Liquids, *Angew. Chem. Int. Edn.*, 19 (1980) 28-41.
- [10] A.K. Soper, M.G. Phillips, A new determination of the structure of water at 25 C, *Chem. Phys.*, 107 (1986) 47-60.
- [11] M.L. Huggins, Hydrogen bridges in organic compounds, *J. Org. Chem.*, 1 (1936) 405-456.
- [12] S. Bratoz, D. Hazi, N. Sheppard, The Infra-Red Absorption Bands Associated with the COOH and COOD Groups in Dimeric Carboxylic Acids. II. The Region from 3700 to 1500 cm⁻¹, *Spectrochim. Acta*, 8 (1956) 249-261.
- [13] D. Hazi, N. Sheppard, The Infra-Red Absorption Bands Associated with the COOH and COOD Groups in Dimeric Carboxylic Acids. I. The Region from 1500 to 500 cm⁻¹, *Proc. Roy. Soc. London A*, 216 (1953) 247-266.
- [14] A.D.H. Clague, The heat of dimerization of some carboxylic acids in the vapour phase determined by a spectroscopic method, *Spectrochim. Acta Part A*, 25 (1969) 593-596.
- [15] C.G. Cannon, The nature of hydrogen bonding. A review of published work and discussion, *Spectrochim. Acta*, 10 (1958) 341-368.
- [16] B. Chen, I. Ivanov, M.L. Klein, M. Parrinello, Hydrogen Bonding in Water, *Phys. Rev. Lett.*, 91 (2003) 215503.
- [17] R.W. Gora, S.J. Grabowski, G. Leszczynski, Dimers of Formic Acid, Acetic Acid, Formamide and Pyrrole-2-carboxylic Acid: an Ab Initio Study, *J. Phys. Chem. A*, 109 (2005) 6397-6405.
- [18] C. Vega, J.L.F. Abascal, Simulating water with rigid non-polarizable models: a general perspective, *Phys. Chem. Chem. Phys.*, 13 (2011) 19663-19688.

- [19] B. Guillot, A reappraisal of what we have learnt during three decades of computer simulations on water, *J. Mol. Liq.*, 101 (2002) 219-260.
- [20] P.J. Linstrom, W.G. Mallard, NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institutes of Standards and Technology WebBook, Gaithersburg MD, 20899.
- [21] F. Rivenq, Ebulliometric Measurements of the Mixture Water and Butyric Acid, *Bull. Soc. Chim. Fr.*, (1962) 1192-1195.
- [22] M.B. Oliveira, M.J. Pratas, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, Description of the Mutual Solubilities of Fatty Acids and Water with the CPA EoS AICHE J., 55 (2009) 1604-1613.
- [23] F. Drouillon, Study of the ternary mixture: water, ethyl alcohol, normal butyl alcohol *J. Chim. Phys.*, 22 (1925) 149-168.
- [24] R.D. Nelson, D.R. Lide, A.A. Maryott, Selected Values of Electric Dipole Moments for Molecules in the Gas Phase. , in: *Natl. Stand. Ref. Data Ser. , Nat. Bur. Stnds. , 1967.*
- [25] K. Kojima, K. Tochigi, K. Kurihara, M. Nakamichi, Isobaric Vapor-Liquid Equilibria for Acetone + Chloroform + Benzene and the Three Constituent Binary Systems, *J. Chem. Eng. Data*, 36 (1991) 343-345.
- [26] C.M. Huggins, G.C. Pimentel, J.N. Shoolery, Proton Magnetic Resonance Studies of Chloroform in Solution: Evidence for Hydrogen Bonding, *J. Chem. Phys.*, 23 (1955) 1244-1247.
- [27] K. Coutinho, N. Saavedra, S. Canuto, Theoretical analysis of the hydrogen bond interaction between acetone and water, *J. Mol. Struct.: THEOCHEM* 466 (1999) 69-75.
- [28] N.S. Bayliss, E.G. McRae, Solvent Effects in the Spectra of Acetone, Crotonaldehyde, Nitromethane and Nitrobenzene, *J. Phys. Chem.*, 58 (1954) 1006-1011.
- [29] K. Kojima, K. Ochi, Y. Nakazawa, Relationship between Liquid Activity Coefficient and Composition for Ternary Systems, *Int. Chem. Eng.*, 9 (1969) 342-347.
- [30] F. Dolezalek, Zur Theorie der binären Gemische und konzentrierten Lösungen., *Z. Phys. Chem.*, 64 (1908) 727-747.
- [31] C. McCabe, A. Galindo, SAFT Associating Fluids and Fluid Mixtures, in: A.R.H. Goodwin, J.V. Sengers, C.J. Peters (Eds.) *Applied Thermodynamics of Fluids*, Royal Society of Chemistry, London, 2010.
- [32] J.J. van Laar, Über Dampfspannungen von binären Gemischen, *Z. Phys. Chem.*, 72 (1910) 723-751.
- [33] J.J. van Laar, Zur Theorie der Dampfspannungen von binären Gemischen, *Z. Phys. Chem.*, 83 (1913) 599-609.
- [34] J. Rodriguez, N.M. Dowell, F. Llovel, C.S. Adjiman, G. Jackson, A. Galindo, Modeling the fluid phase behavior of aqueous mixtures of multifunctional alkanolamines and carbon dioxide using transferable parameters with the SAFT-VR approach, *Mol. Phys.*, 110 (2012) 1325-1348.
- [35] T.L. Hill, *Statistical Mechanics*, McGraw-Hill, New York, 1956.
- [36] T.L. Hill, *Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, 1960.
- [37] H.C. Andersen, Cluster expansions for hydrogen - bonded fluids. I. Molecular association in dilute gases, *J. Chem. Phys.*, 59 (1973) 4714-4725.
- [38] H.C. Andersen, Cluster expansions for hydrogen bonded fluids. II. Dense liquids, *J. Chem. Phys.*, 61 (1974) 4985-4992.
- [39] D. Chandler, L.R. Pratt, Statistical mechanics of chemical equilibria and intramolecular structures of nonrigid molecules in condensed phases, *J. Chem. Phys.*, 65 (1976) 2925-2940.
- [40] L.W. Dahl, H.C. Andersen, A theory of the anomalous thermodynamic properties of liquid water, *J. Chem. Phys.*, 78 (1983) 1980-1993.

- [41] L.W. Dahl, H.C. Andersen, Cluster expansions for hydrogen - bonded fluids. III. Water, *J. Chem. Phys.*, 78 (1983) 1962-1979.
- [42] F. Hirata, Statistical Mechanical Calculation of the Radial Distribution Function for a Water-like Fluid, *Bull. Chem. Soc. Japan*, 50 (1977) 1032-1039.
- [43] J.S. Høye, K. Olaussen, Statistical mechanical model with chemical reaction, *Phys. A*, 104 (1980) 435 - 446.
- [44] A. Ben-Naim, Application of an Approximate Percus–Yevick Equation for Liquid Water, *J. Chem. Phys.*, 52 (1970) 5531-5541.
- [45] A. Ben-Naim, Statistical Mechanics of “Waterlike” Particles in Two Dimensions. I. Physical Model and Application of the Percus–Yevick Equation, *J. Chem. Phys.*, 54 (1971) 3682-3695.
- [46] A. Ben-Naim, Statistical mechanics of water-like particles in two-dimensions II. One component system, *Mol. Phys.*, 24 (1972) 705-721.
- [47] A. Ben-Naim, F.H. Stillinger, Aspects of the Statistical-Mechanical Theory of Water, in: R.A. Horne (Ed.) *Water and Aqueous Solutions: Structure, Thermodynamic and Transport Processes*, Wiley, New York, 1972.
- [48] S.L. Carnie, D.Y.C. Chan, G.R. Walker, The statistical mechanics of ion-dipole-tetrahedral quadrupole mixtures, *Mol. Phys.*, 43 (1981) 1115-1138.
- [49] P.T. Cummings, G. Stell, Statistical mechanical models of chemical reactions II. Analytic solution of the Percus-Yevick approximation for a model of homogeneous association, *Mol. Phys.*, 55 (1985) 33-48.
- [50] G.W.A. Kahibaum, C.G. von Wirkner, Studies on vapor stress measurements. 2nd section 1st part (vol 2a), in, 1897, pp. 1-222.
- [51] Y.V. Kalyuzhnyi, G. Stell, On the effects of association in fluids with spherically symmetric interactions I. Cluster expansions and integral equations, *Mol. Phys.*, 78 (1993) 1247-1258.
- [52] J. Kolafa, I. Nezbeda, Monte Carlo simulations on primitive models of water and methanol, *Mol. Phys.*, 61 (1987) 161-175.
- [53] I. Nezbeda, J. Kolafa, Y.V. Kalyuzhnyi, Primitive model of water II. Theoretical results for the structure and thermodynamic properties, *Mol. Phys.*, 68 (1989) 143-160.
- [54] G.N. Patey, S.L. Carnie, Theoretical results for aqueous electrolytes. Ion – ion potentials of mean force and the solute - dependent dielectric constant, *J. Chem. Phys.*, 78 (1983) 5183-5190.
- [55] W.R. Smith, I. Nezbeda, A simple model for associated fluids, *J. Chem. Phys.*, 81 (1984) 3694-3699.
- [56] G. Stell, Y. Zhou, Chemical association in simple models of molecular and ionic fluids, *J. Chem. Phys.*, 91 (1989) 3618-3623.
- [57] Y. Zhou, G. Stell, Chemical association in simple models of molecular and ionic fluids. II. Thermodynamic properties, *J. Chem. Phys.*, 96 (1992) 1504-1506.
- [58] M.S. Wertheim, Fluids with highly directional attractive forces: II. Thermodynamic perturbation theory and integral equations, *J. Stat. Phys.*, 35 (1984) 35-47.
- [59] M.S. Wertheim, Fluids with highly directional attractive forces: I. Statistical thermodynamics, *J. Stat. Phys.*, 35 (1984) 19-34.
- [60] M.S. Wertheim, Fluids with highly directional attractive forces: IV. Equilibrium polymerization, *J. Stat. Phys.*, 42 (1986) 477-492.
- [61] M.S. Wertheim, Fluids with highly directional attractive forces: III. Multiple attraction sites, *J. Stat. Phys.*, 42 (1986) 459-476.
- [62] W.G. Chapman, G. Jackson, K.E. Gubbins, Phase equilibria of associating fluids. Chain molecules with multiple bonding sites, *Mol. Phys.*, 65 (1988) 1057-1079.

- [63] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, SAFT: Equation-of-state solution model for associating fluids, *Fluid Phase Equilib.*, 52 (1989) 31-38.
- [64] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, New reference equation of state for associating liquids, *Ind. Eng. Chem. Res.*, 29 (1990) 1709-1721.
- [65] E.A. Müller, K.E. Gubbins, An equation of state for water from a simplified intermolecular potential, *Ind. Eng. Chem. Res.*, 34 (1995) 3662-3673.
- [66] A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, Statistical Associating Fluid Theory for chain molecules with attractive potentials of variable range, *J. Chem. Phys.*, 106 (1997) 4168-4186.
- [67] T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C.S. Adjiman, E.A. Müller, G. Jackson, Accurate perturbation theory for chains of Mie soft-core segments (SAFT-VR Mie) for the description of vapour-liquid equilibria and derivative properties, *J. Chem. Phys.*, 139 (2013) 154504.
- [68] I.G. Economou, Statistical Associating Fluid Theory: A successful model for the calculation of thermodynamic and phase equilibrium properties of complex fluid mixtures, *Ind. Eng. Chem. Res.*, 41 (2002) 953-962.
- [69] E.A. Müller, K.E. Gubbins, Molecular-based equations of state for associating fluids: A review of SAFT and related approaches, *Ind. Eng. Chem. Res.*, 40 (2001) 2193-2211.
- [70] S.P. Tan, H. Adidharma, M. Radosz, Recent advances and applications of Statistical Associating Fluid Theory, *Ind. Eng. Chem. Res.*, 47 (2008) 8063-8082.
- [71] V. Papaioannou, T. Lafitte, C. Avendaño, C.S. Adjiman, G. Jackson, E.A. Müller, A. Galindo, Group contribution methodology based on the statistical associating fluid theory for heteronuclear molecules formed from Mie segments, *J. Chem. Phys.*, 140 (2014) 054107.
- [72] S. Dufal, V. Papaioannou, M. Sadeqzadeh, T. Pogiatis, A. Chremos, C.S. Adjiman, G. Jackson, A. Galindo, Prediction of Thermodynamic Properties and Phase Behavior of Fluids and Mixtures with the SAFT- γ Mie Group-Contribution Equation of State, *J. Chem. Eng. Data*, 59 (2014) 3272-3288.
- [73] W.G. Chapman, K.E. Gubbins, C.G. Joslin, C.G. Gray, Theory and simulation of associating liquid mixtures, *Fluid Phase Equilib.*, 29 (1986) 337-346.
- [74] M.N. García-Lisbona, A. Galindo, G. Jackson, A.N. Burgess, Predicting the high-pressure phase equilibria of binary aqueous solutions of 1-butanol, n-butoxyethanol and n-decylpentaerythritol ether (C10E5) using the SAFT-HS approach, *Mol. Phys.*, 93 (1998) 57-72.
- [75] M.N. García-Lisbona, A. Galindo, G. Jackson, A.N. Burgess, An Examination of the Cloud Curves of Liquid-Liquid Immiscibility in Aqueous Solutions of Alkyl Polyoxyethylene Surfactants Using the SAFT-HS Approach with Transferable Parameters, *J. Am. Chem. Soc.*, 120 (1998) 4191-4199.
- [76] M. Kleiner, G. Sadowski, Modeling of Polar Systems Using PCP-SAFT: An Approach to Account for Induced-Association Interactions, *J. Phys. Chem. C*, 111 (2007) 15544-15553.
- [77] M. Kleiner, G. Sadowski, Modeling vapor-liquid equilibria of ethanol + 1,1,1,2,3,3,3-heptafluoropropane binary mixtures using PC-SAFT, *Fluid Phase Equilib.*, 260 (2007) 190-194.
- [78] A. Grenner, I. Tsivintzelis, I.G. Economou, C. Panayiotou, G.M. Kontogeorgis, Evaluation of the Nonrandom Hydrogen Bonding (NRHB) Theory and the Simplified Perturbed-Chain-Statistical Associating Fluid Theory (sPC-SAFT). 1. Vapor-Liquid Equilibria, *Ind. Eng. Chem. Res.*, 47 (2008) 5636-5650.
- [79] I. Tsivintzelis, A. Grenner, I.G. Economou, G.M. Kontogeorgis, Evaluation of the Nonrandom Hydrogen Bonding (NRHB) Theory and the Simplified Perturbed-Chain-Statistical Associating Fluid Theory (sPC-SAFT). 2. Liquid-Liquid Equilibria and

- Prediction of Monomer Fraction in Hydrogen Bonding Systems, *Ind. Eng. Chem. Res.*, 47 (2008) 5651-5659.
- [80] M.P. Breil, G.M. Kontogeorgis, P.K. Behrens, M.L. Michelsen, Modeling of the Thermodynamics of the Acetic Acid–Water Mixture Using the Cubic-Plus-Association Equation of State, *Ind. Eng. Chem. Res.*, 50 (2011) 5795-5805
- [81] G. Jackson, W.G. Chapman, K.E. Gubbins, Phase equilibria of associating fluids. Spherical molecules with multiple bonding sites, *Mol. Phys.*, 65 (1988) 1-31.
- [82] S. Dufal, T. Lafitte, A.J. Haslam, A. Galindo, G.N.I. Clark, C. Vega, G. Jackson, The A in SAFT: Developing the contribution of association to the free energy within a Wertheim TPT1 treatment of generic Mie fluids. , *Mol. Phys.*, 113 (2015) 948-984.
- [83] L.L. Lee, *Molecular Thermodynamics of Nonideal Fluids*, Butterworths, 1988.
- [84] J.A. Barker, D. Henderson, Perturbation theory and equation of state for fluids.II. A successful theory of liquids, *J. Chem. Phys.*, 47 (1967) 4714-4721.
- [85] J.A. Barker, D. Henderson, What is "liquid" ? Understanding the states of matter, *Rev. Mod. Phys.*, 48 (1976) 587-671.
- [86] B.J. Zhang, Calculating thermodynamic properties from perturbation theory I. An analytic representation of square-well potential hard-sphere perturbation theory, *Fluid Phase Equilib.*, 154 (1999) 1-10.
- [87] P. Paricaud, A general perturbation approach for equation of state development: Applications to simple fluids, ab initio potentials, and fullerenes, *J. Chem. Phys.*, 124 (2006) 154505.
- [88] A. Lymperiadis, C.S. Adjiman, A. Galindo, G. Jackson, A group contribution method for associating chain molecules based on the statistical associating fluid theory (SAFT - gamma), *J. Chem. Phys.*, 127 (2007) 234903.
- [89] A. Lymperiadis, C.S. Adjiman, G. Jackson, A. Galindo, A generalisation of the SAFT - gamma group contribution method for groups comprising multiple spherical segments, *Fluid Phase Equilib.*, 274 (2008) 85-104.
- [90] Y. Peng, K.D. Goff, M.C. dos Ramos, C. McCabe, Developing a predictive group-contribution-based SAFT-VR equation of state, *Fluid Phase Equilib.*, 277 (2009) 131-144.
- [91] Y. Peng, H. Zhao, C. McCabe, On the thermodynamics of diblock chain fluids from simulation and heteronuclear Statistical Associating Fluid Theory for potentials of variable range, *Mol. Phys.*, 104 (2006) 571-586.
- [92] J.S. Rowlinson, F.L. Swinton, *Liquids and liquid mixtures*, 3rd ed., Butterworths, London, 1982.
- [93] A.J. Haslam, A. Galindo, G. Jackson, Prediction of binary intermolecular potential parameters for use in modelling fluid mixtures, *Fluid Phase Equilib.*, 266 (2008) 105-128.
- [94] K.E. Bett, J.S. Rowlinson, G. Saville, *Thermodynamics for chemical engineers*, MIT Press, Cambridge, 1975.
- [95] F.E. Pereira, G. Jackson, A. Galindo, C.S. Adjiman, A duality-based optimisation approach for the reliable solution of (p,T) phase equilibrium in volume-composition space, *Fluid Phase Equilib.*, 299 (2010) 1-23.
- [96] G.N.I. Clark, A.J. Haslam, A. Galindo, G. Jackson, Developing optimal Wertheim-like models of water for use in Statistical Associating Fluid Theory (SAFT) and related approaches, *Mol. Phys.*, 104 (2006) 3561-3581.
- [97] J.N. Spencer, G.M. Bodner, L.H. Rickard, *Chemistry: Structure and Dynamics*, 5th ed., Wiley, New York, 2011.
- [98] E.H. Benmekki, G.A. Mansoori, Phase equilibrium calculations of highly polar systems, *Fluid Phase Equilib.*, 32 (1987) 139-149.
- [99] J. Gmehling, J. Li, M. Schiller, A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties, *Ind. Eng. Chem. Res.*, 32 (1993) 178-193.

- [100] F.E. Pereira, G. Jackson, A. Galindo, C.S. Adjiman, The HELD algorithm for multicomponent, multiphase equilibrium calculations with generic equations of state, *Comput. Chem. Eng.*, 36 (2012) 99-118.
- [101] gPROMS v. 3.4.0, in, PSE Ltd., 2011.
- [102] D.A. Fletcher, R.F.M. Meeking, D. Parkin, The United Kingdom Chemical Database Service, *J. Chem. Inf. Comput. Sci.*, 36 (1996) 746-749.
- [103] R.M. Ibberson, W.I.F. David, O. Yamamuro, Y. Miyoshi, T. Matsuo, H. Suga, Calorimetric, dielectric, and neutron diffraction studies on phase transitions in ordinary and deuterated acetone crystals, *J. Phys. Chem.*, 99 (1995) 14167-14173.
- [104] A.V. Korabelnikov, N.F. Otpushchennikov, Acoustic and thermodynamic properties of acetone on saturation line, *Uch. Zap. Kursk. Gos. Pedagog. Inst.*, 91 (1971) 194-208.
- [105] G. Liessmann, W. Schmidt, S. Reiffarth, Recommended Thermophysical Data, Data compilation of the Saechsische Olefinwerke Boehlen Germany, (1995).
- [106] R. Vilcu, B. Coman, Determination of heat capacities of some alcohols and ketones in vapor phase, *Rev. Roum. Chim.*, 20 (1975) 603-609.
- [107] D. Ambrose, J.H. Ellender, H.A. Gundry, D.A. Lee, R. Townsend, Thermodynamic properties of organic oxygen compounds. LI. Vapor pressure of esters and fatty acids, *J. Chem. Thermodyn.*, 13 (1981) 795-802.
- [108] G. Bernardo-Gil, M. Esquivel, A. Ribeiro, Densities and refractive indices of pure organic acids as a function of temperature, *J. Chem. Eng. Data*, 35 (1990) 202-204.
- [109] J.M. Costello, S.T. Bowden, The temperature variation of orthobaric density difference in liquid-vapor systems. IV. Fatty acids, *Recl. Trav. Chim. Pays-Bas*, 77 (1958) 803-810.
- [110] J.J. Jasper, G.B. Miller, The vapor pressure of monofluoroacetic acid, *J. Phys. Chem.*, 59 (1955) 441-442.
- [111] W.O. Pool, A.W. Ralston, Boiling points of n-alkyl acids, *Ind. Eng. Chem. Ind. Ed.*, 34 (1942) 1104-1105.
- [112] C. Spizzichino, Contribution a l'Etude des Tensions de Vapeur et des Chaleurs de Vaporisation des Acides Gras, Esters Methyliques et Alcools Gras a des Pressions Inferieures A 1 mm de Mercure, *J. Rech. C.N.R.S.*, 34 (1956) 1-24.
- [113] E. Wilhelm, A. Inglese, J.-P.E. Grolier, Excess molar enthalpies of (an alkanoic acid+n-heptane, or cyclohexane, or benzene) at T= 298.15 K, *The Journal of Chemical Thermodynamics*, 31 (1999) 1165-1174.
- [114] E. Andereya, J.D. Chase, The Implications of Carboxylic Acid Properties, *Chem. Eng. Technol.*, 13 (1990) 304-312.
- [115] J.C. Brown, A direct method for determining latent heat of evaporation, *J. Chem. Soc.*, 83 (1903) 987-994.
- [116] L.V. Jasperson, L.C. Wilson, J. Brady, W.V. Wilding, G.M. Wilson, Vapor association of monocarboxylic acids from heat of vaporization and pvT measurements, *AIChE Symp. Ser.*, 85 (1989) 102-139.
- [117] S.P. Verevkin, Measurement and Prediction of the Monocarboxylic Acids Thermochemical Properties, *J. Chem. Eng. Data*, 45 (2000) 953-960.
- [118] R.C.F. Schaake, J.C. van Miltenburg, C.G. de Kruif, Thermodynamic Properties of the Normal Alkanoic Acids I. Molar Heat Capacities of Seven Odd-numbered Normal Alkanoic Acids, *J. Chem. Thermodyn.*, 14 (1982) 771-778.
- [119] R.C.F. Schaake, J.C. van Miltenburg, C.G. de Kruif, Thermodynamic Properties of the Normal Alkanoic Acids I. Molar Heat Capacities of Seven Odd-numbered Normal Alkanoic Acids, *J. Chem. Thermodyn.*, 14 (1982) 763-769.
- [120] P.H. van Konynenburg, R.L. Scott, Critical lines and phase equilibria in binary van der Waals mixtures, *Philos. Trans. R. Soc. London, Ser. A*, 298 (1980) 495-540.

- [121] G.C. Benson, Excess Gibbs energy and LVE in propanone and normal alkane binary mixtures. , Int. Data Ser. , Sel. Data Mixtures, Ser. A, (1979) 25.
- [122] J.R. Loehe, H.C.V. Ness, M.M. Abbott, Vapor-liquid equilibrium of ketone and n-alkane mixtures, Int. Data Ser. , Sel. Data Mixtures, Ser. A (1979) 45.
- [123] J. Acosta, A. Arce, J. Martínez-Ageitos, E. Rodil, A. Soto, Vapor-Liquid Equilibrium of the Ternary System Ethyl Acetate + Hexane + Acetone at 101.32 kPa. , J. Chem. Eng. Data, 47 (2002) 849-854.
- [124] R. Barraza, S. Díaz, J. Edwards, P. Tapia, Thermodynamics of the Systems n-Hexane/3-Pentanone, n-Hexane/Acetone and n-Heptane/3-Pentanone Mixtures, Z. Phys. Chem., 117 (1979) 43-54.
- [125] G. Kolasinska, M. Goral, J. Giza, Vapor-liquid equilibria and excess gibbs free energy in binary systems of acetone with aliphatic and aromatic hydrocarbons at 313.15 K, Z. Phys. Chem. Leipzig, 263 (1982) 151-160.
- [126] G. Spinolo, R. Riccardi, Liquid-liquid equilibria in propanone and n-alkane mixtures, Int. Data Ser. Sel. Data Mixtures Ser. A, 2 (1977) 91-94.
- [127] W. Wolff, K. Bernstorff, Die Mischungslücke im System Aceton-n-Heptan und ihre Berechnung aus Aktivitätskoeffizienten. , Z. Phys. Chem., 14 (1958) 208-229.
- [128] A. Zacharias, D. Srinivasan, M.G.S. Rau, Isobaric Vapor-Liquid Equilibria for the Systems Acetone - n-Heptane and n-Hexane - Trichloroethylene, Indian J. Technol., 14 (1976) 162-164.
- [129] A. Lietzmann, B. Loewen, S. Schulz, Excess Molar Enthalpies of Propanone + Heptane, Propanone + Ethanol, Ethanol + Heptane, and 2-Propanol + Water at 283.15, 298.15, 323.15, 343.15, and 363.15 K, J. Chem. Eng. Data, 39 (1994) 785-788.
- [130] G. Marino, M.M. Piñeiro, M. Iglesias, B. Orge, J. Tojo, Temperature Dependence of Binary Mixing Properties for Acetone, Methanol, and Linear Aliphatic Alkanes (C6-C8). J. Chem. Eng. Data, 46 (2001) 728-734.
- [131] L.S. Budantseva, A.Y. Evstigneev, T.M. Lesteva, E.I. Khrapkova, V.I. Chernaya, The Phase Equilibria in the Systems Consisting of Components of the Technical Fractions of Isoprene, Promst. Sint. Kauch (1981) 7-9.
- [132] Y. Kim, P. Uusi-Kyyny, J.P. Pokki, M. Pakkanen, R. Multala, L.M. Westerlund, J. Aittamaa, Isothermal vapour-liquid equilibrium measurements for six binary systems of C4 hydrocarbons + 2-propanone, Fluid Phase Equilib., 226 (2004) 173-181.
- [133] M. Pasanen, A. Zaytseva, P. Uusi-Kyyny, J.-P. Pokki, M. Pakkanen, J. Aittamaa, Vapor Liquid Equilibrium for Six Binary Systems of C4-Hydrocarbons+2-Propanone, Journal of Chemical & Engineering Data, 51 (2006) 554-561.
- [134] S. Sapgir, Recherches sur la theorie des solutions concentrees. VII. Application de l'analyse thermique a des melanges binaires de composes organiques fondant a tres basse temperature, Bull. Soc. Chim. Belg., 38 (1929) 392-408.
- [135] G.I. Egorov, E.L. Gruznov, A.M. Kolker, p-Vm-T-x properties of water-acetone mixtures over the temperature range 298-323 K and pressures from 1 to 1000 bar. Excess thermodynamic quantities. , Zh. Fiz. Khim., 70 (2014) 783-789.
- [136] H.T. French, Excess enthalpies of (acetone + water) at 278.15, 288.15, 298.15, 308.15, 318.15, and 323.15 K, J. Chem. Thermodyn., 21 (1989) 801-809.
- [137] D.F. Othmer, F.R. Morley, Composition of vapors from boiling binary solutions, Ind. Eng. Chem., 38 (1946) 751-757.
- [138] Á. Piñeiro, Á. Olvera, G. García-Miaja, M. Costas, Excess Molar Enthalpies of Tetrahydrofuran or Diisopropyl Ether + 1-Alkanols at 298.15 K, Using a Newly Designed Flow Mixing Cell for an Isothermal Microcalorimeter, J. Chem. Eng. Data, 46 (2001) 1274-1279.

- [139] E.P. Sokolova, A.G. Morachevskii, Thermodynamic Properties of the System Acetone - Water, *Vestn Lenin U Fiz Kh* 16 (1967) 110-115.
- [140] S.J. Lodl, W.A. Scheller, Isothermal vapor-liquid equilibrium data for the system n-heptane - n-valeric acid at 50, 75 and 100 C, *J. Chem. Eng. Data*, 12 (1967) 458-488.
- [141] M.H.S. Radwan, A.A. Hanna, Binary azeotropes containing butyric acids, *J. Chem. Eng. Data*, 21 (1976) 285-289.
- [142] A. Ruiz, Excess enthalpies of (hexane + a carboxylic acid), *J. Chem. Thermodyn.*, 27 (1995) 1227-1234.
- [143] E.H.M. Wright, B.A. Akhtar, Soluble surface films of short-chain monocarboxylic acids on organic and aqueous substrates, *J. Chem. Soc. B* (1970) 151-157.
- [144] M.A. Faucon, Recherches sur les Melanges d'Eau et d'Acides Gras, *Ann. Chim. Phys.*, 19 (1909) 70-152.
- [145] M. Cechova, L. Bartovska, Interfacial tension along the binodal curve in the benzene - ethanol - water and n-hexane - acetone - water ternary systems at 25 C, *Collect. Czech. Chem. Commun.*, 61 (1996) 489-500.
- [146] G.W. Paul, L.E.M. De Chazal, Interfacial tensions in ternary liquid-liquid systems., *J. Chem. Eng. Data*, 12 (1974) 105-107.
- [147] V. Ragaini, V. Raverdino, S. Santi, Liquid-Liquid Equilibrium for the Ternary System n-Hexane - Water - Acetone., *Quad. Ing. Chim. Ital.*, 10 (1974) 19-22.
- [148] T. Treszczanowicz, A.J. Treszczanowicz, T. Kasprzycka-Guttman, Distribution Coefficient of b-Carotene in Systems Composed of Cyclohexane, Water, and 2-Propanone and Methylcyclohexane, Water, and 2-Propanone., *J. Chem. Eng. Data*, 44 (1999) 553-556.
- [149] R.E. Treybal, O.J. Vondrak, Distribution of Ketones in Water-Hydrocarbon Systems., *Ind. Eng. Chem.*, 41 (1949) 1761-1763.
- [150] V.I. Lebed, F.S. Eddin, Physicochemical properties of the solutions of acetic, propionic, butyric, and benzoic acids in water - organic solvents. Part 2. Systems (propionic, butyric, benzoic acids + water + acetone), *Zh. Khim. Nevodnykh Rastvorov*, 1 (1992) 153-165.
- [151] A.E. Dunstan, The Relation between Viscosity and Chemical Constitution - The Viscosity and Fluidity of the Aliphatic Acids, *J. Chem. Soc.*, 107 (1915) 667-672.
- [152] R.V. Hirsch, Dichtebestimmungen von gesättigten Dämpfen und Flüssigkeiten. , *Ann. Phys. (Berlin, Ger.)* 305 (1899) 456-478.
- [153] R.F. Mocharnyuk, Physico-chemical Investigations of Solutions of Certain Acids of the Aliphatic Series in Acetone, *Zh. Org. Khim*, 30 (1960) 1086-1091.
- [154] A. Rose, J.A. Acciari, R.C. Johnson, N.N. Sanders, Automatic calculation of constants of Antoine equation. Caproic and caprylic acid and its methyl esters, *Ind. Eng. Chem.*, 49 (1957) 104-109.
- [155] J. Gmehling, J. Rarey, J. Menke, in: *Pure compound data from Dortmund Data Bank*, 2012.
- [156] D. Hopfe, Thermophysical data of pure substances, in: *D.C.o.F.C. Germany* (Ed.), 1990.
- [157] D. Ambrose, N.B. Ghiassee, Vapor pressures and critical temperatures and critical pressures of some alkanolic acids: C1 to C10, *J. Chem. Thermodyn.*, 19 (1987) 505-519.
- [158] L. Deffet, Recherches sur la Temperature de Congelation des Corps Organiques. XIII. Contribution a l'etude des composes en C7, C8, C9, C10, *Bull. Soc. Chim. Belg.*, 40 (1931) 385-402.

Figures

Figure 1. SAFT- γ Mie molecular models including sites for unlike induced association. In (a) the model of acetone is shown: it comprises three identical segments and three association sites of site types H, e_1 , and e_2 . In (b) the model of propionic acid is shown: it comprises three different segments, one corresponding to the CH_3 group (shaded green), one to the CH_2 group (shaded grey), and one for the COOH group (shaded pink). The COOH group includes five association sites of types H, e_1 , and e_2 .

Figure 2. Fluid-phase equilibria of acetone: (a) vapour-liquid coexistence densities ρ ; and (b) vapour pressures P . The open symbols correspond to the experimental data [20], the filled symbols to the corresponding experimental critical points [20]. The dashed curves represent the SAFT- γ Mie calculations with the non-associating model, and the continuous curves the corresponding calculations with the associating model (cf. the parameters in Tables 2 and 4).

Figure 3. Second-derivative properties of acetone. The symbols correspond to experimental data and the curves to the SAFT- γ Mie predictions (cf. the parameters in Tables 2 and 4): (a) isobaric heat capacities c_P , the squares and continuous curve correspond to the saturated-liquid phase [103, 105] while the circles and dashed curve correspond to the vapour phase at 1 bar [106]; and (b) saturated speed of sound u [104], the squares correspond to the saturated-liquid phase while the circles correspond to the saturated-vapour phase.

Figure 4. Vapour-liquid equilibria of alkyl carboxylic acids: (a) vapour-liquid coexistence densities ρ ; (b) vapour pressures P ; and (c) enthalpies of vaporization ΔH^{vap} . The symbols correspond to the experimental data [50, 105, 107-112, 114-116, 151-154]: butanoic acid (black diamonds), pentanoic acid (red triangles), hexanoic acid (blue circles), heptanoic acid (green circles), octanoic acid (yellow diamonds), nonanoic acid (turquoise triangles), and decanoic acid (purple squares); the filled symbols indicate the corresponding experimental critical points [155, 156]. The continuous curves represent the SAFT- γ Mie calculations carried out with the model parameters presented in Tables 2 to 4. The SAFT- γ Mie representation of the vapour-liquid equilibria of pentanoic, hexanoic, octanoic, and nonanoic acids and the description of the enthalpies of vaporization is fully predictive.

Figure 5. Vapour-liquid and liquid-liquid equilibria of acetone + *n*-alkane binary mixtures.

The symbols represent the experimental data, and the dashed and continuous curves the description with the modified UNIFAC approach and SAFT- γ Mie equation of state, respectively: (a) isothermal pressure-mole fraction (P - x) phase diagram of acetone + *n*-heptane at constant temperatures of $T = 338.15$ K (diamonds) [121], $T = 323.15$ K (triangles) [122], $T = 313.15$ K (squares) [125], and $T = 273.15$ K (circles) [122]; (b) isobaric temperature-mole fraction (T - x) phase diagram of acetone + *n*-heptane at a constant pressure of $P = 101$ kPa [127, 128]; (c) isothermal pressure-mole fraction (P - x) phase diagram of acetone + *n*-hexane at constant temperatures of $T = 283.15$ K (triangles) [124], $T = 268.15$ K (squares) [122], and $T = 253.15$ K (circles) [122]; (d) isobaric temperature-mole fraction (T - x) phase diagram of acetone + *n*-hexane at a constant pressure of $P = 101$ kPa [123, 126]; (e) isothermal pressure-mole fraction (P - x) phase diagram of acetone + *n*-octane at a constant temperature of $T = 313.15$ K [125]; (f) isobaric temperature-mole fraction (T - x) phase diagram of acetone + *n*-octane at a constant pressure of $P = 101$ kPa [126]. The SAFT- γ Mie calculations of the fluid-phase equilibria of acetone + *n*-heptane at $T = 313.15$ K and at $P = 101$ kPa, and of acetone + *n*-hexane and acetone + *n*-octane at all conditions are fully predictive.

Figure 6. Isothermal-isobaric excess properties of mixing for acetone + *n*-alkane binary mixtures at atmospheric pressure ($P = 101$ kPa). The symbols represent the experimental data (excess molar enthalpies [129], excess molar volumes [130]), and the continuous curves the corresponding description with SAFT- γ Mie approach: (a) excess molar enthalpy of mixing of acetone + *n*-heptane at temperatures of $T = 363.15$ K (circles), $T = 343.15$ K (squares), $T = 323.15$ K (triangles), $T = 298.15$ K (diamonds), and $T = 283.15$ K (crosses); (b) excess molar volume of mixing of acetone + *n*-heptane at temperatures of $T = 298.15$ K (circles), $T = 288.15$ K (squares), and $T = 278$ K (triangles). The SAFT- γ Mie calculations of the excess properties of mixing are fully predictive.

Figure 7. Vapour-liquid equilibria of binary mixtures of acetone + branched alkanes. The symbols represent the experimental data, and the continuous curves the corresponding description with the SAFT- γ Mie approach: (a) isobaric temperature-mole fraction (T - x) phase diagram of acetone + 2-methylbutane at $P = 101$ kPa [131]; (b) isothermal pressure-mole fraction (P - x) phase diagram of acetone + 2-methylpropane at temperatures of $T = 364.5$ K (squares) [133], and $T = 318.6$ K (circles) [132]. The SAFT- γ Mie calculations of the fluid-phase equilibria for acetone + 2-methylpropane are fully predictive.

Figure 8. Vapour-liquid equilibria and isothermal-isobaric excess properties of mixing of the acetone + water binary mixture. The symbols represent the experimental data, and the continuous curves the corresponding description with SAFT- γ Mie approach including the unlike induced association sites: (a) isothermal pressure-mole fraction (P - x) phase diagram at constant temperatures of $T = 323.15$ K (triangles) [139], $T = 308.15$ K (circles) [139], and $T = 293.15$ K (squares) [139]; (b) isobaric temperature-mole fraction (T - x) phase diagram at constant pressures of $P = 342.6$ kPa (triangles) [137], $P = 170.3$ kPa (circles) [137], and $P = 101.3$ kPa (squares) [137]; (c) excess molar enthalpy of mixing at $T = 298.15$ K and $P = 101$ kPa (triangles) [138], $T = 288.15$ K and $P = 101.3$ kPa (circles) [136], and $T = 278.15$ K and $P = 101.3$ kPa (squares) [136]; (d) excess molar volume of mixing at $T = 308.15$ K and $P = 100$ kPa (triangles) [135], and $T = 298.15$ K and $P = 100$ kPa (circles) [135]. Other than the fluid-phase equilibria of acetone + water at 323.15 K and 293.15 K, all of the SAFT- γ Mie calculations shown are predictions.

Figure 9. Vapour-liquid equilibria of alkyl carboxylic acids + *n*-alkanes binary mixtures. The symbols represent the experimental data, and the continuous curves the corresponds to predictions obtained with the SAFT- γ Mie approach and models of this work: (a) isobaric temperature-mole fraction (T - x) phase diagram of butanoic acid + *n*-octane at a constant pressure of $P = 101$ kPa [141]; (b) isothermal pressure-mole fraction (P - x) phase diagram of pentanoic acid + *n*-heptane [140] at constant temperatures of $T = 373.15$ K (circles), $T = 348.15$ K (squares), and $T = 323.15$ K (triangles).

Figure 10. Isothermal-isobaric excess molar enthalpy of mixing of *n*-alkyl carboxylic acids + *n*-alkane binary mixtures. The symbols represent the experimental data, and the continuous curves the description with the SAFT- γ Mie equation: (a) butanoic acid + *n*-hexane [142] at atmospheric pressure ($P = 101$ kPa) and temperatures of $T = 298.15$ K (circles), $T = 308.15$ K (squares), and $T = 318.15$ K (triangles); (b) butanoic acid + *n*-heptane at ambient conditions ($T = 298.15$ K and $P = 101$ kPa) [113]; (c) pentanoic acid + *n*-hexane [142] at atmospheric pressure ($P = 101$ kPa) and temperatures of $T = 298.15$ K (circles), $T = 308.15$ K (squares), and $T = 318.15$ K (triangles); (d) hexanoic acid + *n*-hexane [142] at atmospheric pressure ($P = 101$ kPa) and temperatures of $T = 298.15$ K (circles), $T = 308.15$ K (squares), and $T = 318.15$ K (triangles); (e) heptanoic acid + *n*-hexane [142] at atmospheric pressure ($P = 101$ kPa) and temperatures of $T = 298.15$ K (circles), $T = 308.15$ K (squares), and $T = 318.15$ K (triangles); (f) octanoic acid + *n*-hexane [142] at atmospheric pressure ($P = 101$ kPa) and temperatures of $T = 298.15$ K (circles), $T = 308.15$ K (squares), and $T = 318.15$ K (triangles). Other than the *n*-heptane + butanoic acid and *n*-heptane + hexanoic acid cases, the SAFT- γ Mie calculations shown are predictions.

Figure 11. Vapour-liquid equilibria of the butanoic acid + water binary mixture. The symbols represent the experimental data, and the continuous and the dashed curves the description SAFT- γ Mie approach with the four and five unlike induced association site schemes (described in the text), respectively: (a) isobaric temperature-mole fraction (T - x) phase diagram at pressures of $P = 101.3$ kPa (crosses), $P = 79.99$ kPa (diamonds), $P = 53.33$ kPa (triangles), $P = 26.66$ kPa (circles), and $P = 13.33$ kPa (squares) [21]; (b) isothermal pressure-mole fraction (P - x) phase diagram at a temperature of $T = 303.15$ K [143]. Other than the vapour-liquid equilibrium at 13.33 and 101.3 kPa, the SAFT- γ Mie calculations are predictions.

Figure 12. Isothermal-isobaric liquid-liquid equilibria of (a) acetone + water + *n*-hexane, and (b) acetone + water + *n*-heptane ternary mixtures at ambient conditions ($T = 298.15$ K and $P = 100$ kPa). The symbols and the continuous lines represent the experimental data and tie-lines, respectively [145-149], and the dashed curve and lines are the corresponding predictions of the phase diagram and tie-lines obtained using the SAFT- γ Mie approach with the unlike induced association site models of this work.

Figure 13. Isobaric-isothermal density of the acetone + water + butanoic acid ternary mixture at ambient conditions ($T = 298.15$ K and $P = 100$ kPa). The symbols represent the experimental data [150] for different acetone/water molar ratios (indicated in the figure). The continuous lines correspond to the predictions obtained using the SAFT- γ Mie approach with the unlike induced association site models of this work.

Tables

Table 1. Like and unlike group-group interactions required to describe systems comprising linear and branched alkanes, water, carboxylic acids, and acetone. The grey shading indicates group-group interactions developed in previous publications [71, 72, 82], the green shading indicates group-group interactions developed in our current work and the white shading interactions yet to be determined.

		1					
1	CH ₃		2				
2	CH ₂			3			
3	CH				4		
4	H ₂ O					5	
5	CH ₃ COCH ₃						6
6	COOH						

Table 2. SAFT- γ Mie like group interaction parameters ^a.

k	group k	ν_k^*	S_k	λ_{kk}^r	λ_{kk}^a	σ_{kk} [Å]	(ϵ_{kk}/k_B) [K]	$N_{ST,k}$	$n_{k,H}$	n_{k,e_1}	n_{k,e_2}
1	CH ₃	1	0.57255	15.050	6.0000	4.0770	256.77	0			
2	CH ₂	1	0.22932	19.871	6.0000	4.8800	473.39	0			
3	CH	1	0.07210	8.0000	6.0000	5.2950	95.621	0			
4	H ₂ O	1	1.00000	17.020	6.0000	3.0063	266.68	2	2	2	
5	CH ₃ COCH ₃	3	0.72135	17.433	6.0000	3.5980	286.02	3	1	1	1
6	COOH	1	0.55593	8.0000	6.0000	4.3330	405.78	3	1	2	2

^a ν_k^* , S_k , and σ_{kk} denote the number of segments in group k , the shape factor, and the segment diameter of group k , respectively; λ_{kk}^r and λ_{kk}^a represent the repulsive and attractive exponents respectively, and ϵ_{kk} is the dispersion energy of the Mie potential characterizing the like interaction of two k groups; $N_{ST,k}$ is the number of association site types present on group k , while $n_{k,H}$, n_{k,e_1} , and n_{k,e_2} represent the number of H , e_1 , and e_2 association sites. The corresponding association site interaction energy and bonding volume are given in Table 4. The like group parameters for CH₃, CH₂, CH and H₂O are taken from previous work [71, 72, 82].

Table 3. Estimated SAFT- γ Mie unlike group attractive interaction dispersion energies (ε_{kl}) and repulsive exponent (λ_{kl}^r). ^a

k	l	group k	group l	(ε_{kl}/k_B) [K]	λ_{kl}^r	k	l	group k	group l	(ε_{kl}/k_B) [K]	λ_{kl}^r
1	1	CH ₃	CH ₃	256.77	15.050	2	6	CH ₂	COOH	413.74	CR
1	2	CH ₃	CH ₂	350.77	CR	3	3	CH	CH	95.621	8.0000
1	3	CH ₃	CH	387.48	CR	3	4	CH	H ₂ O	101.89	CR
1	4	CH ₃	H ₂ O	274.80	CR	3	5	CH	CH ₃ COCH ₃	637.29	CR
1	5	CH ₃	CH ₃ COCH ₃	233.48	14.449	4	4	H ₂ O	H ₂ O	266.68	17.020
1	6	CH ₃	COOH	255.99	CR	4	5	H ₂ O	CH ₃ COCH ₃	287.26	CR
2	2	CH ₂	CH ₂	473.39	19.871	4	6	H ₂ O	COOH	399.00	CR
2	3	CH ₂	CH	506.21	CR	5	5	CH ₃ COCH ₃	CH ₃ COCH ₃	286.02	17.433
2	4	CH ₂	H ₂ O	284.53	CR	6	6	COOH	COOH	405.78	8.0000
2	5	CH ₂	CH ₃ COCH ₃	299.48	11.594						

^aIn all cases the unlike diameter σ_{kl} and unlike attractive exponent λ_{kl}^a are obtained from the combining rules given in equations 20 and 23, respectively. CR indicates that the combining rule given by equation 23 is used to calculate the unlike repulsive exponent λ_{kl}^r . The CH₃-CH₂, CH₃-CH, CH₂-CH, CH₃-H₂O, CH₂-H₂O, and CH-H₂O unlike interaction parameters are taken from previous work [71, 72].

Table 4. Estimated SAFT- γ
Mie like and unlike group association site interaction energies ($\varepsilon_{kl,ab}^{\text{HB}}$) and bonding volume
($K_{kl,ab}$) parameters^a

k	group k	Site a of group k	l	group l	Site b of group l	($\varepsilon_{kl,ab}^{\text{HB}}/k_B$) [K]	$K_{kl,ab}$ [$\text{\AA}^3$]
4	H ₂ O	H	4	H ₂ O	e ₁	1985.4	101.69
4	H ₂ O	H	5	CH ₃ COCH ₃	e ₁	1558.7	772.77
4	H ₂ O	H	5	CH ₃ COCH ₃	e ₂	417.24	1304.3
4	H ₂ O	e ₁	5	CH ₃ COCH ₃	H	1386.8	188.83
4	H ₂ O	H	6	COOH	e ₁	2450.1	11.141
4	H ₂ O	H	6	COOH	e ₂	214.55	1159.4
4	H ₂ O	e ₁	6	COOH	H	188.61	3075.5
5	CH ₃ COCH ₃	H	5	CH ₃ COCH ₃	e ₁	980.20	2865.2
6	COOH	H	6	COOH	H	6427.9	0.80620

^aThe parameters of the association interactions between water molecules are taken from previous work [71, 72, 82].

Table 5. Percentage average absolute deviations (%AAD) of the SAFT- γ Mie description from the experimental data for the vapour pressures $P_{\text{vap}}(T)$, and saturated liquid densities $\rho_{\text{sat}}(T)$ of acetone and carboxylic acids obtained with the group parameters of Tables 2 to 4.

The asterisk denotes compounds for which the properties have been predicted.

Compound	T Range [K]	N_P	%AAD $P_{\text{vap}}(T)$	Ref.	T Range [K]	N_ρ	%AAD $\rho_{\text{sat}}(T)$	Ref.
Acetone	180-460	29	0.19	[20]	180-460	29	0.25	[20]
butanoic acid	343-452	34	1.98	[107, 110]	273-563	17	0.75	[105, 109]
pentanoic acid*	303-460	19	3.32	[117, 157]	233-533	25	0.88	[105, 109]
hexanoic acid*	356-479	38	2.56	[107, 111, 154]	273-588	27	0.59	[105, 109]
heptanoic acid	348-494	40	2.24	[50, 111]	263-583	16	1.00	[105, 108]
octanoic acid*	403-513	35	2.50	[154, 157]	293-573	22	0.58	[108, 109]
nonanoic acid*	372-528	11	2.59	[111]	288-323	7	0.80	[151, 158]
decanoic acid	350-543	13	3.98	[111, 112]	313-573	14	0.23	[109]
Average			2.42				0.64	