Polymer-surfactant interactions

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1998

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Interactions between single-tailed surfactants and hydrophobically-modified polymers

Isothermal titration microcalorimetry and fluorescence spectroscopy have been used to investigate interactions between hydrophobically-modified water-soluble polymers and single-tailed surfactants having anionic or cationic headgroups. It appears that individual amphiphilic molecules adsorb onto hydrophobic microdomains formed by the polymers in aqueous solutions. The length of the alkyl side-chain of the polymer determines the number and strength of the (inter-)polymeric associations, and it appears to be the most important factor for efficient polymer/surfactant interactions. Interestingly, anionic surfactants interact stronger with uncharged polymers than their cationic counterparts. This phenomenon most likely reflects the different hydration characteristics of the cationic and anionic headgroups.

2.1 A brief review of polymer-surfactant interactions

Mixtures of water-soluble polymers and surfactants find numerous applications in mineral processing and petroleum engineering. In addition, a large number of end-products such as paints, shampoos and liquid detergents contain both surfactants and polymers. In all cases, the issue is the fine-tuning of the viscosities of (aqueous) solutions by a careful choice of a certain polymer in combination with a specific surfactant at well-chosen concentrations.

2.1.1 ‘Classical’ polymer-surfactant interactions. From 1957 onwards, the interactions between micelles and water-soluble neutral homopolymers have been studied in detail. The interaction of poly(ethylene oxide), PEO, with sodium n-dodecylsulfate (SDS) micelles has been of particular interest. The main features of these ‘classical’ polymer-surfactant interactions have been summarized in excellent review articles. Therefore, we will review only the major points.

As has been established using viscosimetry, surface tensiometry, NMR spectroscopy, neutron scattering, fluorescence spectroscopy, and isothermal titration calorimetry, PEO ‘induces’ micellization of the surfactant onto the polymer chain. In the presence of PEO, surfactant molecules aggregate cooperatively to form polymer-bound micelles at a critical aggregation concentration (C₁) which is lower than the CMC in aqueous solution. Interestingly, the micelles which are formed at C₁ have a smaller aggregation number and a lower degree of counterion binding than micelles in the absence of polymer. The stoichiometry of the complex is more or less defined: saturation occurs at a well-defined concentration of surfactant (C₂) above which ‘free’ micelles are formed. Typically, C₂ exceeds the CMC of the surfactant (in the absence of polymer) by a factor of 5.

The morphology of the complex formed between surfactant micelles and nonionic water-soluble polymers was established by Cabane. According to his model, a ‘necklace’ is formed where the micelles are the beads, and the polymer is the string (Figure 2.1). Segments of the polymer bind to the surface
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Figure 2.1 A two-dimensional representation of a PEO-SDS complex. The black dots are SDS micelles. Taken from ref. [7].

region of the surfactant micelles, so that the core of the micelle is shielded from the surrounding water for ca. 30% of its surface. Stabilization of the interface between the hydrophobic core and water is considered to be a major driving force for polymer-micelle interaction. Nevertheless, 90% of the polymer resides in the bulk water.

In applications, use is made of the so-called ‘polyelectrolyte effect’. As multiple ionic micelles bind to an uncharged polymer molecule, parts of the backbone of the polymer repel each other due to electrostatic repulsions. Thereby, the polymer coils become more elongated (‘rod-like’), and the viscosity of the solution increases.

2.1.2 Interactions between hydrophobically-modified polymers and single-tailed surfactants in aqueous solutions. Hydrophobically-modified water-soluble polymers (i.e. ‘polysoaps’) are capable of spontaneous aggregation through intra- and intermolecular association of their alkyl side chains. Intrapolymeric hydrophobic association occurs at the lowest polymer concentrations, provided that the number of alkyl side chains per molecule exceeds a certain critical value. For example, the reduced viscosity of aqueous solutions of hydrophobically-modified poly(N-ethyl-4-vinyl-pyridinium bromide)s significantly decreases as the dodecyl content is increased beyond 10 mol%, indicating the formation of compact globules (i.e. intramolecular domains). The flexibility of the main chain is another factor determining the formation of intrapolymeric hydrophobic microdomains. Intermolecular association of hydrophobic side-chains depends on the concentration of polymer in solution. For example, using polarity-sensitive probes, the critical aggregation concentration (CAC) of poly(acrylamide-co-methyl-n-dodecyl-diallylammonium bromide) containing 2 mol% of hydrophobes was determined as 10 unit mM;
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Figure 2.2 Effect of SDS concentration on the viscosity of HEUR solutions of different concentrations. Reproduced from [16].

the CAC of hydrophobically-modified poly(N-ethyl-4-vinyl-pyridinium bromide) containing 10 mol% of dodecyl groups is $5 \times 10^{-4}$ M. The formation of interpolymeric hydrophobic microdomains is accompanied by an increase of the intrinsic viscosity of the polymer solution.

Quite generally, if the polysoap concentration exceeds the critical overlap concentration, addition of surfactant enhances the viscosity even further until a maximum is reached, at approximately the CMC. When the surfactant concentration is increased beyond the CMC, the viscosity steadily drops. Figure 2.2 graphically illustrates the dependence of solution viscosity on the concentration of added SDS, for several concentrations of $\alpha,\omega$-pentadecyl-end-capped ethylene oxide-urethane (HEUR) block copolymers. The following model for polysoap-surfactant interactions has been proposed to account for these observations. The initial viscosity increase is attributed to an increase in both the number and the strength of the hydrophobic interchain liaisons resulting from adsorption of individual surfactant molecules onto interpolymeric hydrophobic microdomains (Figure 2.3, Region 1 and 2). The general observation that increasing the number and/or length of the polymer hydrophobes greatly enhances the (maximum) viscosity is consistent with the following interpretation: increasing the hydrophobicity of the polysoap promotes interpolymeric association and thereby the tendency of surfactant molecules to adsorb. The viscosity decrease at higher surfactant concentrations has been explained by the fact that as the CMC is exceeded, each polymer hydrophobe may become individually solubilized by a single micelle. As a consequence, the interpolymeric network is broken down (Figure 2.3, Region 3).
conformational energy of the polymer is lowered if the hydrophobes reside in a larger number of micelles rather than in a smaller number of hydrophobic microdomains.

The viscosifying effect of added single-tailed amphiphiles occurs even if electrostatic forces between the polymer backbone and the surfactant are repulsive, as in SDS-hydrophobically-modified poly(sodium acrylate) interactions.\textsuperscript{16, 22} Again, the conclusion is that the driving force for the formation of the mixed hydrophobic clusters in Regions 1 and 2 is hydrophobic interactions.

Clearly, ‘classical’ polymer-surfactant interactions are radically different from the interactions between single-tailed surfactants and polysoaps, despite the fact that the hydrophobic effect plays a pivotal role in both cases. In case of SDS and PEO, polymer-bound \textit{micelles} are involved, and to have an appreciable viscosifying effect, the surfactant concentration should exceed the CMC (or $C_1$). The opposite is true when polysoaps are involved: the viscosifying effect is most pronounced at low amphiphile concentrations, where the surfactants are present as \textit{monomers}.

2.1.3 \textbf{Motivation and aim of this research.} The above-mentioned model for ‘associative thickening’ (Region 1, 2) of polysoap solutions with added surfactants appears to be broadly consistent with experimental observations. However, little systematic effort has been made to validate the model with regard to its implications for polymer-surfactant interactions at a molecular level.\textsuperscript{23} The theory implies that when surfactant is added to an aqueous solution containing hydrophobically-modified polymer, the surfactant monomers should not aggregate cooperatively to form polymer-bound micelles. Instead, one expects to observe a continuous association process of the amphiphilic molecules with the associated hydrophobic moieties of the polymers. Moreover, the tendency to form mixed aggregates should depend on the hydrophobicity of the polymer. These are the most important working hypotheses that we liked to test.
Figure 2.3  Schematic representation of the interactions of polysoaps with single-tailed surfactants at three different surfactant concentrations corresponding to Regions 1, 2 and 3. Polymeric hydrophobic microdomains are denoted by the black dots. Taken from ref. [17].
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\[\begin{align*}
\text{CMP} & : \quad \text{CH}_3\text{-(CH}_2\text{)}_{10}\text{-CH}_2\text{C}\text{H}_2\text{O-P-O^\prime Na}^+ \\
\text{DTAB} & : \quad \text{CH}_3\text{-(CH}_2\text{)}_{10}\text{-CH}_2\text{N}\text{^\prime CH}_3 \text{ Br}^-
\end{align*}\]

\[\begin{align*}
\text{PSA-CX}[Y] & : \quad \text{CH}_2\text{-CH}_{100-y}\text{-CH}_3 \\
\text{LMAM}[Z] & : \quad \text{CH}_2\text{-CH}_{100-z}\text{-CH}_3
\end{align*}\]

**Scheme 2.1** Structures of the compounds that have been studied.

Our motivation for the present study is not only scientific interest. Polysoaps are present in the wash liquor, \(^{24}\) where they might form microdomains. Amphiphilic molecules may bind to these domains, and the concomitant reduction of free surfactant in solution may adversely affect wash performance.

We have investigated polysoap-surfactant interactions using two different (complementary) techniques: fluorescence spectroscopy, using pyrene as a probe, and ultrasensitive isothermal titration microcalorimetry. The polysoaps are hydrophobically-modified poly(sodium acrylate) or poly(acrylamide) having different numbers of hydrophobic side chains, with varying lengths. As surfactants, we used an (anionic) analog of sodium n-dodecyl phosphate, CMP, and the cationic amphiphile DTAB (Scheme 2.1).

The hydrophobically-modified poly(sodium acrylate)s are called PSA-CX[Y] to indicate the number of carbon atoms in the hydrophobic side chains of the polymer (X). The degree of hydrophobic modification is expressed as the fraction of all monomeric units which have a hydrophobic moiety, multiplied by 100. The result is the number Y. The hydrophobically-modified poly(acrylamide)s are copolymers of acrylamide and lauryl methacrylate of different composition, and are therefore called LMAM[Z], where Z is the degree of hydrophobic modification.

### 2.2 The application of fluorescence spectroscopy to the study of polymer-surfactant interactions

The research plan aimed to study the influence of hydrophobic interactions on the association of single-tailed surfactants with hydrophobic microdomains. A prerequisite is that the hydrophobicity of the microdomains can be quantified. A key problem involves the definition and quantification of
hydrophobicity. The use of a fluorescent probe, pyrene, provides some answers to these questions.

2.2.1 Some important aspects of pyrene spectroscopy. Pyrene is a nonpolar polyaromatic molecule with a modestly low solubility in water (ca. $6 \times 10^{-7}$ mol l$^{-1}$). The fluorescence spectrum of pyrene possesses a vibrational band structure which, due to the Ham effect, exhibits a strong sensitivity to the polarity of the environment. The relative intensities of the peaks at 372 and 385 nm ($I_1$ and $I_3$, respectively) undergo significant changes upon going from solutions in nonpolar to solutions in polar solvents. In particular, $I_1$ increases with solvent polarity, while $I_3$ remains essentially unaffected. Thus, $I_1/I_3$ increases from 0.64 to 1.45 on going from cyclohexane to ethanol; in water, $I_1/I_3 = 1.95$.

Pyrene has also been used as a probe to determine critical micelle concentrations. Below the CMC, pyrene resides in water. As the surfactant concentration is increased through the CMC, micelles start to form. The apolar pyrene molecules partition into (the core of) the micelles, and as a result, $I_1/I_3$ decreases to 1.2. The fluorescence spectra of pyrene in water, and solubilized in micelles, are shown in Figure 2.4. The figure reveals that not only the intensity ratio $I_1/I_3$ is changed as pyrene is transferred from water to a micelle. The total fluorescence intensity of pyrene in micelles is larger than in water. This effect has been only recently explored, and is accounted for by the fact that the lifetime of the excited state of pyrene is shorter in water than the fluorescence lifetime of pyrene molecules solubilized in hydrophobic microenvironments.

Consequently, pyrene can be used equally well to probe hydrophobic microdomains formed by polysoaps. Thus, $I_1/I_3$ is a quantitative measure of the micropolarity at the binding site of the probe. The total fluorescence intensities provide information concerning the ‘packing’ of hydrophobic chains in the microdomains. If the alkyl chains are closely packed, water is largely excluded from the microdomains, and the total fluorescence intensity is high. Another effect of close-packing of alkyl chains is to increase the microviscosity of the hydrophobic domains. This slows down the diffusive motion of pyrene and quencher (dissolved oxygen) in the aggregates, which makes quenching of pyrene fluorescence less efficient than in ‘open’ aggregates. (The solutions were not degassed prior to fluorescence
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**Figure 2.4** Fluorescence spectrum of pyrene in pure water and solubilized in Triton X-100 micelles. [Pyrene] = $10^{-6}$ - $10^{-7}$ M.

Apart from characterizing the microdomains, the effect of added surfactant can be investigated. Does a surfactant aggregate cooperatively, to form micelles, or does it associate continuously with the polymeric domains? Is the ‘hydrophobicity’ of the microdomains changed as surfactant is added?

Before considering the experimental data, a final point needs to be addressed. The reported spectroscopic parameters only reflect the properties of the binding site of the probe if all pyrene molecules are bound to the hydrophobic domains. For example, if part of the probe molecules reside in the water phase and the remainder is bound to micelles (or hydrophobic microdomains), the reported value of $I_3/I_1$ is between 2 (corresponding to water) and ca. 1.2, the ‘intrinsic’ $I_3/I_1$ in micelles. Thus, knowledge of a partitioning constant for the distribution of the probe in the two phases is required, so that the ‘intrinsic’ spectroscopic parameters, characteristic of the hydrophobic pseudophase, can be calculated. This point is often overlooked in the scientific literature.

We have not determined partitioning coefficients. However, the polymer concentration has been chosen such that effectively all pyrene molecules are bound to the hydrophobic microdomains, assuming that most polymeric side chains are involved in hydrophobic associations. As an example, the binding constant of pyrene to microdomains formed from poly(disodium maleate-co-n-dodecyl vinyl ether) is $4.10^4$ M$^{-1}$, expressed in moles of associated side chains per litre of solution. As the dodecyl side-chain is replaced by a decyl group, the **Table 2.1** Pyrene $I_3/I_1$ and total fluorescence intensities for 160 unit mM aqueous solutions of hydrophobically-modified poly(sodium acrylate)s at 25 °C.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$I_3/I_1$</th>
<th>Total fluorescence intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triton X-100 (&gt; CMC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pure water</td>
<td></td>
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<table>
<thead>
<tr>
<th></th>
<th>Binding Constant</th>
<th>PSA: Poly(acrylamide)</th>
<th>PSA-C9[4]: Poly(sodium acrylate)</th>
<th>PSA-C12[4]: Poly(sodium acrylate)</th>
<th>PSA-C12[8]: Poly(sodium acrylate)</th>
<th>PSA-C18[4]: Poly(sodium acrylate)</th>
<th>LMAM[0]: Poly(acrylamide)</th>
<th>LMAM[1.5]: Poly(acrylamide)</th>
<th>LMAM[3]: Poly(acrylamide)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>1.95</td>
<td>not applicable</td>
<td>1.94</td>
<td>1 (by definition)</td>
<td>1.44</td>
<td>1.30</td>
<td>1.24</td>
<td>1.24</td>
<td>1.16</td>
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<tr>
<td>PSA</td>
<td>1.94</td>
<td>1 (by definition)</td>
<td>1.44</td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
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<td>1.9</td>
</tr>
<tr>
<td>PSA-C9[4]</td>
<td>1.44</td>
<td>1.5</td>
<td>1.30</td>
<td>4.4</td>
<td>1.24</td>
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<tr>
<td>LMAM[0]</td>
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<td>1 (by definition)</td>
<td>1.16</td>
<td>1.9</td>
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<td>1.12</td>
<td>2.5</td>
<td></td>
<td></td>
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<tr>
<td>LMAM[3]</td>
<td>1.12</td>
<td>2.5</td>
<td></td>
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\(^a\) Total fluorescence intensities in PSA-CX[Y] solutions are related to the intensity of pyrene in the presence of poly(sodium acrylate). \(^b\) Total fluorescence intensities in the presence of LMAM[Z] are related to the intensity of pyrene in the presence of poly(acrylamide).

Binding constant is reduced to $6.10^3 \text{ M}^{-1}$. These values compare favorably with the binding constants of pyrene to micelles formed from SDS ($K = 3.10^4 \text{ M}^{-1}$) and sodium decyl sulfate ($K = 1.10^{-1} \text{M}^{-1}$), respectively.\(^{25}\) These similarities suggest that the affinity of pyrene for hydrophobic clusters composed of single-tailed amphiphilic moieties mainly depends on the length of the n-alkyl chain. Now, the lowest concentration of hydrophobic side chains used in the present study was 2.4 mM. Therefore, the fraction of bound pyrene molecules exceeds the fraction of pyrene molecules in water by a factor of about $10^2$.

### 2.2.2. Examination of microdomains formed from hydrophobically-modified poly-(sodium acrylate)s and poly(acrylamide)s using pyrene as a probe

$I/I_0$ and total fluorescence intensities of pyrene (at ca. $10^{-7} \text{M}$) in aqueous solutions containing 160 unit mM (ca. 1.5 wt%) of PSA-CX[Y] and 160 unit mM (ca. 1.5 wt%) of LMAM[Z] are reported in Table 2.1.

Poly(sodium acrylate) and poly(acrylamide) do not form hydrophobic microdomains: $I/I_0$ values are virtually identical to those of pyrene in pure water. The poly(sodium acrylate)s bearing 4% of octadecyl groups or 8% of dodecyl groups form hydrophobic microdomains quite efficiently. $I/I_0$ is similar to the value of 1.2 found for surfactant micelles. Moreover, the total fluorescence intensity is high, indicating tight packing of the polymer hydrophobes in the microdomains. For PSA-C9[4], the total fluorescence intensity is low, and the reported $I/I_0$ is moderately high. Thus it appears that poly(sodium acrylate)s bearing 4% of nonyl chains form hydrophobic microdomains rather less efficiently. These results are in full agreement with the hypothesis that microdomain formation is driven by hydrophobic interactions. The longer the hydrophobic side chains are, or the larger the number of hydrophobes per polymer, the more hydrophobic are the microdomains.

Notably, $I/I_0$ in the presence of LMAM[1.5] is even lower than for solutions containing the same concentration of PSA-C12[8], despite the fact that the concentration of (dodecyl) hydrophobes is 5 times less. This result is explained by the notion that in case of the charged poly(sodium acrylate)s, microdomain formation is hampered by electrostatic repulsions. For hydrophobic association of PSA-CX[Y] to occur, Coulombic repulsions between approaching parts of the charged backbone have to be overcome.
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Figure 2.6 Total fluorescence intensity of pyrene as a function of CMP concentration in the presence of PSA-CX[Y] at 160 unit mM.

Therefore, the concentration of hydrophobes has to be larger to form microdomains efficiently. Finally, in agreement with the above-mentioned observations, hydrophobic microdomains formed from LMAM[3] are less polar and more tightly packed than those formed from LMAM[1.5].

2.2.3 Interactions between single-tailed surfactants and polysoaps as probed by pyrene. Plots of $I/I_0$ against CMP concentration, in the presence of 160 unit mM of PSA-CX[Y], are presented in Figure 2.5. In the presence of poly(sodium acrylate), a steep drop of $I/I_0$ is observed near the critical aggregation concentration at ca. 0.3 mM. Hence, micellization of the surfactant occurs at a concentration that is much lower than the CMC in the absence of the polymer (3 mM, see below). The lowering of the CMC is a result of salt effects. The concentration of sodium ions in solution is increased by the presence of PSA. Therefore, the degree of counterion binding to the CMP micelles is larger, hence, electrostatic repulsions between the headgroups are reduced, and micellization is favored. Direct (‘classical’) interactions between the poly(sodium acrylate) backbone and CMP can be excluded because of the unfavorable electrostatic repulsions.

When CMP is added to a 160 unit mM solution of PSA-C9[4], $I/I_0$ is decreased quite steeply, to become constant at 1.2, as the CMP concentration reaches ca. 0.3 mM. The plot reflects micellization of CMP molecules. Apparently, the polymeric microdomains are not capable of binding individual surfactant molecules. In the presence of PSA-C12[8] or PSA-C18[4], $I/I_0$ is low, and remains low if CMP is added. Although this result can be accounted for in terms of a continuous association of CMP molecules with the hydrophobic microdomains, in fact, the ratio of $I_0/I_0$ measured in a micellar solution of CMP cannot be distinguished from $I_0/I_0$ ratios determined for the hydrophobic microdomains formed by these polymers. Hence, the obtained results are not conclusive. The same trends are observed if the total fluorescence intensity is plotted against the concentration of CMP (Figure 2.6). In the presence of poly(sodium acrylate), the total fluorescence intensity decreases slightly with added CMP, until the CMC is reached.
Figure 2.7  Pyrene I$_1$/I$_3$ as a function of the concentration of CMP, in the presence of various hydrophobically-modified poly(acrylamide)s at 160 unit mM.

Figure 2.8  Total fluorescence intensity of pyrene as a function of CMP concentration in the presence of hydrophobically-modified poly(acrylamide)s at 160 unit mM.

As the probe is solubilized into the micelles, the total fluorescence intensity increases, according to
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Figure 2.5  Pyrene $I_1/I_3$ as a function of the concentration of CMP, in the presence of various hydrophobically-modified poly(sodium acrylate)s at 160 unit mM.

expectation. The aggregation behavior of CMP in the presence of PSA-C9[4] is very similar, indicating that CMP forms micelles. In the presence of PSA-C12[8] or PSA-C18[4], the plot does not show a break; the total fluorescence intensities remain constant, suggesting that added CMP does not micellize.

With reference to $I_1/I_3$ (Figure 2.7) or the total intensity of pyrene (Figure 2.8) as a function of the concentration of added CMP in the presence of hydrophobically-modified poly(acrylamide)s, similar features are apparent. In the case of a 160 unit mM solution of LMAM[0], the plot shows a clear break at the CMC of the surfactant in aqueous solution, which is 3 mM. The fact that LMAM[0] does not affect the CMC of the anionic amphiphile is in line with previous studies stating the absence of ‘classical’ polymer-surfactant interactions between poly(acrylamide) and SDS. In case of LMAM[1.5] or LMAM[3], $I_1/I_3$ increases slightly, and the total fluorescence intensity decreases upon addition of CMP. Added surfactant appears to continuously associate with the polymeric microdomains to form mixed clusters which are slightly more ‘open’ than the polymeric microdomains in the absence of surfactant. The introduction of charge into the hydrophobic associates upon binding of CMP molecules, leading to Coulombic repulsions, is responsible for this effect.

2.3 Surfactant-polysoap interactions studied by titration calorimetry

As it appears, fluorescence spectroscopy using pyrene as a probe provides valuable information with regard to the nature of hydrophobic microdomains. However, details concerning polymer-surfactant interactions are not revealed because the fluorescence spectra of pyrene solubilized in polymeric microphases and in surfactant micelles are similar. Isothermal titration microcalorimetry provides additional insights into polymer-surfactant interactions.  

2.3.1 Principles of titration calorimetry. Solution microcalorimeters are normally arranged as
Figure 2.9  Schematic representation of the Omega titration microcalorimeter.

twins and function as differential instruments. One of the calorimetric vessels contains the reaction system, and is called the sample cell. The reference cell is filled with the same solvent used to make up the solution in the measuring cell. Hence, the heat capacities of the filled cells are (approximately) the same. The microcalorimeter owes its prefix to its power sensitivity of 1 µW or better. Thus, it can accurately detect heat flow differences of (less than) approximately 1 µJ s⁻¹.

The MicroCal Omega titration microcalorimeter is a power compensation calorimeter and is fully described in the literature. Two coin-shaped cells, having a volume of ca. 1.3 ml, are permanently mounted on either side of a semiconducting thermocouple plate. The thermopile functions as a differential thermometer. The temperature increases slightly during an experiment by heating the reference cell by a small, constant power. The temperature difference between sample and reference cells is monitored and a proportional power fed to the sample cell is adjusted to keep the temperature of the cells the same. Thus, if injection of a small aliquot of solution from the spinning syringe into the sample cell is exothermic, the control system stops heating the sample cell until the temperature of the sample cell has ‘caught up’ with the temperature of the sample cell. The recorded quantity is the rate of heating of the sample cell over the time required to bring sample and reference cells back on a common temperature ramp. The signal from the control unit is integrated, yielding the heat q associated with a given injected aliquot from the syringe into the sample cell. A diagrammatic representation of the apparatus is given in Figure 2.9.

Analysis of the calorimetric data is based on the condition that following each injection of δn_j⁰ moles of substance-j from the syringe, the solution in the sample cell undergoes spontaneous chemical reaction to
reach a unique and stable minimum in the Gibbs energy. As a result, the composition of the sample cell changes by an amount $d\xi$. The following is the key equation for titration microcalorimetry:

$$\left[ \frac{q}{\delta n_j^0} \right]^{(j+1)} = \left[ \frac{\delta H}{\delta \xi} \right]_{T,p} \cdot \left[ \frac{d\xi}{dn_j^0} \right]^{(j)}$$

The left-hand side is the recorded heat accompanying the change in equilibrium composition of the solution in the sample cell from that after injection $I$ to that after injection $I + 1$. The right-hand side is a product of two terms: the differential of the enthalpy of the sample cell with respect to the composition, and the dependence of composition on the amount of injected substance. Neither of the terms is known a priori, and in order to interpret the titration microcalorimetric data we require a model for the chemical reactions or molecular reorganizations occurring in the sample cell. The Origin software package that accompanies the Omega titration calorimeter has built-in software routines to convert the dependence of $q/\delta n_j^0$ on injection number into a plot of the enthalpy change per mole of injectant ($\Delta_{\text{mix}}H$) as a function of concentration of injectant.$^{43}$

2.3.2 Titration microcalorimetry as a tool to study polymer-surfactant interactions. Until recently, calorimetry has not contributed significantly to the understanding of polymer-surfactant interactions and surfactant aggregation. The situation changed when modern high sensitivity titration microcalorimeters became available. The first microcalorimetric experiments were focused on ‘classical’ polymer-surfactant interactions.$^{44}$ Although the interpretation of the observed heat effects was far from straightforward, the concentrations corresponding to the onset of micellization and to saturation of the binding could be satisfactorily reproduced.$^{10}$ In a key development, the interactions of hydrophobically-modified poly(ethylene oxide)$^{8}$ and ethyl(hydroxyethyl) cellulose$^{8}$ (HM-EHEC) with single-tailed amphiphiles were studied. These interactions closely resemble ‘classical’ polymer-surfactant interactions, since the degree of hydrophobic modification of the polymers was only 0.1% or lower, and the surfactants were able to interact with the polymer backbones in the usual ‘beads-on-a-string’ manner. To our knowledge, no microcalorimetric studies have been published regarding the interactions between hydrophobically-modified polymers and single-tailed surfactants, where polymer-surfactant interactions occur by virtue of the presence of hydrophobic side chains only.

2.3.3 CMP and hydrophobically-modified poly(acrylamide). Figure 2.10 (circles) shows an enthalpogram characterizing the micellization of CMP in aqueous solution. Several microcalorimetric studies of micellization of surfactant molecules in aqueous solutions have been described in the literature.$^{45}$ At surfactant concentrations below the CMC, micelles break up upon injection into the cell. At surfactant concentrations higher than the CMC, micelles are only diluted in a solution of micelles. Since this heat effect is more exothermic than the breaking up of micelles, micellization of CMP in ‘pure’ water is weakly exothermic, by 0.7 kJ.mol$^{-1}$. For CMP in pure water, the transition occurs at 3.0 mM.$^{46}$ The latter corresponds with the CMC of 2.9 mM determined as the surfactant concentration where the plot of conductivity vs. [CMP] shows a clear break (Figure 2.10, squares).$^{47}$

As shown Figure 2.11, in the presence of poly(acrylamide) the CMC hardly changes,
The critical micelle concentration of CMP in pure water at 30 °C as determined from titration microcalorimetry and conductivity data.

Plot of the enthalpy of transfer of CMP from water into 160 unit mM hydrophobically-modified poly(acrylamide); [CMP]$_{syringe}$ = 30 mM; but the enthalpy of micellization becomes more exothermic. A possible explanation notes that the
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Surfactant monomers have a higher enthalpy: during the break-up of micelles, surfactant monomers are released into the solution. They are hydrated at the cost of the hydration of the polymer, or vice versa, leading to an endothermic effect. Since the transition occurs at the same concentration as in the absence of LMAM[0], and is still cooperative, there is no indication for direct polymer-micelle interactions.

Clearly, the hydrophobically-modified poly(acrylamide)s interact with the surfactant. No cooperative transition is observed in case of LMAM[1.5] or LMAM[3]. Instead, the plot resembles a binding isotherm. CMP micelles disintegrate into monomers, which continuously associate with the hydrophobic domains. These findings are consistent with the results from the fluorescence probe studies.

The surfactant monomer-polymer interaction enthalpy approaches the enthalpy corresponding to dilution of the CMP solution into aqueous solution as the surfactant concentration is increased. This pattern is due to increasing electrostatic repulsions between the bound ionic surfactant molecules resulting in saturation of the hydrophobic binding sites. The CMP-water curve is approached at higher surfactant concentrations for LMAM[3] than for LMAM[1.5], because the hydrophobic side chains are responsible for the interaction.

The occurrence of a ‘binding isotherm’ together with ‘saturation of the binding’ is a rather common observation. A peculiar feature, however, is the fact that the enthalpic effects accompanying the binding of surfactant molecules to hydrophobic microdomains are exothermic. As was discussed in Section 1.4, hydrophobic interactions per se are quite generally endothermic near room temperature. Did we encounter some artifact? Most likely this is not the case. The data are consistent with observations in the (scarce) literature that the interactions of SDS with hydrophobically-modified poly(ethylene oxide), or hydrophobically-modified ethyl(hydroxyethyl)cellulose, are more exothermic (or less endothermic) than those of SDS with the non-modified analogs, PEO and EHEC. Moreover, examples are known of enthalpy-controlled binding of hydrophobic guests into nonpolar cavities, such as the complexation of benzene in cyclophane host molecules.
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Figure 2.12  Plot of the enthalpy of transfer of CMP from water into 160 unit mM of hydrophobically-modified poly(sodium acrylate); [CMP]_{syringe} = 10 mM.

Figure 2.13  Plot of the enthalpy of transfer of CMP from water into 160 unit mM of hydrophobically-modified poly(sodium acrylate); [CMP]_{syringe} = 30 mM.
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We contend that the ‘binding state’ of water molecules in the hydrophobic microdomains is changed as surfactant molecules are adsorbed, in a way similar to that which has been proposed for the hydration change of a hydrophobic pocket upon complexation of a nonpolar guest. Thus, water molecules in hydrophobic cavities, or water molecules near the hydrophobic core of the polymeric microdomains, are likely oriented such that hydrogen bonds are sacrificed (as compared with bulk water). Upon binding of an apolar solute, some of these ‘unhappy’ water molecules are displaced and liberated into bulk water, whereby the total number of hydrogen bonds in the system is increased. This process is enthalpically favorable.

2.3.4 CMP and hydrophobically-modified poly(sodium acrylate)s. The plot of $\Delta_{\text{obs}} H$ vs. CMP concentration shows a clear break near 0.4 mM (Figure 2.12). This concentration is in excellent agreement with CMC of the surfactant (in the presence of 160 unit mM of PSA) as determined using pyrene as a probe.

Association of surfactant molecules in the presence of nonyl-modified poly(sodium acrylate) is still highly cooperative, which is in line with the results of probe experiments mentioned above. PSA-C9[4] forms hydrophobic microdomains rather inefficiently, and added surfactant molecules form micelles rather than adsorb onto hydrophobic agglomerates formed by the polymer. Interestingly, however, the CMC decreases from 0.4 to 0.3 mM, and the enthalpy of micellization becomes more exothermic by 0.7 kJ mol$^{-1}$ in going from PSA-C9[4] to PSA. These observations strongly point to a ‘classical’ stabilization of CMP micelles by nonyl-modified poly(sodium acrylate), where the polymer stabilizes the micelle as in PEO-SDS interactions.

The picture becomes completely different when the polymer contains lauryl or stearyl side chains. In these cases, no transition was observed that might point to a cooperative micellization process. This result was anticipated, because the polymers form efficient hydrophobic microdomains (vide supra), to which adsorb surfactant molecules. The continuous association of surfactants with hydrophobic microdomains is exothermic. The magnitudes of the heat effects are not so strongly dependent on surfactant concentration as in the case of the interactions with hydrophobically-modified poly(acrylamide)s, probably because the concentration of hydrophobic microdomains is larger in case of the poly(sodium acrylate)s, due to their larger hydrophobe content. On the other hand, interactions of CMP with PSA-C12[8] are less exothermic than those with LMAM[3], even though the latter polymer contains less hydrophobic side chains per unit mol. A likely explanation involves the absence of an electrostatic constraint in the polymer-surfactant interaction.

Interestingly, adsorption of surfactant monomers onto PSA-C18[4] is more exothermic than the interaction of CMP with PSA-C12[8] in the same concentration region. Probably, the concentration of hydrophobic domains in a 160 unit mM solution of PSA-C12[8] is larger than in a solution containing PSA-C18[4]. However, the microdomains formed by the polymer bearing octadecyl side chains will offer better binding sites for the surfactant molecules. If the affinity of the CMP molecules for microdomains from PSA-C18[4] is larger than the binding affinity of CMP to microdomains formed by PSA-C12[8], then the fraction of surfactant bound per injection will be larger in case of PSA-C18[4]. Hence, the difference in $\Delta_{\text{obs}} H$ per injection can be accounted for. Finally, we note there is a limit to the amount of surfactant that can be adsorbed: the heat effects become less exothermic if the surfactant concentration is increased beyond a critical value (Figure 2.13).

Figure 2.14 provides conclusive evidence that interaction between surfactant monomers and
Figure 2.14  Plot of the enthalpy of transfer of CMP from water into 160 unit mM of hydrophobically-modified polymer; [CMP]_{syringe} = 2 mM.
interactions between single-tailed surfactants and hydrophobically-modified polymers occurs. In the foregoing experiments, including those reported in the literature, the concentration of added surfactant was always higher than the CMC, so that mostly micelles were injected into the polymer solution, and it was assumed that they disintegrated into monomers. In the present experiment, the syringe only contains surfactant monomers since the surfactant concentration lies

![Diagram](image_url)

**Figure 2.15** Plot of the enthalpy of transfer of DTAB from water into 160 unit mM of hydrophobically-modified poly(acrylamide); [DTAB]syringe = 153 mM.
well below the CMC. Most significantly, the same trends for the interactions between individual CMP molecules and hydrophobically-modified polymers are obtained: the interactions are most favorable in case of the uncharged hydrophobically-modified poly(acrylamide) LMAM[3], and interactions with PSA-C18[4] are accompanied by more exothermic heat effects than those with PSA-C12[8].

2.3.5 DTAB and hydrophobically-modified poly(sodium acrylate)s. The cationic surfactants form precipitates with the poly(sodium acrylate)s even at very low concentrations. Charge neutralization of both the polymer and the surfactant renders the molecules water-insoluble. The formation of insoluble precipitates in the titration cell of the microcalorimeter is highly undesirable for reasons of reproducibility and the lifetime of the apparatus. Therefore, only few, preliminary, microcalorimetric experiments were undertaken (data not shown). The results provide strong evidence that the binding of the cationic surfactant to the negatively charged polymer is driven by entropy: the heat effects accompanying binding (and precipitation) are endothermic by ca. 20 kJ mol\(^{-1}\). This result is not an unusual. For example, the binding of Ca\(^{2+}\) ions to the surface of vesicle bilayers composed of negatively-charged surfactant molecules (having phosphate headgroups) is entropy-driven,\(^ {57}\) and so is the complexation of Ca\(^{2+}\) ions by some (poly)phosphates.\(^ {58}\) In all cases, dehydration of the ionic groups is the most important contribution to the observed enthalpic effects.\(^ {59}\) Liberation of water molecules (\(\Delta S > 0\)) is the driving force for the reaction. Heat effects vanish completely at a surfactant-to-polymer ratio where charge neutralization has occurred. Finally, the observed heat effects disappear as charge neutralization has occurred, again reflecting the predominance of electrostatic interactions.

**Figure 2.16** Plot of the enthalpy of transfer of DTAB monomers from water into 160 unit mM of hydrophobically-modified poly(acrylamide); [DTAB]\(_{\text{sysinge}}\) = 10 mM.

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2.3.6 DTAB and hydrophobically-modified poly(acrylamide). We finally consider the interactions between cationic surfactants and hydrophobically-modified poly(acrylamide). Cationic surfactants interact less strongly with PEO, poly(propylene oxide) (PPO) or poly(vinyl pyrrolidone) (PVP) than anionic surfactants. The reason is still obscure. One explanation involves the notion that hydration shell overlap between cationic surfactants and polymers is not favorable. An alternative proposition invokes the bulkiness of the headgroups of cationic surfactants, appreciably shielding the hydrophobic core of the micelle from water. Therefore, the driving force (hydrophobic interactions) for the conventional polymer-micelle interaction is reduced.

As can be seen from Figure 2.15, micellization of DTAB in water is rather similar to micellization in a 160 mM solution of poly(acrylamide). Thus, there is no evidence for direct interactions of DTAB micelles or monomers with LMAM[0]. To some extent, DTAB monomers do adsorb onto microdomains formed in solutions of hydrophobically-modified poly(acrylamide). Additional evidence was obtained from an experiment where the syringe contained only DTAB monomers, and no micelles (Figure 2.16). As anticipated, the enthalpy of binding is most exothermic for LMAM[3] and diminishes as the degree of hydrophobic modification decreases. Interestingly, the magnitudes of the heat effects are only -2 kJ mol⁻¹ at most, whereas in the case of CMP, heat effects of -7 kJ mol⁻¹ have been observed. Furthermore, one cannot deny that the sigmoidal features of the DTAB titration curve are typical of micellization. However, the line shapes indicate that the cooperativity of the aggregation process decreases with increasing hydrophobic modification of the polymer. This result might hint at the adsorption of DTAB monomers onto hydrophobic microdomains, and, as is shown below, this process does indeed occur. Presumably, multiple adsorption equilibria occur simultaneously.

The results indicate that the interactions between cationic micelle-forming surfactants and hydrophobically-modified poly(acrylamide) are much less favorable than those between hydrophobically-modified poly(acrylamide) and anionic micelle-forming surfactants. Interactions between hydrophobically-modified poly(acrylamide) and cationic surfactants resemble the classical SDS-PEO interactions where micelles are stabilized by the polymer through shielding of their interfaces from bulk water. Therefore, it is not surprising that no saturation behavior is observed (Figure 2.17).
Figure 2.17  Plot of the enthalpy of transfer of DTAB from water into 40 and 160 unit mM of hydrophobically-modified poly(acrylamide); [DTAB]$_{syringe}$ = 153 mM.

2.4 Conclusions

The following conclusions regarding interactions of single-tailed surfactants with hydrophobically-modified polymers are drawn:

1) In general, interactions between anionic micelle-forming surfactants and hydrophobically-modified water-soluble polymers are fundamentally different from those between these surfactants and uncharged polymers such as PEO, PPO and PVP. In the latter case, the interactions involve polymer molecules wrapped around entire micelles. In the case of hydrophobically-modified polymers, surfactant monomers preferentially adsorb onto hydrophobic microdomains, thereby strengthening the associations of the alkyl side chains.

2) Association of surfactant molecules with hydrophobic microdomains is driven by hydrophobic interactions. The efficiency of the interaction increases with the polymer hydrophobe content and/or the length of the alkyl side chains. In case of PSA-C9[4], hydrophobic interactions are too weak for surfactant adsorption to occur, and polymer-surfactant interactions follow the ‘classical’ pattern as observed for SDS/PEO. However, if the poly(sodium acrylate) bear 4% of octadecyl, or 8% of dodecyl chains, anionic surfactants interact with the negatively charged hydrophobic microdomains, despite the unfavorable electrostatic interactions.

Acknowledgements
We wish to thank Mr. A. Wagenaar who kindly provided the surfactant CMP. Mr. M. Collavo (University of Padova) synthesized the hydrophobically-modified poly(acrylamide) when he visited the University of Groningen as an Erasmus student.
2.5 Experimental part

Materials. Poly(sodium acrylate)s [A] were obtained from National Starch. The pH of the supplied polymer solutions was adjusted to 9 so that the acidic groups were completely converted into their sodium salts. The polymers that were used in the microcalorimetric studies possess molecular weights of about 8000 (GPC) except for PSA-C9[4] which had a molecular weight of 27000. Poly(acrylamide)s [B] were synthesized by radical copolymerization of acrylamide (Servapor, 99%) and lauryl methacrylate (Aldrich, 96%) according to a literature procedure. The raw polymeric material was dissolved in a minimum amount of water and precipitated in methanol. This procedure was repeated. The polymer was dissolved in water and freeze-dried. The complete removal of acrylic monomers was ascertained by ¹H-NMR. The percentage of hydrophobic moieties incorporated into the polymer molecules was determined by measuring the intensity of the terminal alkyl chain CH₃ peak as compared to the intensity of all the peaks in the ¹H-NMR spectrum. It appeared that in all cases approx. 50% of the hydrophobic monomer feed was incorporated into the polymer. The synthesis of CMP has been described. DTAB [3], 99%, was purchased from Merck and was used without further purification. Pyrene (Aldrich, 99+%) was used as received.

Microcalorimetry. An Omega Isothermal Titration Microcalorimeter (Microcal Inc., Northampton, MA, USA) was used to measure the enthalpies of polymer-surfactant interaction. In a typical experiment, a 250 µl stirred syringe was filled with surfactant solution. Each time, a few µl were injected into the measuring cell containing the polymer solution (approx. 1% w/w). A plot was constructed of the enthalpy per injection versus the surfactant concentration, at approximately constant polymer concentration; the temperature was 30.0 ± 0.1 °C. In some cases, particularly when the anionic hydrophobically-modified poly(sodium acrylate)s were used, the observed interaction enthalpies were corrected for the enthalpies of dilution of the polymer by the added water, which were measured in separate experiments.

Fluorescence spectroscopy. Pyrene fluorescence spectra were recorded at 30 ± 1 °C, using an Aminco SLM SPF-500C spectrofluorometer equipped with a thermostated cell holder. Pyrene was excited at 335 nm (slit width: 5 nm). The emission spectrum was recorded from 360 to 530 nm (slit width: 1 nm, step size: 0.5 nm, filter: 2).

Dilute aqueous solutions of pyrene were prepared by sonifying 500 ml of water with ca. 0.5 g of pyrene for 1 hour. Excess pyrene was filtered off, and the filtrate was diluted with 500 ml of water to dissolve any pyrene dimers, if present.

Conductometry. The onset of micellization of the surfactant CMP was indicated by a clear break in the conductivity vs. [CMP] plot. Conductivity was measured using a Wayne-Kerr Autobalance Universal Bridge B642 fitted with a Philips black platinum electrode PW 9512/01 (cell constant: 1.41 cm⁻¹). The temperature was kept constant at 30.0 ± 0.1 °C using a Lauda R2 circulating water thermostat bath equipped with a magnetic stirring device. The solutions were thermostated for at least 15 min before starting the measurements. The surfactant concentration was varied by adding 10 µl aliquots of a concentrated solution to the contents of the cell; concentrations were corrected for volume changes.

2.6 Notes and references

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15. The critical overlap concentration is denoted as \(c^* (= [\eta]^{-1})\). It corresponds to the polymer concentration where interchain interactions start to occur. See, for example, Winnik, F.M. *Macromolecules*, 1989, 22, 734.


19. Polysoaps with perfluorinated alkyl chains show enhanced aggregation properties as compared with their hydrogenated counterparts, due to the greater hydrophobicity of a -CF₂ group compared to a -CH₂ moiety: Petit, F.; Iliopoulos, I.; Audebert, R.; Szönyi, S. *Langmuir* 1997, 13, 4229.


21. After drying aqueous solutions of hydrophobically-modified poly(acrylamide)s (2 wt.%), (hydrophobic) clusters were observed by transmission electron microscopy. In the presence of 25
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24. In general, hydrophobically-modified polymers may be added to laundry detergents in order to stabilize a concentrated liquid formulation (Chapters 5 and 6).


33. The same principles underlie the lower critical micelle concentration of uncharged surfactants as compared with their charged counterparts. See, for example, Israelachvili, J.N. In *Surfactants in Solution*, Mittal, K.L.; Bothorel, P. (Eds.); Plenum Press: New York, 1986.


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42. Actually, a very small temperature difference between the sample cell and the reference cell is maintained. Electronic devices operate more effectively on a signal rather than no signal.

43. For a detailed thermodynamic analysis, see Blandamer, M.J. *Biocalorimetry: Applications of Calorimetry in the Biological Sciences*, Ladbury, J.E.; Chowdhry, B.Z. (Eds.), Wiley: Chichester, 1998, in press.


46. As shown by the (nonzero) slope of the enthalpogram at concentrations < CMC, the surfactant solution in the syringe is thermodynamically non-ideal. In these situations, the CMC is taken as the concentration where ΔH is maximal: Bijma, K. Ph. D. Thesis; University of Groningen: Groningen, 1995.


54. The concentration of microdomains will be higher in case of PSA-C12[8] as compared with PSA-C18[4], since the hydrophobe content is twice as large (the number of hydrophobes per molecule is not very different).


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