Modelling the phase behaviour of polymer-solvent mixtures and surfactant systems with the SAFT-γ Mie EoS

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One of the most desired features in thermodynamic tools is a predictive capability, hence thermodynamic modelling frameworks have been developed towards decreasing the need for experimental data for the determination of molecular model parameters. Using gSAFT® software within gPROMS® platform, an assessment of the predictive capability of the SAFT-γ Mie EoS (a group contribution approach, GC) is carried regarding the phase equilibrium of complex materials. The systems examined are: polymer-solvent systems (PS, PVAc, PVME, PE, among others) and non-ionic (n-alkyl polyoxyethylene ether, CnE) surfactant mixtures. The paucity of pure-component vapour-liquid experimental (VLE) data poses a challenge in the modelling of these systems, as these are typically used to develop the required model parameters. This is usually tackled by using experimental data for fluid-phase behaviour of binary and/or multi-component mixtures. The GC formalism advantageously allows the characterisation of target systems once the parameters for the functional groups that describe them have been obtained (e.g. by studying simpler data typically available, including pure-component VLE). The modelling of polymer-solvent systems was very successful - nearly all polymer systems studied were accurately predicted without using binary polymer data to adjust the interaction parameters. Pure-surfactant VLE and CnE/water binary mixtures are easily correlated to by the developed models, and sometimes even transferable to similar systems, but CnE-alkane binaries are very difficult to reproduce, and ternary water-CnE-alkane mixtures are non-replicable. The Critical Micellar Concentration (CMC) of CnE-water systems was also modelled, and the dependency of the CMC on surfactant chain length was well captured.

Introduction

In the chemical industry, predictive approaches have become increasingly important for process design, which can be considerably affected by the accuracy of the description of the thermodynamic properties. Since a predictive capability is one of the most sought out features of Thermodynamic tools, methodologies have been developed towards decreasing the need for experimental data. Group contribution (GC) approaches are an important class of highly predictive thermodynamic frameworks, developed based on the assumption that the properties of a given compound can be determined from the chemically distinct functional groups which are included in the molecule (and the group’s contribution to the molecular properties assumed to be independent of its position in the structure). The Statistical Associating Fluid Theory (SAFT) is an advanced molecular-based equation of state (EoS) which allows for the prediction of thermodynamic properties of complex materials using physically-realistic models of molecules (molecules are described as chains of tangentially bonded spherical segments); this family of EoS is believed to be more versatile than the more widely used engineering methodologies such as cubic equations of state or activity coefficient models. Process Systems Enterprise’s (PSE Ltd.) gSAFT® software is a commercial implementation of one of the most recent SAFT-based EoS: SAFT-γ Mie EoS, developed by Imperial College London. This version of SAFT is a Group Contribution approach, and its use within gPROMS process modelling platform is expected to open up new ways to address industrially relevant processes involving complex materials such as polymers and surfactants, addressed in this work.

Several thermodynamic models have been proposed in the literature to describe the phase behaviour of polymer systems, such as activity coefficient models and equations of state (EoS). More traditionally applied EoS, such as cubic equations of state, accurately describe simple nearly-spherical molecules (alkanes, CO, etc.) but they have been proven to poorly describe polymer systems (1). Thus, recently, significant efforts have been focused on the statistical associating fluid theory (SAFT); given the fact that SAFT describes molecules as chains of

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tangentially bond spherical segments, it appears to be a more suitable alternative when it comes to the description of polymers.

Many versions of the SAFT EoS have been applied to describe the phase behaviour of such systems. Huang and Radosz (2) proposed a version of the SAFT EoS that has been applied to a wide range of polymers (3)–(6). Sandowski et al. developed PC-SAFT, the perturbed chain SAFT equation, which successfully described the phase behaviour of a multiplicity of polymer systems (6)–(11). The SAFT-VR approach, proposed by Gil-Villegas et al. (12) (13), successfully described a wide range of systems (14)–(19). The main challenge when modelling polymer systems with EoS is determining the model parameters, since pure-component parameters are generally determined by regression to experimental pure-component VLE data. In case of polymers, pure-component data is scarce. Thus, identifying pure-component parameters for polymers is more difficult, and paired with a higher degree of uncertainty compared to other more volatile substances (20) as VLE data is not available. To overcome these difficulties, several approaches have been proposed to obtain parameters for different types of polymers within a heterosegmented SAFT model (using copolymer-SAFT (21) and PC-SAFT (22)). However, in those approaches it is required to include experimental data for mixtures comprising polymers – reducing the predictive ability of the equation. A final alternative is the recast of SAFT theories within the group contribution formalism. Such theories can obtain parameters for functional groups from simpler substances for which pure-component VLE experimental data are typically available, and transfer the determined parameters to polymeric systems. The most extensive work on the subject was made by Peng et al., who demonstrated the ability of GC-SAFT-VR (a group contribution approach) to predict the VLE and LLE of polymer solutions and accurately capture the effects of polymer molecular weight and molecular topology on phase behaviour without the need to fit to experimental polymer mixture data (23). Here, the molecules are described by heterosegmented chains in which each type of segment represented a functional group comprised in the molecules – an approach similar to SAFT-γ Mie.

Surfactants (abbreviation of surface active agents) are amphiphilic molecules, i.e. with both a hydrophilic and a hydrophobic part, which allow these molecules to be miscible in both water and oil. Several peculiar properties of surfactants are directly related to their characteristic structure (e.g. the formation of micelles or adsorption to surfaces/interfaces). The non-ionic n-alkyl polyoxyethylene ether (C,E) surfactants, when in aqueous solution, exhibit a region of liquid-liquid immiscibility (closed-loop) which is bounded by an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST) (Figure 1). The UCST is the highest temperature at which phase separation occurs – above that, the components of a binary mixture are fully miscible (24). This UCST is also found in alkane-C,E mixtures. In the same way, one can define LCST as the temperature above which phase separation occurs, but bellow which the system presents only one phase. Hirschfelder et al. (25) were the first to postulate that directional forces such as hydrogen bonding were responsible for the LCST. Since the SAFT EoS accounts for this type of directional interactions, it is particularly suited to model the phase behaviour of aqueous surfactant solutions.

![Figure 1](image_url)

Figure 1 – Typical phase diagram for a C,E-water system, displaying a closed-loop behaviour.

Cases where the phase behaviour of surfactant systems was modelled is considerably less abundant in the literature, and, in spite of different SAFT versions have been used in water-C,E mixtures (26)–(27), no group contribution theory was ever implemented. Besides the LLE in aqueous solutions, the liquid-phase behaviour of microemulsions of water, C,E and alkanes has been modelled using the SAFT-HS approach (28), the Peng-Robinson EoS and the UNIQUAC gE model (29), and the Flory-Huggins Theory (30). In 2011, Schreckenberg (31) studied both C,E binary and ternary mixtures with the SAFT-VR EoS.

**SAFT-γ Mie**

In the SAFT approach, molecules are modelled as chains formed from spherical monomeric segments (either with hard cores – e.g. square-
well, or soft cores (e.g. Lennard-Jones) which are not allowed to overlap but are fused to each other forming chains of spheres; association happens between bonding sites with short-range interactions placed in those monomeric segments. Consequently, the SAFT approach comprehends two types of asymmetry: the chain contribution for the nonsphericity of molecules, and the association contribution for anisotropic interactions (32). A general form of the SAFT theory may be presented in terms of the perturbation in the Helmholtz free energy:

\[
\frac{A}{Nk_BT} = \frac{A_{\text{ideal}}}{Nk_BT} + \frac{A_{\text{monomeric}}}{Nk_BT} + \frac{A_{\text{interaction}}}{Nk_BT} + \frac{A_{\text{association}}}{Nk_BT} \tag{1}
\]

Where \(A_{\text{ideal}}\) is the free energy of the ideal polyatomic gas system, \(A_{\text{monomeric}}\) the residual free energy due to the formation of spherical monomeric segments (includes repulsive and attractive/dispersive interactions), \(A_{\text{interaction}}\) refers to the energy due to the formation of a chain of tangentially bonded monomeric segments, \(A_{\text{association}}\) is the free energy due to the association between molecules, \(N\) is the total number of molecules, \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature. This convenient division of the SAFT theory when it is written in terms of Helmholtz free energy translates into a versatility which has led to many different variations in the theory, most involving just a change in the monomer term.

SAFT-\(\gamma\) Mie is a generalization of the SAFT-VR Mie (introduced by Laffite et al. (33)), formulated within the framework of a group contribution approach. In this version, molecules are modelled as comprising distinct functional groups based on a fused heteronuclear molecular model (Figure 2). The interactions between functional groups are described the Mie potential of variable attractive and repulsive range:

\[
\Phi_{\text{Mie}}(r) = C\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{\lambda^R} - \left( \frac{\sigma}{r} \right)^{\lambda^A} \right] \tag{2}
\]

Where \(\sigma\) is the segment diameter (at which the potential is zero), \(\varepsilon\) is the depth of the potential well, \(\lambda^R\) and \(\lambda^A\) are the repulsive and attractive exponents (which characterise both the softness/hardness and the range of the interaction, allowed to vary freely), while the factor \(C\) ensures that the minimum of the interactions is -\(\varepsilon\):

\[
C = \frac{\lambda^R}{\lambda^R - \lambda^A} \left( \frac{\lambda^R}{\lambda^R - \lambda^A} \right)^{\lambda^R} \tag{3}
\]

In the SAFT-\(\gamma\) Mie EoS, each non-associating group \(k\) is described by the following set of parameters: the number of segments \(n_k\), shape factor \((S_k)\), translates the extent to which the segments of a given group \(k\) contribute to the overall molecular properties), segment diameter \((\sigma_{kk})\), dispersion energy \((\varepsilon_{kk})\), and repulsive and attractive exponents of the potential \((\lambda_{kk}^R\) and \(\lambda_{kk}^A\) \(\) (Table 1).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_k)</td>
<td>Number of identical segments in the group</td>
</tr>
<tr>
<td>(\sigma_{kk})</td>
<td>Diameter of the segments ((m))</td>
</tr>
<tr>
<td>(\varepsilon_{kk})</td>
<td>Energy of interaction between segments of the group ((J))</td>
</tr>
<tr>
<td>(\lambda_{kk}^R), (\lambda_{kk}^A)</td>
<td>Attractive and repulsive exponents of the potential</td>
</tr>
<tr>
<td>(S_k)</td>
<td>Shape factor</td>
</tr>
</tbody>
</table>

When speaking of associating groups, like water, the association energy \((\varepsilon_{kk}^{HB})\) and bonding volume \((K_{kk}^{HB})\) are added to the previous list. While the number of segments is determined by a trial-and-error approach, the rest of the parameters are estimated from appropriate experimental data.

For mixtures, a method is needed to obtain cross-interaction (unlike) parameters. Every cross-interaction parameters could be adjusted to optimise the description of experimental mixture data, but usually this is not done, since a large number of cross-interaction parameters can lead to a large number of unnecessary degrees of freedom and fitting to experimental data reduces the predictive capability of the EoS. Thus, the unlike non-associating interactions – the segment diameter \((\sigma_{kl})\) and the repulsive and attractive exponents of the potential \((\lambda_{kl}^R\) and \(\lambda_{kl}^A)\) – are calculated by means of combining rules as in Table 2, but the unlike dispersion energy \((\varepsilon_{kl}^{\text{disp}})\) is also treated as an adjustable parameter. For unlike association interactions, the cross association energy \((\varepsilon_{kl}^{\text{assoc}})\) and the bonding volume \((K_{kl}^{\text{assoc}})\) are also estimated by regression to experimental data.
Table 2 - SAFT-γ Mie combining rules for unlike parameters; *associating compounds (34).

<table>
<thead>
<tr>
<th>Unlike parameter</th>
<th>Combining rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Segment diameter</td>
<td>( \sigma_{kl} = (\sigma_{kk} + \sigma_{ll}) / 2 )</td>
</tr>
<tr>
<td>Effective hard-sphere</td>
<td>( d_{kl} = (d_{kk} + d_{ll}) / 2 )</td>
</tr>
<tr>
<td>dispersion energy</td>
<td>( \epsilon_{kl} = \sqrt{\frac{\sigma_{kk} \sigma_{ll}}{\sigma_{kl}}} ) ( \sqrt{\epsilon_{kk} \epsilon_{ll}} )</td>
</tr>
<tr>
<td>Repulsive and attractive exponents</td>
<td>( \lambda_{kl} = 3 + \sqrt{(\lambda_{kk} - 3)(\lambda_{ll} - 3)} )</td>
</tr>
<tr>
<td>Range of association</td>
<td>( r_{kl}^e = (r_{kk}^e + r_{ll}^e) / 2 )</td>
</tr>
<tr>
<td>site-site interaction</td>
<td>*</td>
</tr>
<tr>
<td>Association energy</td>
<td>( \epsilon_{kl}^{H\beta} = \frac{\epsilon_{kk}^{H\beta} \epsilon_{ll}^{H\beta}}{\sqrt{\epsilon_{kk}^{H\beta} \epsilon_{ll}^{H\beta}}} )</td>
</tr>
</tbody>
</table>

Polymer-Solvent Systems

gSAFT is a property package used in gPROMS® platform products (e.g. gPROMS ModelBuilder®, used in this project). It implements both the SAFT-VR and SAFT-γ Mie equations of state. Prior to this work, a multitude of SAFT-γ Mie functional groups and respective interactions/cross-interactions had already been determined. When studying the phase behaviour of several polymer-solvent systems, each molecule was divided into the previously existing functional groups. An initial attempt was made to predict all the systems with this set of group parameters. It is noteworthy that some of the cross-interaction parameters between groups were not yet determined, thus being calculated automatically as per combining rule (Table 3).

Original SAFT-γ Mie group parameters

A large set of systems was accurately described when modelling with the set of parameters that had been determined prior to this project. Most of those systems had all their group interactions already estimated, namely: PS+toluene (Figure 3), PS+n-nonane (Figure 4), Poly(1-heptene)+toluene (Figure 5), Poly(1-decene)+toluene (Figure 6), PE+toluene (Figure 7), and PVAc+toluene (Figure 8). However, two systems were accurately predicted even with interactions as per combining rule: PVME+ benzene (Figure 9), and PVME+ ethylbenzene (Figure 10).

Table 3 - Polymer solvent systems and their interactions missing in the original set of parameters – when simulating these systems, the listed interactions' parameters are automatically estimated as a combining rule.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Missing interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(styrene) (PS)</td>
<td>toluene</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>n-nonane</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>propyl acetate</td>
<td>COO:aCH ; COO:aCCH</td>
</tr>
<tr>
<td></td>
<td>2-butanone</td>
<td>C=O:aCH ; C=O:aCCH</td>
</tr>
<tr>
<td></td>
<td>3-pentanone</td>
<td>C=O:aCH ; C=O:aCCH</td>
</tr>
<tr>
<td>Poly(n-butyl methacrylate) (PBMA)</td>
<td>benzene</td>
<td>COO:aCH ; C=aCH ; COO</td>
</tr>
<tr>
<td></td>
<td>ethylbenzene</td>
<td>COO:aCH ; C=aCH ; C=COO ; C:CH2 ; aCCH2:C00</td>
</tr>
<tr>
<td>Poly(ethylene) (PE)</td>
<td>toluene</td>
<td>-</td>
</tr>
<tr>
<td>Poly(vinyl acetate) (PVAc)</td>
<td>benzene</td>
<td>COO:aCH</td>
</tr>
<tr>
<td></td>
<td>toluene</td>
<td>COO:aCH ; COO:aCCH ; CH:aCCH</td>
</tr>
<tr>
<td></td>
<td>methyl acetate</td>
<td>-</td>
</tr>
<tr>
<td>Poly(1-decene)</td>
<td>toluene</td>
<td>-</td>
</tr>
<tr>
<td>Poly(1-heptene)</td>
<td>toluene</td>
<td>-</td>
</tr>
<tr>
<td>Poly(vinyl methyl ether) (PVME)</td>
<td>benzene</td>
<td>eO:aCH</td>
</tr>
<tr>
<td></td>
<td>ethylbenzene</td>
<td>eO:aCH ; eO:aCCH2</td>
</tr>
<tr>
<td></td>
<td>toluene</td>
<td>eO:aCH ; eO:aCCH3 ; aCH3</td>
</tr>
</tbody>
</table>
Parameter estimations

In spite of the success in modelling two systems with missing interactions, with increasing number of interactions as per combining rule, the systems were being more and more poorly described. Thus, a few parameter estimations were carried in this work. For instance, the PS + propyl acetate system had both COO\textsubscript:aCH and COO\textsubscript:aCCH as per combining rule. The first was estimated by regression to binary VLE experimental data of ethyl acetate + benzene, butyl acetate + benzene, and ethyl acetate + toluene (this last one was included so as to enable the simultaneous estimation of the also missing COO:aCCH\textsubscript3 interaction). The interaction energy obtained was ε\textsubscript{aCH:COO}/k\textsubscript{B} = 519.460K. To estimate the COO:aCCH interaction, the experimental VLE data for cumene + methyl acetate and cumene + propyl acetate was used; however, the small shape factor of the aCCH group (S\textsubscript{aCCH} = 0.207) made its contribution to the applied systems very insignificant and so a wide range of interaction energies would allow a proper fit of the model to the experimental VLE data. Nonetheless, the numerous repetition of this functional group in the polymer made its contribution much more important in this system, and so the interaction had to be estimated by fitting to the polymer data itself (ε\textsubscript{aCCH:COO}/k\textsubscript{B} = 203.051K) (Figure 11).
Figure 11 - PS ($M_n=290000\text{g/mol}$) + propyl acetate, comparison between original predictions (dashed lines) and the new model including both $\varepsilon_{\text{aCH:COO}}$ and $\varepsilon_{\text{aCC:H:COO}}$ (continuous lines). ● - experimental data (23).

Furthermore, at this point the PVAc + benzene system also had all its interactions included in the refined set of group parameters (aCH:COO) (Figure 12).

Having both $\varepsilon_{\text{aCH:COO}}$ and $\varepsilon_{\text{aCC:H:COO}}$ (669,943K) been estimated simultaneously, PVAc + toluene, another previously poorly described system, had only CH:aCH3 as per combining rule. This interaction was estimated by regression to experimental binary VLE data of 2-propanol + m-xylene, being $\varepsilon_{\text{aCC:H:CH}3}$=568.798K (Figure 13).

Poly(n-butyl methacrylate) (PBMA) + benzene was then studied. Previously lacking three interactions (COO:aCH; C:aCH; C:COO), only two are still not included in the set of group parameters. To estimate the aCH:C parameters, experimental binary VLE data of benzene+dimethylbutane and benzene+trimethylpentane was used, achieving an interaction energy of 180,713K. The C:COO interaction was left as per combining rule, since the system was already accurately modelled (Figure 14).

Two PS + ketone systems were studied as well. Initially missing two interactions, even after estimating C=O:aCH, using both acetone + benzene and 2-butanone + ethylbenzene experimental VLE data, the model predictions
were not perfect (Figure 16). The issue might be either related to some other parameter determined prior to this work (which were all left untouched) or in the experimental data itself, since the origin of the plot should be included and in the PS+3-pentanone system it appears not to be (and both systems’ data came from the same source). Finally, the PVME + toluene system was modelled (Figure 17), leaving two interactions as per combining rule (eO:aCH and eO:aCCH3), and having already estimated CH:aCCH3. All the estimated interaction parameters have been summarized in Table 4.

### Table 4 – Summary of the estimated parameters while studying polymer-solvent systems.

<table>
<thead>
<tr>
<th>Group Pair [k:l]</th>
<th>( \epsilon_{kl}/k ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aCH : COO</td>
<td>519.460</td>
</tr>
<tr>
<td>aCCH3 : COO</td>
<td>669.943</td>
</tr>
<tr>
<td>aCCH2:COO</td>
<td>203.051</td>
</tr>
<tr>
<td>CHaCCH3</td>
<td>568.798</td>
</tr>
<tr>
<td>C=CH</td>
<td>180.713</td>
</tr>
<tr>
<td>aCCH2:COO</td>
<td>562.076</td>
</tr>
<tr>
<td>aCH : C=O</td>
<td>450.286</td>
</tr>
<tr>
<td>aCCH3 : C=O</td>
<td>581.102</td>
</tr>
</tbody>
</table>

### Surfactant Mixtures

After the proven ability to describe polymer-solvent systems, the possibility of using SAFT-\( \gamma \) Mie to model an even more complex type of molecules was studied: the non-ionic \( n \)-alkyl polyoxyethylene ether surfactants, \( \text{H}-[\text{CH}_2]_{i} - [\text{OCH}_2\text{CH}_2]_{j} - \text{OH} \). These surfactants, consisting of a linear block-copolymer chain, are also called \( \text{C}_i \text{E}_j \) - where \( C_i \) is the alkane hydrophobic chain, and \( E_j \) denotes the polyoxyethylene hydrophilic chain. Both the number of carbon atoms in the alkane chain (\( i \)) and the amount of oxyethylene molecules in the polyoxyethylene chain (\( j \)) can take any value, which enables the study of many similar systems with very different properties.

The ultimate goal of studying surfactants is usually to build a ternary “fish diagram” in which the amount of surfactant necessary to add to a water-oil system so as to achieve a single phase is easily read. Thus, ternary systems were studied, starting from the pure surfactant and the water and oil binaries.

#### Original SAFT-\( \gamma \) Mie group parameters

Firstly, a test to the original set of parameters was carried towards verifying if it would accurately describe surfactant aqueous solutions and ternary systems. Note that all the groups in which the components were divided (Figure 18) has been determined prior to this work, as well as their like and unlike interactions. However, the results in Figure 19 clearly show this set of parameters is
not applicable. So as to access the reason for this behaviour, pure-component VLE was predicted and compared to experimental data – results showed that there was a considerable deviation between the model and the data, which increased with the surfactant length. CiEj-alkane binaries were also studied, and the original model failed to predict the LLE which experimentally was found to be characteristic to these mixtures.

**Correlation to experimental data**

Before changing the segmentation of the surfactant molecules, a first attempt was made to estimate cross-interaction parameters while keeping the same groups, and verify if there was any chance that this SAFT approach was able to accurately capture the closed-loop behaviour. Thus, the H2O:cO interaction was optimized by fitting to C6E5+H2O LLE experimental data (Table 5), and tested on other CiEj-water systems as in Figure 21.

**Table 5 – H2O:cO parameter estimation results by regression to C6E5+Water LLE experimental data.**

<table>
<thead>
<tr>
<th>Group Pair [kJ]</th>
<th>Dispersion</th>
<th>Association</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\epsilon_{ij}/k_B$ (K)</td>
<td>$\epsilon_{ij}^{\text{like}}/k_B$ (K)</td>
</tr>
<tr>
<td>H2O : cO</td>
<td>304.868</td>
<td>1798.286</td>
</tr>
</tbody>
</table>

Although results are accurate, using surfactant data directly seemed necessary to get sufficiently accurate models thus causing a lack of predictive capability.

**Re-segmentation and parameter estimations**

Since the CH$_2$ group was common to alkanes, the alkane-like surfactant hydrophobic chain, and the surfactant hydrophilic chain, this was assumed to be the main cause for the poor prediction of pure surfactants, alkane-CiEj systems and ternary mixtures. Therefore, a re-segmentation was carried in two approaches.

- **CH$_2$ surfactant**

  In this first approach (Figure 21), a new CH$_2$surf group was developed, as equivalent to each of the CH$_2$ groups within the hydrophilic chain. A model was created for this group, by estimating the like group parameters by regression to experimental pure-component (C6E5 VLE) and binary CiEj-alkane (C6E5 + n-dodecane LLE) data. This model proved to describe pure...
C,Ei accurately, and found LLE for the C,Ei-alkane systems – so a further step was taken towards modelling C,Ei-water phase behaviour using C,Ei-H₂O LLE experimental data to estimate H₂O:CH₃surf and H₂O:O (since optimizing only the first revealed issues in modelling the hydrogen-bonding-related LCST).

However, in spite of predicting the LLE in the C,Ej-alkane systems and being transferable to several H₂O-C,Ej mixtures, this approach would not describe the first systems very accurately, and actually failed in predicting ternary systems.

- CH₂CH₂O

Since keeping small segments was proven unsuccessful when predicting ternary systems, another approach was taken into account: dividing the hydrophilic chain into larger segments, thus introducing a simple connectivity effect in the model (Figure 22). Taking the same steps as in the CH₂surf approach, a model was developed for this group and its interactions with itself, CH₂, CH₃, OH and H₂O, using the same sets of data as before. Nonetheless, this approach revealed to model the studied systems even more inaccurately: the LCST in several water-C,Ei binaries was not being found, and the no three-phase immiscibility region was being modelled in the ternary mixtures. Thus, this attempt was also discarded.

**Modelling the Critical Micellar Concentration**

There are several theoretical approaches for the thermodynamic treatment of micelle formation in surfactant solutions, which can be classified into phenomenological models (empirical or semi-empirical methods, relying exclusively on the availability of experimental data), and molecular thermodynamic methods (which describe surfactant solutions’ properties using molecular thermodynamic principles and molecular structure characteristics [36]). For the development of a CMC-predictive model, a molecular thermodynamic method has been chosen (as it relates more closely to this project): Chen’s Method. Chen et al. [37] [38] proposed a simple thermodynamic framework for micelle formation in aqueous surfactant solutions, in which the CMC was considered to be a phase separation (Figure 23), comprising an “aqueous phase” and a “micellar phase”. Hence, the CMC is treated as a phase boundary calculation so that the surfactant chemical potential (μₛ) is equal in both phases:

$$\mu^a(T, P, x^a) = \mu^m(T, P, x^m)$$  \hspace{1cm} (4)

Where aq refers to the aqueous phase and m to the micelle phase, and xₛ is the surfactant mole fraction. This may be re-written as:

$$\mu^a_{pure} + RT \ln (x^a) = \mu^m_{pure} + RT \ln (x^m)$$  \hspace{1cm} (5)

Where γₛ is the activity coefficient of the surfactant. Assuming the surfactant is pure within the “micelle phase”, and that both phases have the same reference state, Equation (5) simplifies to:

$$x^a y^m = 1$$  \hspace{1cm} (6)

This γₛaq, the activity coefficient of the surfactant in solution, is easily calculated by gSAFT. Thus, by applying this equation to a gPROMS model, given a specific T (298.15 K) and P (0.1 MPa), and a range of surfactant global concentration (for at the CMC, the “micellar phase” is approximated to zero), the surfactant mole fraction for which the equation equals to unity will be the predicted value for the CMC. The model, using the original groups and parameters, was tested for a set of surfactants with the same hydrophilic chain length and different hydrophobic chain lengths, and the trend was accurately predicted (Figure 24).
Conclusions

The VLE of polymer-solvent systems is very accurately predicted by the SAFT-\(\gamma\) Mie EoS, and the wide range of polymers (comprising several different function groups) studied has also proven the EoS captures the effects of polymer molecular weight and branching on phase behavior. Although not all group parameters had been determined prior to this work, several systems were initially accurately described by it without any parameter estimation; and from the ones that did not, some improved greatly just after one or two estimations even when leaving some interactions as per combining rule – thus, combining rules are often enough to describe the unlike interactions.

Surfactant experimental data seems to be necessary in order to achieve sufficiently accurate models regardless of the approach taken. This caused a clear lack of predictive capacity.

The difference in predicting polymer and surfactant mixtures is believed to rest in the inability to include the groups’ connectivity in the models, since SAFT-\(\gamma\) Mie does not take the position of the functional groups within the molecule into account. While the groups in polymers are repeated numerous, the particular order in which the groups are linked to each other in reality will not significantly influence the model. On the other hand, surfactants’ phase behaviour is deeply linked to their inherent amphiphilicity, which in its turn relates to the particular way in which the functional groups are organized in the molecule. Consequently, in a future work, a way of including this effect in the approach should be developed.

Finally, the model developed to predict the CMC was considered qualitatively accurate, but quantitatively inaccurate. As future work, another attempt at this model is advised, applying a different approach as Chen’s comprises quite a few approximations which may not be completely valid in this case. Also, one advises decreasing the platform’s tolerance (of \(10^{-3}\)), and using another set of experimental data with which to compare the modelled predictions.

References


