Macroscopic modelling of the surface tension of polymer-surfactant systems

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Abstract

Polymer-surfactant mixtures are increasingly being used in a wide range of applications. Weakly-interacting systems, such as SDS/PEO and SDS/PVP, comprise ionic surfactants and neutral polymers, while strongly-interacting systems, such as SDS/POLYDMDAAC and C12TAB/NaPSS, comprise ionic surfactants and oppositely charged ionic polymers. The complex nature of interactions in the mixtures leads to interesting and surprising surface tension profiles as the concentrations of polymer and surfactant are varied. The purpose of our research has been to develop a model to explain these surface tension profiles and to understand how they relate to the formation of different complexes in the bulk solution. In this paper we show how an existing model based on the law of mass action can be extended to model the surface tension of weakly-interacting systems, and we also extend it further to produce a model for the surface tension of strongly-interacting systems. Applying the model to a variety of strongly-interacting systems gives remarkable agreement with the experimental results. The model provides a sound theoretical basis for comparing and contrasting the behaviour of different systems and greatly enhances our understanding of the features observed.

1 Introduction

Polymer-surfactant mixtures are increasingly being used in a wide range of domestic, industrial and technological applications. The mixtures are in general aqueous-based and polymers are added to the systems to control rheology and stability and to manipulate surface adsorption. Interactions within the mixture are driven by hydrophobic, dipolar and electrostatic forces. The complex nature of these interactions and the desire to understand them has led to a wealth of research on the subject, both experimental and theoretical; see for example the papers by Goddard [1, 2, 3]. The most widely studied interactions have been those between neutral polymers and ionic surfactants, which are referred to as "weakly-interacting" systems, as interactions between the polymer and the surfactant are mainly driven by weak hydrophobic forces. Anionic surfactants have attracted most interest; the interaction between the surfactant and the polymer generating interesting behavioural features. The variation of surface tension as bulk surfactant concentration is increased displays a plateau; see for example data presented in references [4, 5, 6, 7, 8]. Systems containing a neutral polymer and a cationic surfactant tend to produce less complex behaviour and consequently have been studied less, and are summarised in the review in reference [9]. In general, systems containing neutral polymers are well understood. When ionic surfactants are introduced into solutions containing ionic polymers of the opposite sign, the strong electrostatic interactions produce systems with yet more complex behaviour. These systems are referred to as "strongly-interacting" systems, as the attractive electrostatic forces are extremely important in the interactions between the polymer and the surfactant. The variation of surface tension as bulk surfactant concentration is increased is more complex and can even show a peak, as is illustrated in the data in references [10, 11, 12, 13]. We note that all measurements described in the references above are carried out under static conditions.

We will briefly review what is known about how the polymer-surfactant interaction modifies the surface tension and adsorption behaviour for different interactions.

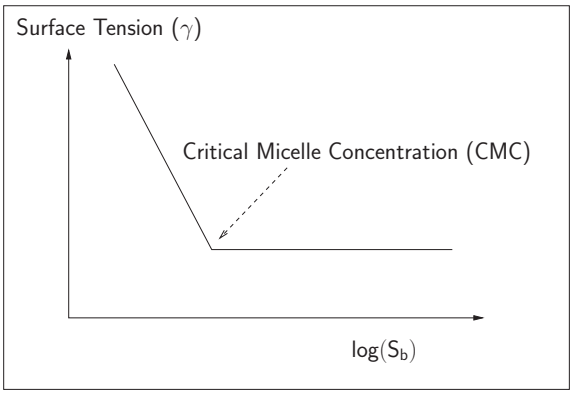


Figure 1: Schematic representation of surface tension, γ, versus log(bulk surfactant concentration, S_b) for a solution containing ionic surfactant only.

1.1 Surface tension of surfactant-only systems

The preference of surfactant molecules either to adsorb at the surface or to form complexes in the bulk leads to interesting variations in the surface tension. A schematic representation of how surface tension, γ, varies as surfactant bulk concentration, S_b, increases is shown in figure 1. The qualitative shape of this graph is well understood. At low concentrations, the surfactant adsorbs to the surface. The presence of surfactant at the surface disrupts the hydrogen bonds between the water molecules and thus lowers the surface tension. As surfactant concentration is increased, more molecules adsorb at the surface, thus lowering the surface tension further. At a certain concentration of surfactant, the *critical micelle concentration* (CMC), it is energetically more favourable for the surfactant to form micelles in the solution. As a result, as the concentration of surfactant is increased beyond this point, the surface tension is almost constant, since there is little or no change in the concentration of surfactant at the surface, nor in the free monomer concentration in equilibrium with the surface.

1.2 Surface tension of weakly-interacting polymer-surfactant systems

Introducing neutral polymers into a solution containing ionic surfactant causes a marked change in the behaviour of the surface tension. The most widely studied solutions are SDS/PEO [4, 5], and SDS/PVP [6, 7, 8]. Sodium dodecyl sulfate (SDS) is an anionic surfactant, while poly(ethyleneoxide) (PEO) and poly(vinylpyrrolidone) (PVP) are neutral polymers.

The surface tension profile for a generic weakly-interacting system is shown schematically in figure 2. Figure 3 shows how it changes with polymer concentration for the SDS/PVP system, [7, 8]. The SDS/PEO system is very similar, [4]. There are two places where there are striking changes in the graph of the surface tension; the CMC and another point at lower surfactant concentrations, the *critical aggregation concentration* (CAC). The CAC is understood to be the point at which the polymer and surfactant start to form mixed aggregates in the bulk. The aggregates take the form of surfactant micelles associating with the polymer molecules, in a "necklace" formation, see for example [14].

Below the CAC, the surface tension decreases monotonically. In this region, the surface tension is less than the surface tension of the surfactant-only system for the same bulk surfactant concentration. This is consistent with some cooperation in the interaction between the polymer and surfactant at the surface.

Above the CAC, there is no significant change in the surface tension for a range of increasing surfactant concentrations. The length of this plateau, (CMC-CAC), increases linearly with polymer concentration [5, 8]. At a certain concentration between the CAC and the CMC, the surface tension starts to decrease again. At this point the polymer is saturated with micellar aggregates, and adding additional surfactant results in an increase in free monomer in the bulk and increased adsorption on the surface. This continues until the surfactant concentration reaches the CMC, where it becomes more energetically favourable for the surfactant molecules to form free micelles in the bulk. Surfactant adsorption at the surface decreases significantly and the surface tension varies negligibly as the bulk concentration is increased.

The exact nature of the interaction between the polymer and the surfactant

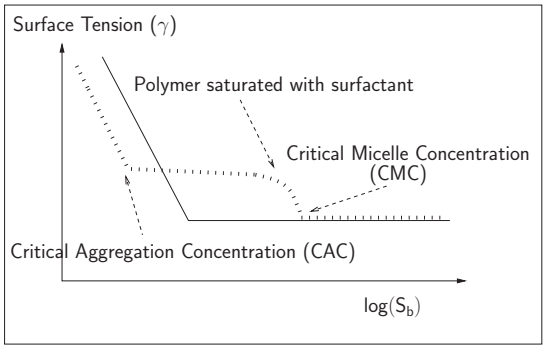


Figure 2: Schematic representation of surface tension against log(bulk surfactant concentration) for a generic weakly-interacting system. This is represented by the dotted line. The solid line corresponds to a polymer-free solution.

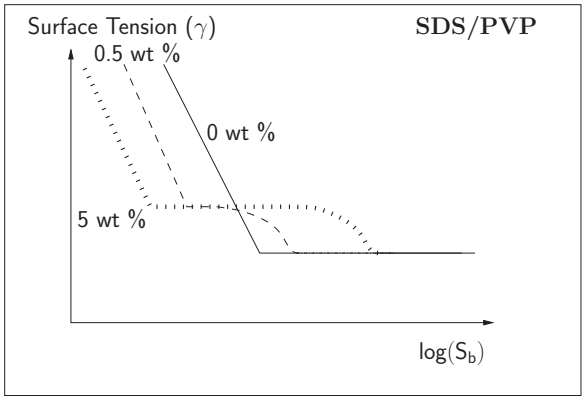


Figure 3: Schematic representation of surface tension against log(bulk surfactant concentration) for the SDS/PVP system. The three lines correspond to solutions containing 0 wt %, 0.5 wt % and 5 wt % of the polymer PVP.

molecules is not clear. The more hydrophobic the polymer, the higher the level of interaction appears to be, as indicated in [15]. PVP is more hydrophobic than PEO, so the interaction is stronger in the SDS/PVP system. The interaction between the ionic charge of the surfactant and the dipole of the polymer may also be important. In part, this may explain why there is such a difference between systems containing cationic surfactants and those containing anionic surfactants.

1.3 Surface tension of strongly-interacting polymer-surfactant systems

The main difference between systems containing neutral polymers and those containing ionic polymers is the existence of strong electrostatic forces in the latter. These dominate the interaction between the polymers and the surfactant. The surface tension behaviour corresponding to these systems can look broadly similar to the neutral polymer system; however the suggested rationale for the underlying mechanics is very different.

Typical ionic polymer systems studied include C_nTAB/NaPSS, [11, 12, 13], and SDS/POLY-DMDAAC/NaCl, [10]. The alkyltrimethylammonium bromides (C_nTAB) are cationic surfactants, where the subscript n denotes the number of carbon atoms in the hydrocarbon chain. Sodium poly(styrene sulfonate) (NaPSS) is an anionic polymer and poly(dimethyldiallylammonium chloride) (POLY-DMDAAC) is a cationic polymer. Neither of these polymers is surface-active on its own.

Typical surface tension profiles for these systems as bulk surfactant concentration varies are more complex, as shown in figures 4 to 7 and clearly show the existence of a hump in the surface tension profile, [10, 11, 12, 13]. We have marked typical points T_1 and T_2 on the C_{14}TAB graph and the significance of these will be discussed further below.

In all cases, there is a pronounced lowering of surface tension at lower surfactant concentrations when the polymer is introduced, compared with the no polymer case. It appears that adsorption of polymer-surfactant complexes occurs at surfactant concentrations well below the concentration at which surfactant on its own would be expected to adsorb significantly. These polymer-surfactant complexes are formed by the cooperative binding of sur-

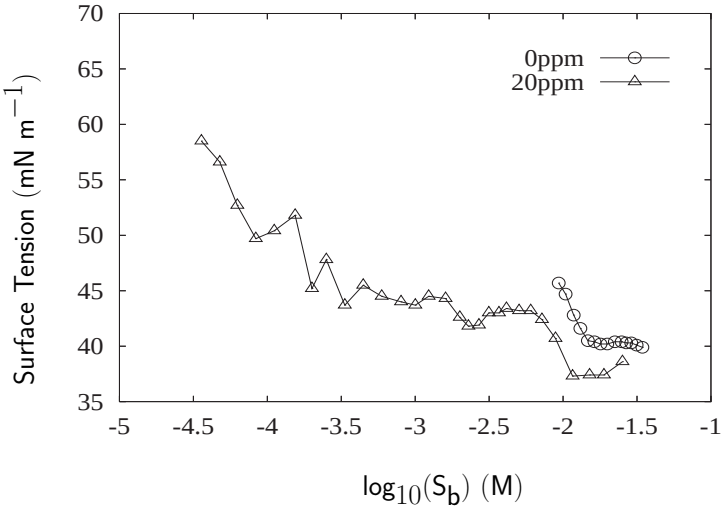


Figure 4: Surface tension of the C_{12}TAB/NaPSS system with no polymer and polymer concentration 20ppm. Experimental data from reference [13].

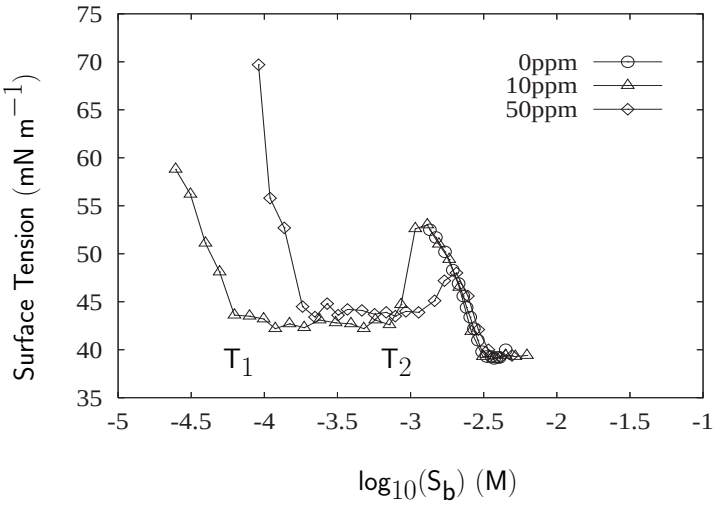


Figure 5: Surface tension of the C_{14}TAB/NaPSS system with no polymer and polymer concentrations 10ppm and 50ppm. Experimental data from reference [13].

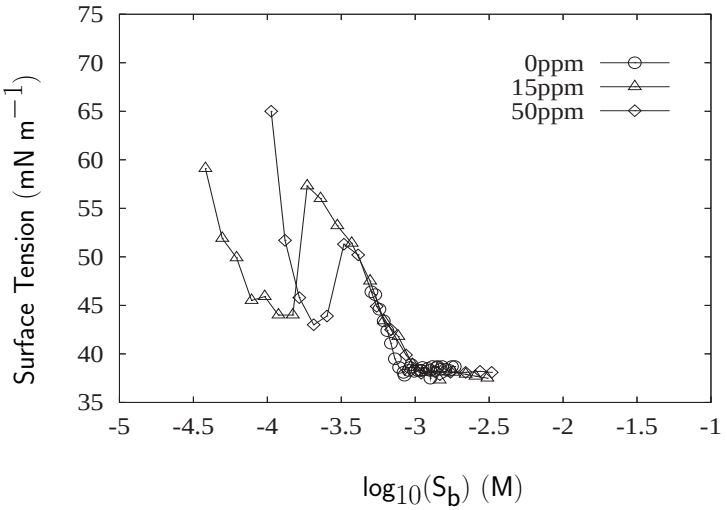


Figure 6: Surface tension of the C_{16}TAB/NaPSS system with no polymer and polymer concentrations 15ppm and 50ppm. Experimental data from reference [13].

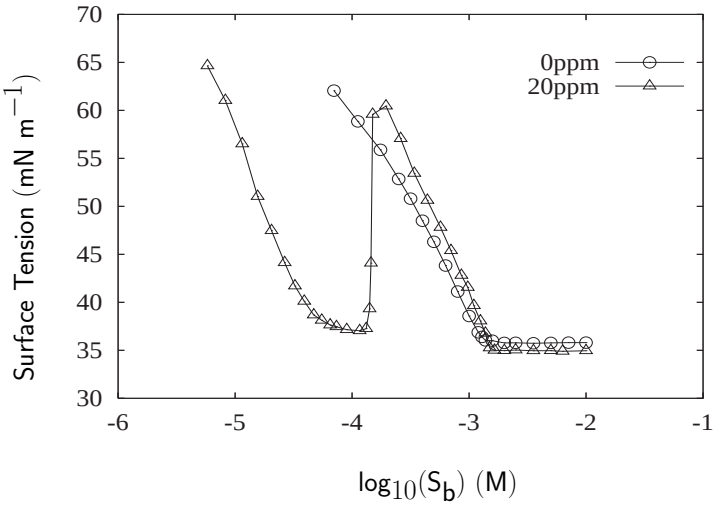


Figure 7: Surface tension of the SDS/POLY-DMDAAC/NaCl system with no polymer and polymer concentration 20ppm. Experimental data from reference [13].

factant monomers onto the polymer backbone. At first glance the point T_1 would appear to be similar to the CAC in the weakly-interacting systems above. However the interpretation given to this point in reference [12] is that this is the point where surface-active polymer complexes containing only singly-bound monomers start to form. The CAC, where the surfactant binds to the polymer in micellar form, occurs at higher surfactant concentrations, but does not correspond to any significant change in the surface tension profile. This may be because the interaction between the polymer and the surfactant is so strong at the surface that changes in the bulk have relatively little effect.

Taylor et al. [12, 13] rationalised these surface tension profiles using three different polymer-surfactant aggregates. They define three different complexes, a surface-active complex consisting of surfactant monomers bound to the polymer backbone, P_S; a surface-active polymer-surfactant complex containing a bilayer or a layer of micelles, which binds onto the underside of the P_S complex, P'_S; and a non-surface-active polymer-micellar aggregate where surfactant molecules cooperatively adsorb to the polymer backbone in the form of micelles to form a necklace-like structure, P_{S_M}. The relative stability of the species may be approximately measured by the overall value of surfactant concentration at which they start to form. The complex P_S forms at very low concentrations due to the electrostatic interaction between the polymer and surfactant and this complex is assumed to be highly surface-active. The sublayer P'_S forms at higher concentrations of surfactant, while P_{S_M} will not generally form until the surfactant concentration has reached the CAC. The formation of the P_{S_M} complex is unlikely to have a large effect on the surface tension, as the P_S complexes are expected to be too strongly bound to be removed from the surface, and there is surplus polymer in the solution. However it is possible that when the formation of the P_{S_M} complex is almost complete, some of the P_S complex is removed from the surface, leading to the rise in surface tension at T_2. In the scenario where the P'_S complex has adsorbed to the underside of the P_S complex, a significant rise in surface tension does not generally occur. The adsorption of the P'_S complex offsets the possible steep rise in surface tension.

As discussed by Taylor et al. [12, 13] the relative stability of the P'_S and P_{S_M} complexes is all-important. If the P'_S complex is more stable than the P_{S_M} complex, that is forms at lower surfactant concentrations, then the hump

in surface tension is likely to be suppressed. However if the P_{S_M} complex is more stable, then it is unlikely that the P'_S complex will ever form, so there is nothing to prevent the hump occurring. We may relate this to the C_nTAB systems by noting that, as n increases the CAC of the system appears to reduce, making the P_{S_M} complex increasingly stable and reducing the gap in stability between P_S and P_{S_M}. This agrees with the fact that the hydrophobicity of the surfactant molecule increases with n. The smaller the gap in stability between P_S and P_{S_M}, the less likely that the P'_S complex will form. Hence there is a steep hump for the C_{16}TAB system and a minimal hump in the C_{12}TAB system. Clearly this is a simple picture, but it seems to encapsulate the main features experimental observations.

1.4 Macroscopic models for interaction of polymers and surfactants

As yet no quantitative theoretical model exists to explain the more complex surface tension behaviour observed in the strongly-interacting systems. In this paper, we use the assumptions of Taylor et al. [12, 13] described above to derive a simple model using the law of mass action to explain how the surface tension changes as the bulk concentrations of surfactant and polymer are changed. Gilanyi and Wolfram [16] used the law of mass action approach to describe polymer-surfactant interactions in "weakly-interacting" systems. The law of mass action is used to evaluate the competition between the formation of polymer-surfactant micellar aggregates and the formation of free surfactant micelles, and the effects of surfactant counterion binding was also included. They did not, however, relate the calculated concentrations to the surface tension.

First, in section 3, we show how, using the Gibbs equation and the Langmuir isotherm, we can use Gilanyi and Wolfram's model (neglecting counterion binding) to predict surface tension behaviour. In section 4 we then extend their model to include surface-active polymer-surfactant complexes, P_S, and show how the inclusion of such complexes helps to describe additional features of both weakly- and strongly-interacting systems.

The main uncertainty with these models is the estimation of the reaction constants, which must be adjusted to match the experimental data. Na-

garajan [17, 18] derived thermodynamic formulas to estimate these reaction coefficients by considering contributions to the free energy of formation of polymer-surfactant aggregates. Ruckenstein et al. [19, 20] and Nikas and Blankstein [21] performed a similar analysis, but considered slightly different contributions to the free energy. However in all these papers, the analysis was only performed for systems involving neutral polymers, and was not expressed in terms of the resulting surface tension.

2 Surface tension and adsorption

The main analytical tool in understanding how the surface tension is related to the concentrations of species in the bulk and at the surface is the Gibbs adsorption equation, [22], which is given by

$$d\gamma = -RT \sum_i \Gamma_i d(\log C_i), \tag{1}$$

where γ is the surface tension, Γ_i is the surface excess concentration of solute i, C_i represents the concentration of solute i in the bulk evaluated just below the surface, R is the Universal Gas Constant and T is the absolute temperature. One critical assumption in (1) is that the "activities" of the solutes may be replaced by the concentrations, which is only true if the concentrations of the solutes are small, that is if the solutions are dilute.

If we can relate the surface excess concentrations to the bulk concentrations, then it is straightforward to determine the surface tension. If the surface is in thermodynamic equilibrium with the subsurface layer, then the most widely used model for single species is the Langmuir isotherm,

$$\Gamma = \Gamma_\infty \frac{k_C C}{1 + k_C C}, \tag{2}$$

where k_C is a constant measuring the ability to adsorb and Γ_∞ is the maximum surface concentration of this solute that can occur.

If the solution contains many species competing to adsorb and each species excludes the same area on the surface, then the Langmuir isotherm becomes

(see for example [23])

$$\Gamma_i = \Gamma_\infty \frac{k_{C_i} C_i}{1 + \sum_j k_{C_j} C_j}. \tag{3}$$

Substituting from (3), into (1), we obtain

$$d\gamma = -RT \sum_i \Gamma_\infty \frac{k_{C_i} C_i}{1 + \sum_j k_{C_j} C_j} d(\log C_i). \tag{4}$$

This formula may be integrated exactly to give us the Szyszkowski equation of state

$$\gamma - \gamma_0 = -RT\Gamma_\infty \log\left(1 + \sum_j k_{C_j} C_j\right), \tag{5}$$

where γ_0 is the surface tension of the solution in the absence of all solutes and Γ_∞ is the single maximum surface excess concentration. Throughout this paper we shall make the assumption that all species encountered exclude the same area from the surface so that the Szyszkowski equation of state holds. This is a clearly a simplification, but nevertheless enables us to obtain interesting results. For solutions containing different sized molecules, which exclude different areas from the surface, thermodynamically consistent isotherms should be derived from an appropriate free energy calculation. We do not explore this approach in this paper.

3 Macroscopic model of competition between polymer-surfactant micelle aggregates and free surfactant micelles

Firstly we shall consider the formation of free micelles. Micelles formed in solution generally have a reasonably homogeneous structure and we shall assume that the micelles are all composed of the same number of monomers

N. This number tends to be large, around 50-80. We shall denote the concentrations (in mol m^{-3}) of free surfactant monomers and micelles by S and S_N respectively. We model the formation of micelles as a single-step reaction of the form

$$NS \underset{k_{-0}}{\overset{k_{+0}}{\rightleftharpoons}} S_N, \tag{6}$$

for some reaction constants, k_{+0} and k_{-0}. We note that this is a simplification, particularly as polydispersity is not included, but it provides us with the simplest model with the minimum number of parameters.

Secondly we consider the polymer-surfactant aggregates. We assume that the aggregates take the form of surfactant micelles attached to the polymer chains, in a sort of necklace formation, as has been seen in experimental work. These micelles have a lower aggregation number M, and, for simplification, we shall assume that the same number n attach to each polymer chain. This is a simpler version of the model of Nikas et al. [21] who assume that first one micelle attaches to all polymers, then a second, then a third and so on, until the maximum number n is reached. The concentration of free and aggregated polymer molecules shall be denoted by P_f and P_{S_M} respectively. We shall assume that the formation of aggregates is described by the single-step reaction

$$P_f + nMS \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} P_{S_M}, \tag{7}$$

for some reaction constants, k_{+1} and k_{-1}.

Invoking the "law of mass action", which implies that the rate, j_{S_N}, at which surfactant changes phase from monomer to micelle is

$$j_{S_N} = k_{+0}S^N - k_{-0}S_N, \tag{8}$$

and similarly the rate, $j_{P_{S_M}}$, at which polymer and surfactant combine to form aggregates is

$$j_{P_{S_M}} = k_{+1}P_f\ S^{nM} - k_{-1}P_{S_M}. \tag{9}$$

At thermodynamic equilibrium we must have that $j_{S_N} = j_{P_{S_M}} = 0$ and therefore the following relations must hold,

$$S_N = K_0 S^N, \tag{10}$$
$$P_{S_M} = K_1 P_f \, S^{nM}, \tag{11}$$

where $K_0 = k_{+0}/k_{-0}$ and $K_1 = k_{+1}/k_{-1}$.

In addition, we know the total bulk concentrations of the surfactant and polymer, denoted by S_b and P_b, and these must satisfy the following relations,

$$S_b = S + NS_N + nMP_{S_M}, \tag{12}$$
$$P_b = P_f + P_{S_M}. \tag{13}$$

We therefore have four equations for the four unknowns, S, S_N, P_f and P_{S_M}. Solving for S, we obtain

$$S_b = S + NK_0 S^N + nMP_b \left(\frac{K_1 S^{nM}}{1 + K_1 S^{nM}} \right). \tag{14}$$

This has the same form as the equation derived by Nikas et al. [21] from thermodynamic arguments, but is slightly different from that derived by Ruckenstein et al. [19], who use a combination of thermodynamic reasoning to describe the free micelle formation and an adsorption isotherm to describe the complexation of the surfactant with the polymer.

The dimensions of K_0 are $(\text{mol m}^{-3})^{-(N-1)}$, and those of K_1 are $(\text{mol m}^{-3})^{-nM}$. Following the example of [24], let us define

$$S_{CMC} = \left(\frac{1}{NK_0} \right)^{\frac{1}{N-1}} \text{ mol m}^{-3}, \tag{15}$$
$$S_{CAC} = \left(\frac{1}{K_1} \right)^{\frac{1}{nM}} \text{ mol m}^{-3}, \tag{16}$$

where, as we shall see, we can identify S_{CMC} with the Critical Micelle Concentration and S_{CAC} with the Critical Aggregation Concentration. We can then re-write equation (14) as

$$S_b = S + S_{CMC}\left(\frac{S}{S_{CMC}}\right)^N + nMP_b\left(\frac{\left(\frac{S}{S_{CAC}}\right)^{nM}}{1+\left(\frac{S}{S_{CAC}}\right)^{nM}}\right). \tag{17}$$

It is also easy to show that P_f, P_{S_M} and S_N are given by the formulae

$$P_f = P_b\left(\frac{1}{1+\left(\frac{S}{S_{CAC}}\right)^{nM}}\right), \tag{18}$$

$$P_{S_M} = P_b\left(\frac{\left(\frac{S}{S_{CAC}}\right)^{nM}}{1+\left(\frac{S}{S_{CAC}}\right)^{nM}}\right), \tag{19}$$

$$S_N = \left(\frac{S_{CMC}}{N}\right)\left(\frac{S}{S_{CMC}}\right)^N. \tag{20}$$

We summarize this system of reactions with a pictorial representation of each species in figure 8. The only surface-active species is the free surfactant, so the Szyszkowki equation, (5), becomes, in this case,

$$\gamma - \gamma_0 = -RT\Gamma_\infty \log\left(1 + k_S S\right). \tag{21}$$

It is straightforward to plot the surface tension versus total surfactant concentration for any particular case. Using typical values for the parameters, we obtain the plot in figure 9, which shows a comparison between the surfactant-only case and the case where polymer is present. This plot does indeed exhibit many of the features encountered in weakly-interacting systems. When $S_b \sim S_{CAC}$, micelles start to form complexes with the polymer, which leads us to identify S_{CAC} with the Critical Aggregation Concentration. Then for $S_{CAC} < S_b < S_{CAC} + nMP_b$, the "polymer aggregation plateau", the free

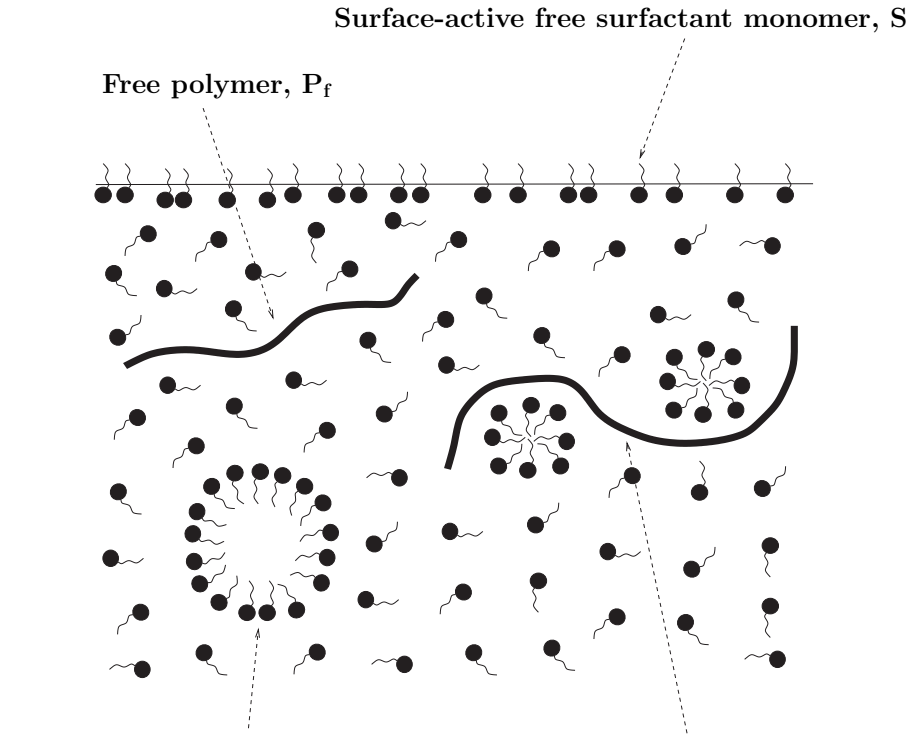


Figure 8: Schematic of species found in weakly-interacting systems.

monomer concentration $S \sim S_{CAC}$, corresponding to the fact that additional monomers prefer to form complexes with the polymer. The concentration $S_{CAC} + nMP_b$ corresponds to the point where the polymers become saturated with surfactant and from there the free monomer concentration starts to increase until it reaches S_{CMC} when free micelles start to form in the solution. This happens when $S_b = S_{CMC} + nMP_b$. This point can be identified with the Critical Micelle Concentration. Above $S_{CMC} + nMP_b$, $S \sim S_{CMC}$.

It is interesting to note that the length of the polymer aggregation plateau and the CMC both increase with nMP_b. This is what we would expect and is consistent with experimental results for the weakly-interacting systems. The CAC in the model does not change with polymer concentration, which agrees with the behaviour of the SDS/PEO system, but does not model the movement observed in the SDS/PVP system. This suggests that the parameter K_1, which we have taken to be constant, may not actually be a constant for the SDS/PVP system, but may vary with polymer concentration.

4 Extension of model to include surface-active polymer-surfactant monomer aggregate

The model presented in section 3 does not include the additional polymer-surfactant complexes, formed by an electrostatic interaction between single surfactant monomers and the polymer backbone, which were discussed earlier in the context of strongly-interacting mixtures. We denote the concentration of this surface-active aggregate by P_S. We retain the other species, S, S_N, P_f and P_{S_M}, in the model and we stress that the only two surface-active species will be S and P_S.

As in the previous model, the free micelles and the polymer-micelle complex are assumed to obey the reactions of the form (6), (7). For the polymer-monomer complex, P_S, we suppose that L monomers attach to each polymer molecule, where it is chemically reasonable to suppose that $L < nM$. Then for a single-step reaction we have

$$P_f + LS \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} P_S, \tag{22}$$

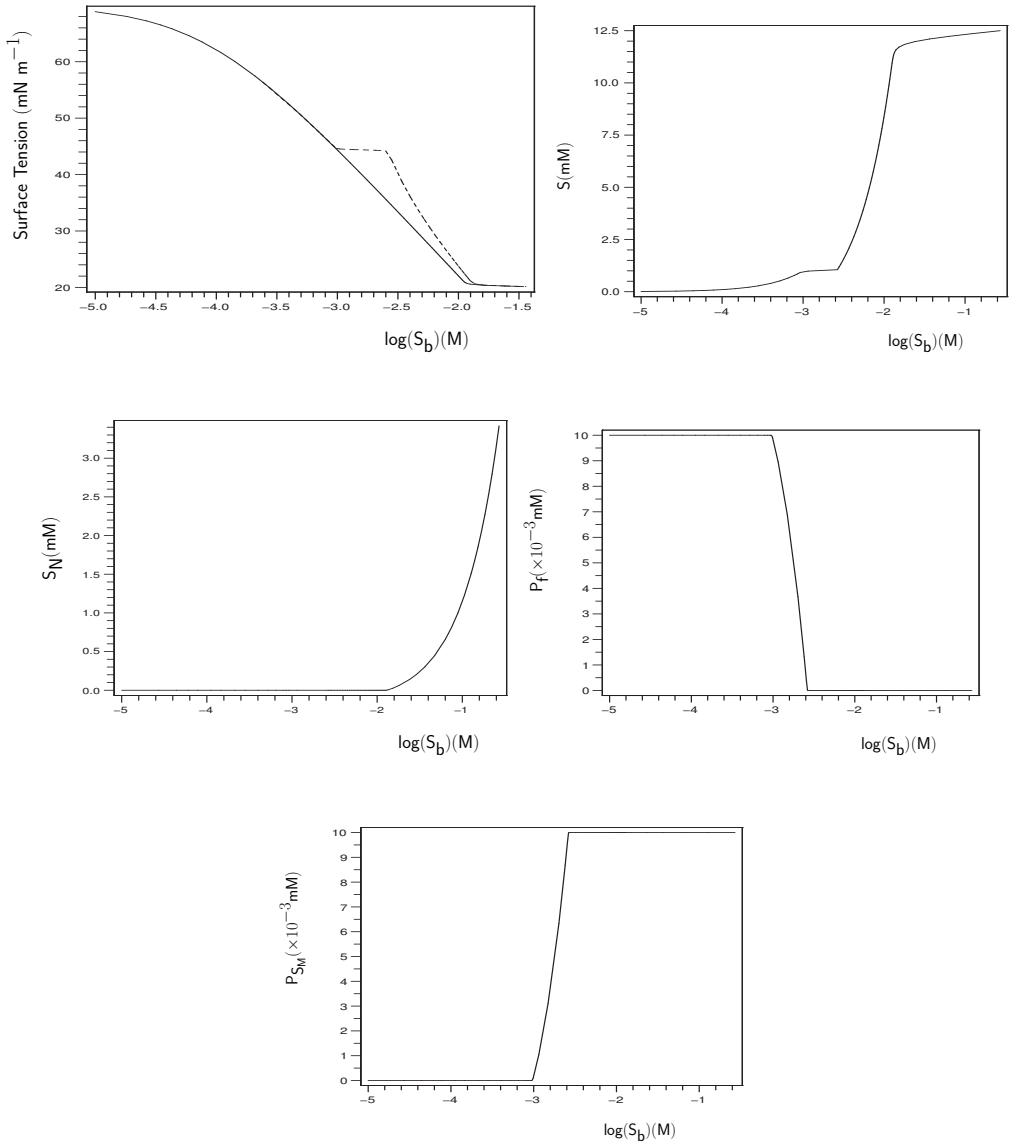


Figure 9: Surface tension versus log(bulk surfactant concentration) plotted using formulae (17) and (21). The lines are for bulk polymer concentrations 0 mM (solid) and 1×10^{-2} mM (dashed). The other graphs show how the concentrations of the different species, S, S_N, P_f and P_{S_M} vary. Parameters used are $N = 75$, $M = 20$, $n = 8$, $S_{CMC} = 12$ mM, $S_{CAC} = 1$ mM, $\Gamma_\infty = 4 \times 10^{-6}$ mol m^{-2}, $\gamma_0 = 70$ mN m^{-1}, $k_S = 12$ m^3 mol^{-1}.

for some reaction constants, k_{+2} and k_{-2}. As previously, for simplicity we assume that these complexes form in a single-step reaction. Using the law of mass action, and assuming equilibrium, we have the following relationships

$$\begin{aligned} S_N &= K_0 S^N, && (23)\\ P_{S_M} &= K_1 P_f\ S^{nM}, && (24)\\ P_S &= K_2 P_f\ S^L, && (25) \end{aligned}$$

where $K_0 = k_{+0}/k_{-0}$ etc.

As before, the total bulk concentrations of surfactant and polymer, denoted by S_b and P_b, must be conserved. Therefore they must satisfy the following relationships,

$$\begin{aligned} S_b &= S + NS_N + nMP_{S_M} + LP_S, && (26)\\ P_b &= P_f + P_{S_M} + P_S. && (27) \end{aligned}$$

We therefore have five equations for the five unknowns, $S,\ S_N,\ P_f,\ P_{S_M}$, and P_S. Solving for S, we obtain

$$S_b = S + \frac{NS^N}{K_0} + P_b \left(\frac{\dfrac{nMS^{nM}}{K_1} + \dfrac{LS^L}{K_2}}{1 + \dfrac{S^{nM}}{K_1} + \dfrac{S^L}{K_2}} \right), \qquad (28)$$

with the same notation as before, and defining

$$S_{ELE} = \left(\frac{1}{K_2} \right)^{\frac{1}{L}}\ \text{mol m}^{-3}, \qquad (29)$$

we may re-write (28) as

$$S_b = S + S_{CMC}\left(\frac{S}{S_{CMC}}\right)^N + P_b\left(\frac{nM\left(\frac{S}{S_{CAC}}\right)^{nM} + L\left(\frac{S}{S_{ELE}}\right)^L}{1+\left(\frac{S}{S_{CAC}}\right)^{nM} + \left(\frac{S}{S_{ELE}}\right)^L}\right). \quad (30)$$

It is trivial to show that the equations for P_f, P_S, P_{S_M} and S_N are as follows

$$\begin{aligned} P_f &= P_b\left(\frac{1}{1+\left(\frac{S}{S_{CAC}}\right)^{nM} + \left(\frac{S}{S_{ELE}}\right)^L}\right), & (31)\\ P_S &= P_b\left(\frac{\left(\frac{S}{S_{ELE}}\right)^L}{1+\left(\frac{S}{S_{CAC}}\right)^{nM} + \left(\frac{S}{S_{ELE}}\right)^L}\right), & (32)\\ P_{S_M} &= P_b\left(\frac{\left(\frac{S}{S_{CAC}}\right)^{nM}}{1+\left(\frac{S}{S_{CAC}}\right)^{nM} + \left(\frac{S}{S_{ELE}}\right)^L}\right), & (33)\\ S_N &= \left(\frac{S_{CMC}}{N}\right)\left(\frac{S}{S_{CMC}}\right)^N. & (34) \end{aligned}$$

We summarize this system of reactions with a pictorial representation of each species in figure 10. To understand how S and P_S affect surface tension, we use the coupled Langmuir isotherm (3)

$$\begin{aligned} \Gamma_{P_S} &= \Gamma_\infty\left(\frac{k_{P_S}P_S}{1+k_S S + k_{P_S}P_S}\right), & (35)\\ \Gamma_S &= \Gamma_\infty\left(\frac{k_S S}{1+k_S S + k_{P_S}P_S}\right), & (36) \end{aligned}$$

where, recall, we have assumed that the maximum concentration of both surfactant and polymer-monomer complex that can exist at the surface is the same, that is Γ_∞.

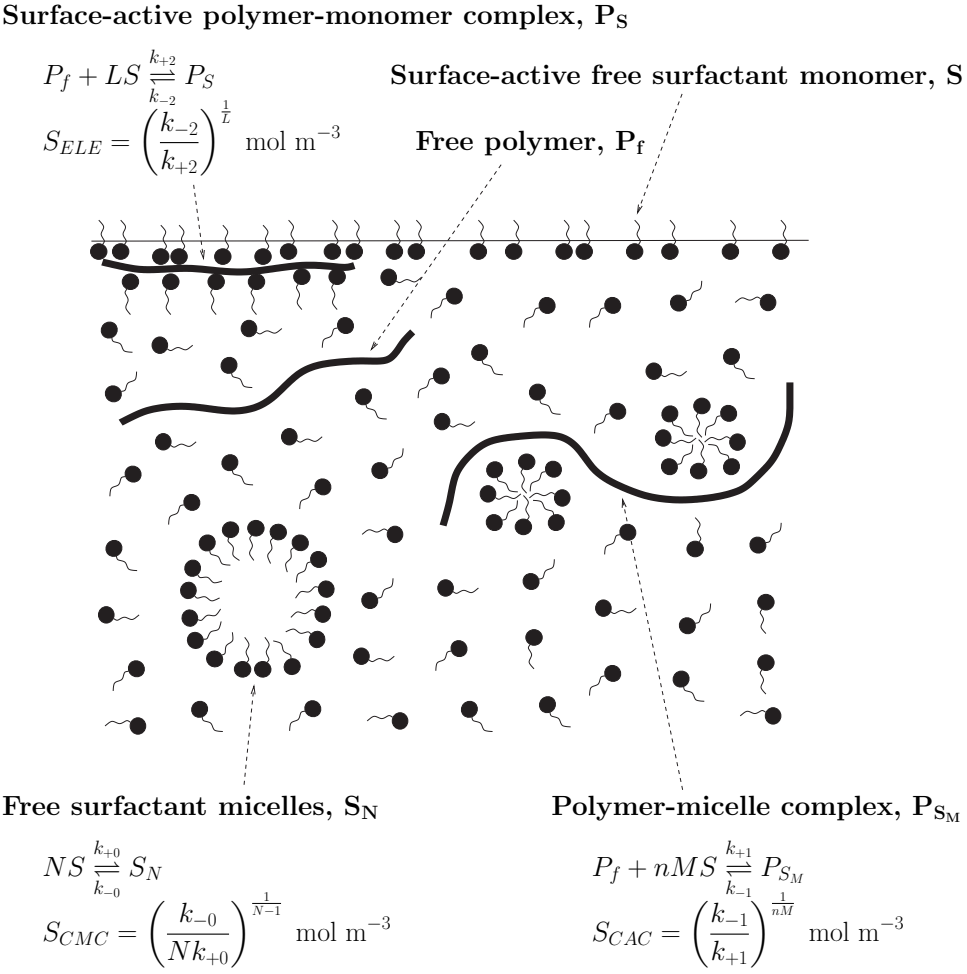


Figure 10: Schematic of species found in strongly-interacting systems.

The Gibbs adsorption isotherm, (4), linking the surface tension to the bulk concentrations therefore becomes

$$d\gamma = -RT\Gamma_\infty \left(\frac{k_{P_S} P_S}{1 + k_S S + k_{P_S} P_S} \right) d\log(P_S) - RT\Gamma_\infty \left(\frac{k_S S}{1 + k_S S + k_{P_S} P_S} \right) d\log S, \quad (37)$$

which we can integrate to give the Szyszkowski equation, (cf. 5),

$$\gamma - \gamma_0 = -RT\Gamma_\infty \log(1 + k_S S + k_{P_S} P_S). \quad (38)$$

We have taken parameters to model the experimental data presented in references [10] and [13], and we show the results for four of their experiments in the figures 11-15 below. In the surface tension graphs, the solid lines are the model predictions and the dots are the experimental data. We see that the model replicates a wide variety of features encountered in polymer-surfactant systems as represented by the C_nTAB/NaPSS and SDS/POLYDMDAAC systems and in fact provides a remarkable agreement for all the systems. In every figure shown, we can see that the first steep downturn in the surface tension graph corresponds to the surfactant concentration at which the surfactant starts to combine with the polymer to form the surface-active polymer-monomer complex, P_S. At this point the free polymer concentration, P_f, declines to zero and all the polymer is contained in the P_S complex. As the bulk surfactant concentration increases, the surface tension declines slightly as the free surfactant monomer concentration, S, continues to increase. This decrease is slight and we see what might be described as a plateau in the surface tension graph. The length of this plateau depends on when it becomes more energetically favourable for the polymer to form complexes with the surfactant in micellar form, P_{S_M}, rather than in monomer form, P_S. We can see that at the bulk surfactant concentration where P_{S_M} starts to form, the concentration of P_S declines to zero, reducing the amount of surface-active species. As a result the surface tension increases again until it reaches a peak, when all the P_S complex has turned into the P_{S_M} complex. We can see qualitatively that the length of the plateau in the graph of the surface tension, (and indeed, the length of the plateau in the graph of P_S

concentration), depends on the relative sizes of S_{ELE} and S_{CAC}, the size of which are in some way a measure of the relative stability of the P_S and P_{S_M} complexes respectively. As bulk surfactant concentration is increased beyond the point where the surface tension has reached a peak, the concentration of P_{S_M} remains constant as the polymer is saturated with surfactant micelles, while the free surfactant monomer concentration, S, increases. This leads to the surface tension decreasing again, which continues until the free surfactant monomer concentration is large enough to allow the formation of free surfactant micelles, S_N. Here the concentration of S_N increases from zero and the free surfactant concentration, S, levels off, although it does still show a slight increase. As a result the surface tension graph also levels off and only decreases slightly.

We have not used any optimisation procedure to choose the parameters in the model to match the experimental data. The parameters to a certain extent choose themselves. The nine parameters to which we need to assign values are N, nM, L, S_{CMC}, S_{CAC}, S_{ELE}, Γ_∞, k_S and k_{P_S}. We have included nM as one parameter instead of two separate ones as they only ever appear multiplied together in the model. We have taken N and S_{CMC} from experimentally measured data for pure surfactant without polymer, [25]. If we then consider the points T_1 to T_5 labelled in the surface tension graph for the SDS/POLYDMDAAC system in figure 11, we can understand the general procedure that must be followed when applying the model to the experimental data. Making the model match the gradient between T_4 and T_5, and also capture the position of the point T_5, establishes the values of Γ_∞ and k_S. Fixing the points T_1 and T_2 involves selecting S_{ELE} and L appropriately, and the drop in the surface tension between T_1 and T_2 fixes the parameter k_{P_S}. Then choosing nM and S_{CAC} (and varying L too if necessary) determines the position of the points T_3 and T_4. This is a simplification of the process, as further adjustments can then be made to the parameters to improve the agreement. Also for some systems nM may affect the fixing of point T_5. However it is clear that a procedure similar to this will always be used. More detail on the effect of the parameters on the behaviour of the model will appear in a forthcoming paper [26].

One problem with the model is that it does not replicate well the surface tension at lower surfactant concentrations. This is most likely due to the fact that we have modelled the binding of monomers to the polymer as a single-

step reaction. In reality these complexes are more likely to form gradually with first one surfactant monomer binding to the polymer, then two and so on. This would lead to a more gradual decrease in the surface tension graph, rather than the steep decrease encountered using the model specified here. Developments to incorporate such refinements are currently in progress.

Penfold et al., [27], have recently applied the model to describe and quantify the variations in the surface tension and adsorption behaviour for the sodium alkyl sulfates and the oppositely charged polyelectrolyte, POLYDMDAAC. In particular they have investigated the role of alkyl chain length (from C10 to C14) and the effect of added electrolyte on the surface tension and adsorption behaviour. The model is shown to reproduce the principal features of the experimental results for this range of systems. From the values of S_{CAC} and S_{ELE} estimated from the model, they were able to evaluate the relative free energy of formation of the surface and solution complexes. From this they were able to quantify how the competition between the formation of surface and solution complexes varied systematically with surfactant alkyl chain length and electrolyte. Furthermore their analysis highlighted the dangers and difficulties associated with interpreting such surface tension data using a more conventional approach.

5 Summary and conclusions

The aim of this paper was to produce a theoretical model to describe the variations in surface tension as the concentration of bulk surfactant is changed for strongly-interacting polymer-surfactant systems, that is, systems containing polymer and surfactant which are oppositely charged. To date no theoretical framework exists which enables any sort of description of these systems. Building on the models of Gilanyi and Wolfram [16], Ruckenstein et al. [19] and Nikas and Blankstein [21], we have succeeded in producing a simple model which can reproduce most of the range of surface tension variations encountered. Gilanyi and Wolfram [16] had originally used a similar model to describe the concentrations of different species encountered in weakly-interacting systems, that is systems containing ionic surfactants and neutral polymers. We have shown that by using the Gibbs equation and the Langmuir isotherm, this model may also be used to describe surface

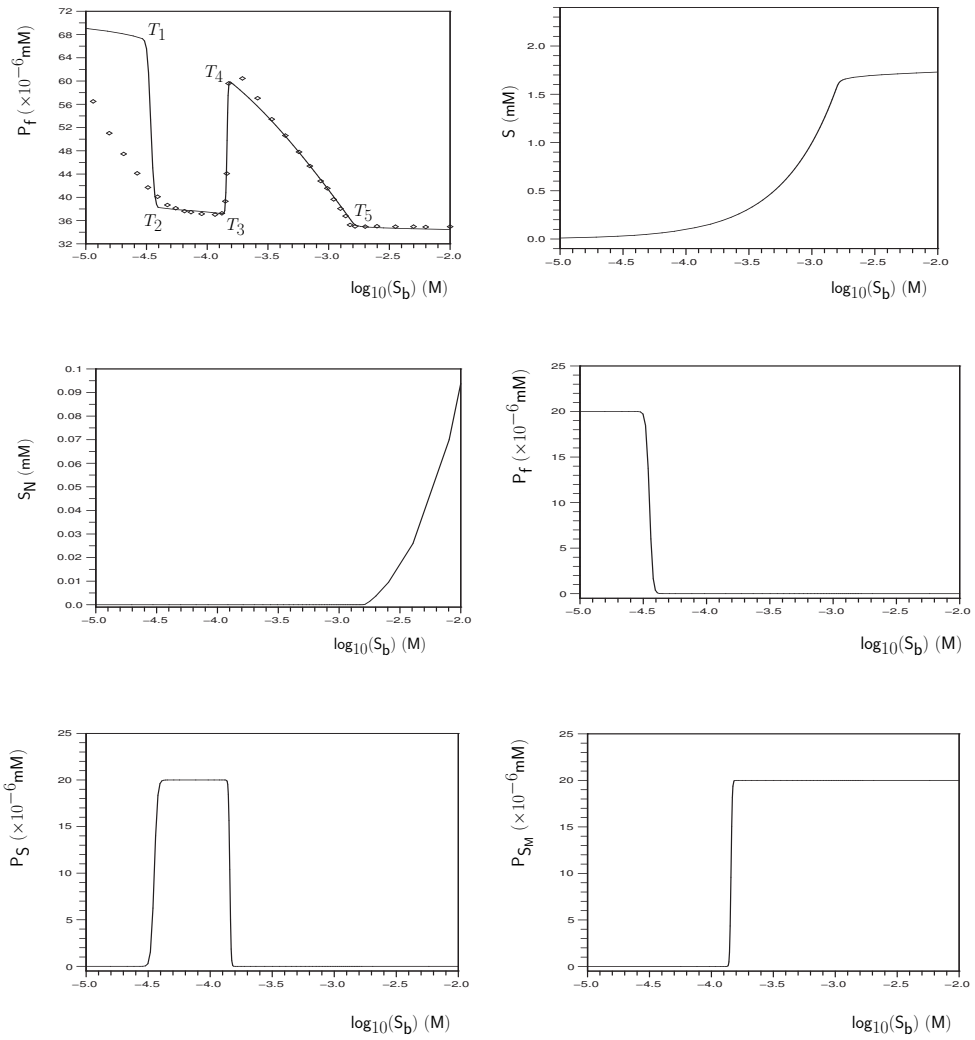


Figure 11: SDS/POLYDMDAAC/0.1M NaCl system [10]. Surface tension and concentrations of the different species. Parameters used in the model are $N = 90$, $M = 20$, $n = 8$, $L = 40$, $S_{CMC} = 1.7$ mM, $S_{CAC} = 0.1$ mM, $S_{ELE} = 0.035$ mM, $\Gamma_\infty = 5.5 \times 10^{-6}$ mol m^{-2}, $\gamma_0 = 70$ mN m^{-1}, $k_S = 7.3$ m^3 mol^{-1}, $k_{P_S} = 4.6 \times 10^5$ m^3 mol^{-1}. The bulk polymer concentration $P_b = 2 \times 10^{-5}$ mM, corresponding to 20ppm.

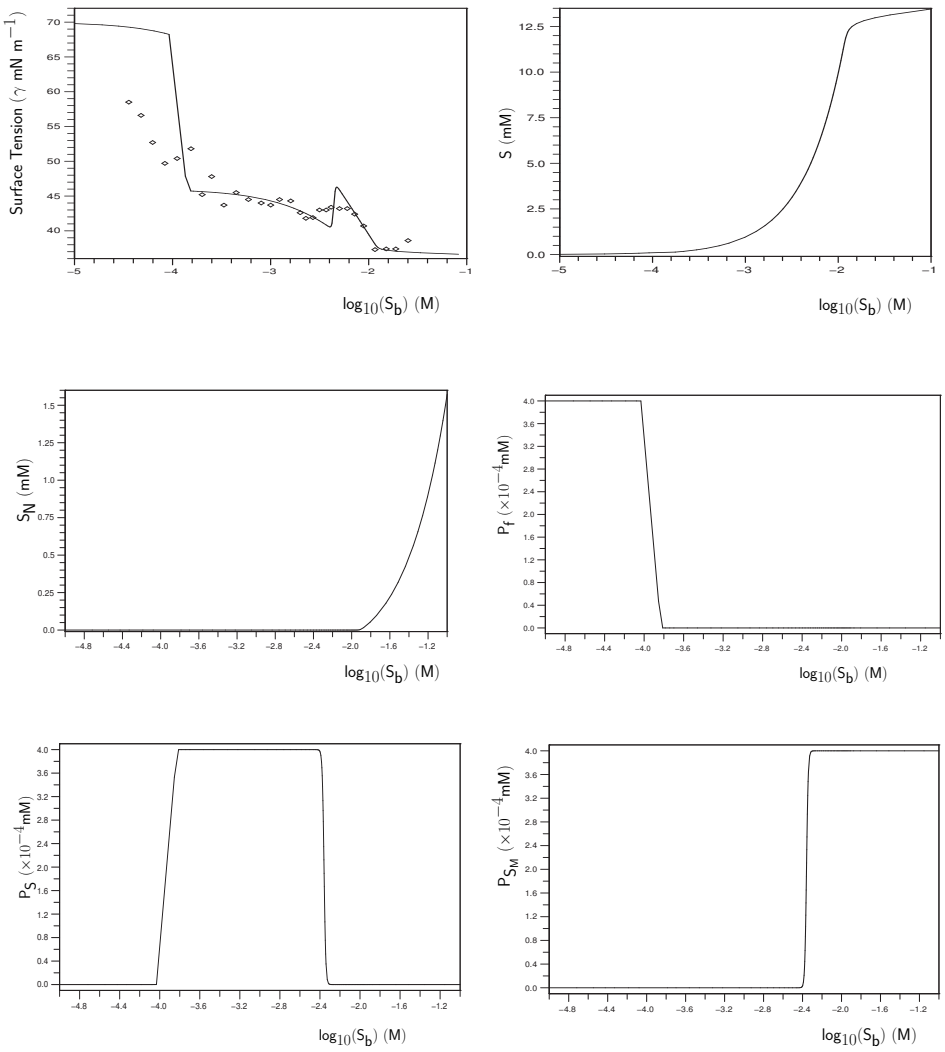


Figure 12: C12TAB/NaPSS system [13]. Surface tension and concentrations of the different species. Parameters used in the model are $N = 55$, $M = 20$, $n = 8$, $L = 108$, $S_{CMC} = 13$ mM, $S_{CAC} = 0.34$ mM, $S_{ELE} = 0.1$ mM, $\Gamma_\infty = 4 \times 10^{-6}$ mol m^{-2}, $\gamma_0 = 70$ mN m^{-1}, $k_S = 2.1$ m^3 mol^{-1}, $k_{P_S} = 2.6 \times 10^4$ m^3 mol^{-1}. The bulk polymer concentration $P_b = 4 \times 10^{-4}$ mM, corresponding to 20ppm.

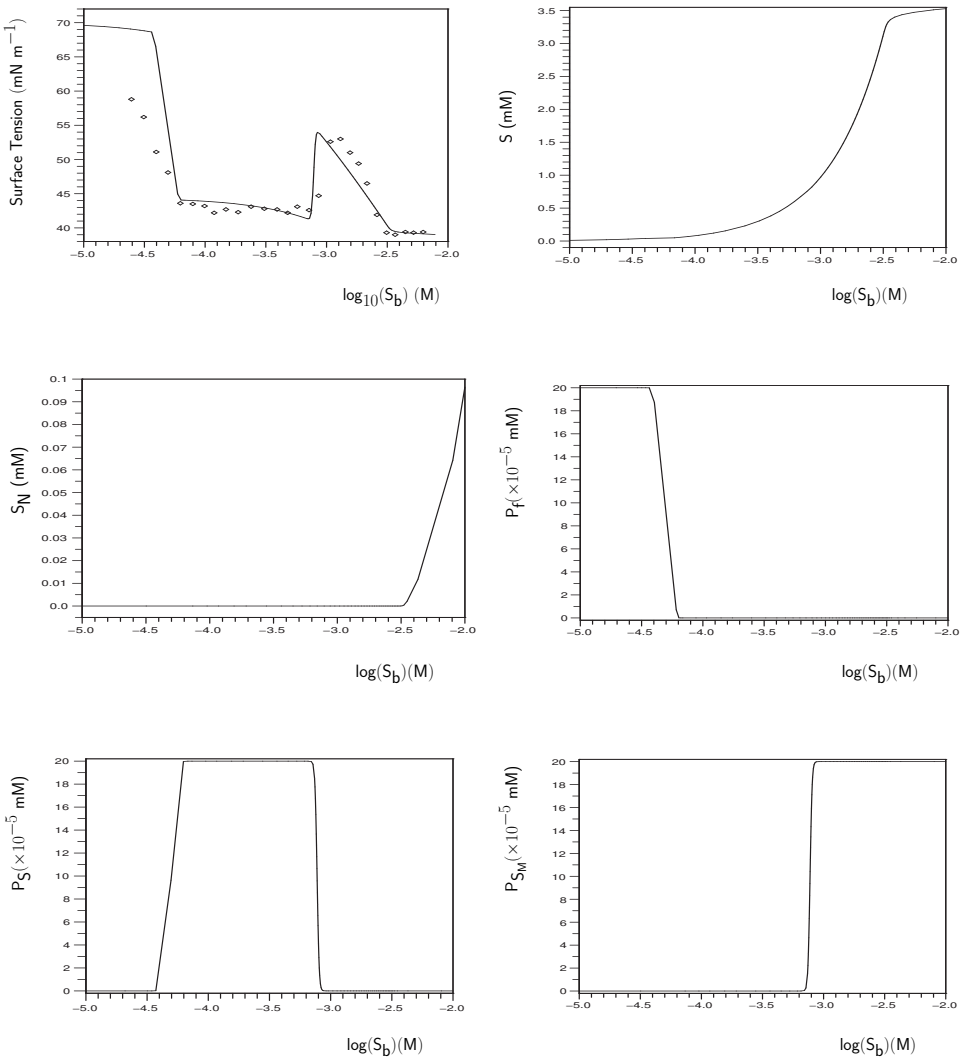


Figure 13: C14TAB/NaPSS system [13]. Surface tension and concentrations of the different species. Parameters used in the model are $N = 70$, $M = 20$, $n = 8$, $L = 80$, $S_{CMC} = 3.5$ mM, $S_{CAC} = 0.12$ mM, $S_{ELE} = 0.04$ mM, $\Gamma_\infty = 5 \times 10^{-6}$ mol m^{-2}, $\gamma_0 = 70$ mN m^{-1}, $k_S = 3.2$ m^3 mol^{-1}, $k_{P_S} = 3.5 \times 10^4$ m^3 mol^{-1}. The bulk polymer concentration $P_b = 2 \times 10^{-4}$ mM, corresponding to 10ppm.

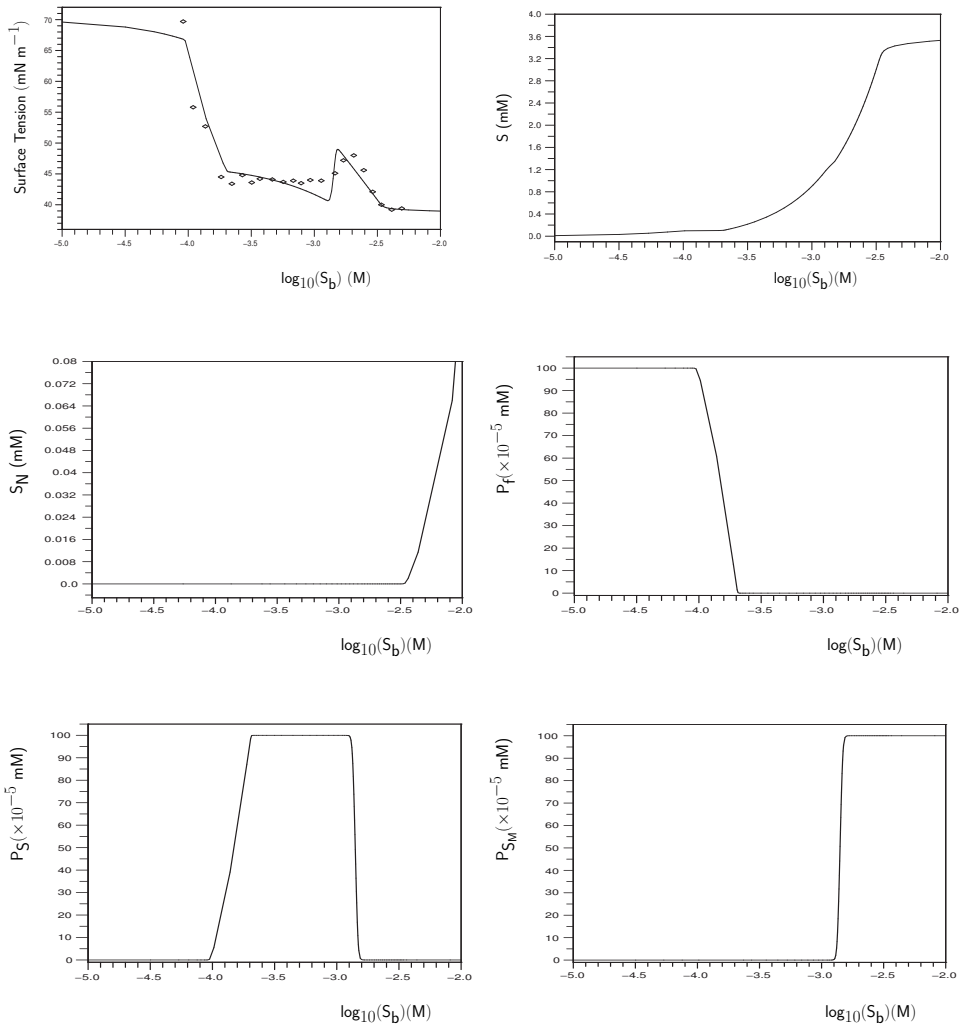


Figure 14: C14TAB/NaPSS system [13]. Surface tension and concentrations of the different species. Parameters used in the model are $N = 70$, $M = 20$, $n = 8$, $L = 100$, $S_{CMC} = 3.5$ mM, $S_{CAC} = 0.26$ mM, $S_{ELE} = 0.1$ mM, $\Gamma_\infty = 5 \times 10^{-6}$ mol m^{-2}, $\gamma_0 = 70$ mN m^{-1}, $k_S = 3.2$ m^3 mol^{-1}, $k_{P_S} = 6 \times 10^3$ m^3 mol^{-1}. The bulk polymer concentration $P_b = 1 \times 10^{-3}$ mM, corresponding to 50ppm.

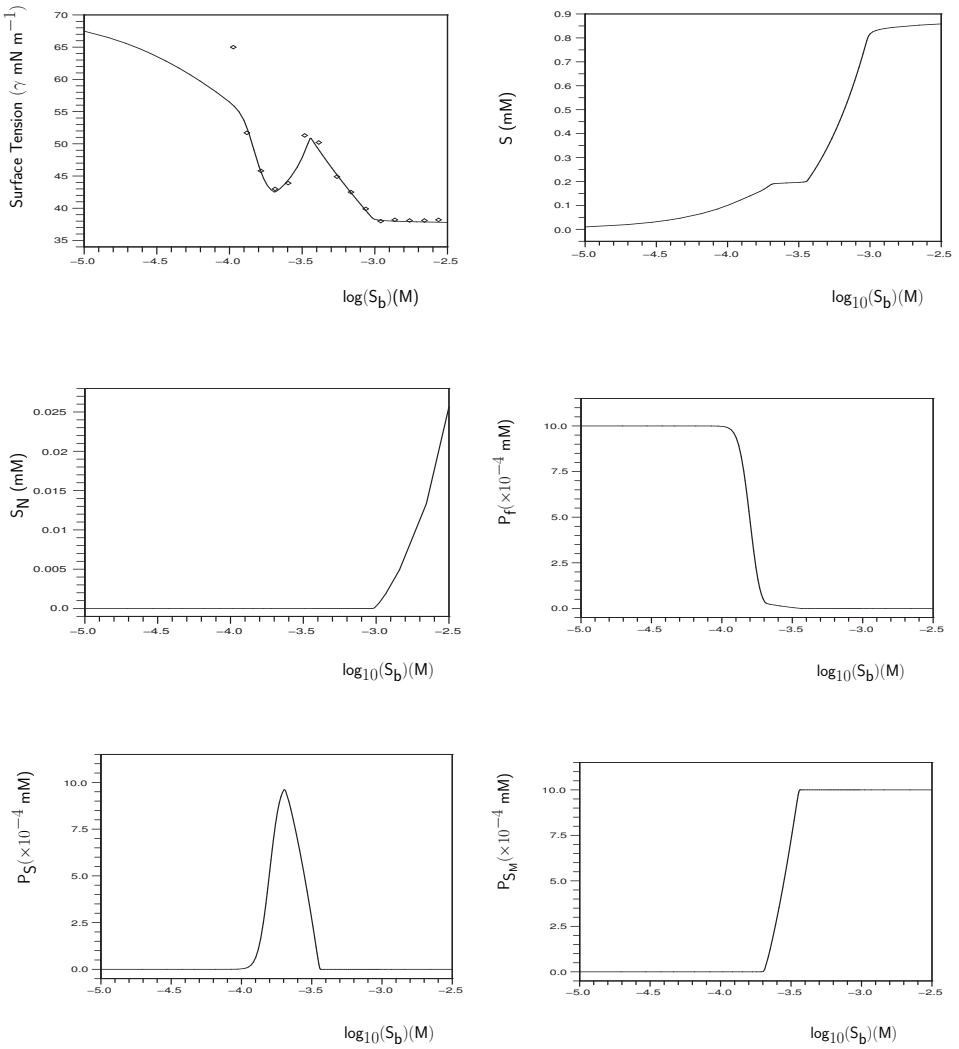


Figure 15: C16TAB/NaPSS system [13]. Surface tension and concentrations of the different species. Parameters used in the model are $N = 90$, $M = 20$, $n = 8$, $L = 15$, $S_{CMC} = 0.85$ mM, $S_{CAC} = 0.19$ mM, $S_{ELE} = 0.15$ mM, $\Gamma_\infty = 4 \times 10^{-6}$ mol m^{-2}, $\gamma_0 = 70$ mN m^{-1}, $k_S = 29$ m^3 mol^{-1}, $k_{P_S} = 1 \times 10^4$ m^3 mol^{-1}. The bulk polymer concentration $P_b = 1 \times 10^{-3}$ mM, corresponding to 50ppm.

tension behaviour and we have also extended their basic model to describe strongly-interacting systems. The important additional feature required was the inclusion of the highly surface-active complex formed by electrostatic binding of single surfactant monomers to the polymer backbone, which we have called P_S. The model expresses in mathematical form the hypotheses put forward to describe the data in references [12, 13]. The competition between the formation of the polymer-monomer complex, P_S, and the formation of the polymer-micelle complex, P_{S_M}, is the main cause of formation of a peak in the surface tension graph. This is determined by the relative size of the parameters S_{ELE} and S_{CAC}, which are dependent on the reaction constants for the formation of each species.

The simplicity of the model means that it has limitations. In reality, the assumption that the surface-active species have the same excluded area on the surface is incorrect, and the Langmuir isotherm, (3), for multiple species is therefore thermodynamically inconsistent. To find a thermodynamically consistent isotherm, one would need to start from an expression for the free energy of the surface. In addition, modelling the formation of the polymer-monomer complex, P_S, as a single-step reaction is too simplistic and, as a result, the model fails to match the experimental surface tension graph at low surfactant concentrations. The model could be refined by modelling the formation of polymer-monomer complexes as a series of reactions adding one monomer at a time, which would replicate more realistically the chemistry involved. Investigating these limitations in the model will be the subject of future research.

In theory the parameters in the model could be evaluated from thermodynamic principles, but this is beyond the scope of this paper. Here we have simply chosen the parameters to match the experimental data and we have provided several different examples of the model agreement with experimental data. The variations in parameters required to match the experimental data are physically reasonable and justified. In order to understand the model more precisely, it is clearly desirable to investigate systematically how the model depends on the variation of the different parameters. By exploiting the large parameters L and nM, it is possible to perform asymptotic analysis to gain further insight into the behaviour of the model as parameters are changed. We have performed this analysis and it will appear in a forthcoming paper [26]. However, here the real strength is that, for the first time, it is

possible to analyse quantitatively and compare different strongly-interacting systems using a model based on a sound theoretical framework. In particular it provides the opportunity to correlate the surface tension and adsorption data obtained from the strongly-interacting systems and to provide a realistic interpretation of complex surface tension data. It enables the competition between the formation of solution and surface polymer-surfactant complexes to be quantified in terms of a free energy, and provides a framework in which predictions could be made.

References

[1] Goddard E. D. *Colloids Surf.* **1986**, *19*, 255-300.

[2] Goddard E. D. *Colloids Surf.* **1986**, *19*, 301-329.

[3] Goddard E. D. *J. Colloid Interface Sci.* **2001**, *256*, 228-235.

[4] Cooke D. J.; Dong C. C.; Lu J. R.; Thomas R. K.; Simister E. A.; Penfold J. *J. Phys. Chem. B* **1998**, *102*, 4912-4917.

[5] Jones M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36-42.

[6] Lange V. H. *Kolloid-Z. u. Z. Polymere* **1971**, *243*, 101-109.

[7] Purcell I. P.; Thomas R. K.; Penfold J.; Howe A. M. *Coll. Surf. A* **1995**, *94*, 125-130.

[8] Purcell I. P.; Lu J. R.; Thomas R. K.; Howe A. M.; Penfold J. *Langmuir* **1998**, *14*, 1637-1645.

[9] Hayakawa K.; Kwak J. C. T. In *Cationic Surfactants*; Rubingh D. N., Holland P. M., Eds.; Marcel Dekker Inc., 1991; Chapter 5.

[10] Staples E.; Tucker I.; Penfold J.; Warren N.; Thomas R. K.; Taylor D. J. F. *Langmuir* **2002**, *18*, 5147-5153.

[11] Taylor D. J. F.; Thomas R. K.; Penfold J. *Langmuir*, **2002**, *18*, 4748-4757.

[12] Taylor D. J. F.; Thomas R. K.; Hines J. D.; Humphreys K.; Penfold J. *Langmuir* **2002**, *18*, 9783-9791.

[13] Taylor D. J. F.; Thomas R. K.; Li P. X.; Penfold J. *Langmuir* **2003**, *19*, 3712-3719.

[14] Cabane B.; Duplessix R. *Colloids Surf.*, **1985**, *13*, 19-33.

[15] Breuer M. M.; Robb I. D. *Chem. Ind.* **1972**, *13*, 530-535.

[16] Gilanyi T.; Wolfram A. *Colloids Surf.* **1981**, *3*, 181-198.

[17] Nagarajan R. *Adv. Coll. Interface Sci.* **1986**, *26*, 205-264.

[18] Nagarajan R. *J. Chem. Phys.* **1989**, *90:3*, 1980-1994.

[19] Ruckenstein E.; Huber G.; Hoffmann H. *Langmuir* **1987**, *3*, 382-387.

[20] Ruckenstein E. *Langmuir* **1999**, *15*, 8086-8089

[21] Nikas Y. J.; Blankstein D. *Langmuir* **1994**, *10*, 3512-3528.

[22] Everett D. H. *An Introduction to the Study of Chemical Thermodynamics*, 2nd ed.; Longman Group Limited, 1971.

[23] Raff L. M. *Principals of Physical Chemistry*, 1st ed.; Prentice-Hall, Inc., 2001.

[24] Breward C. J. W.; Howell P. D. *Euro. J. Appl. Math.* **2004**, *15*, 511-531.

[25] van Os N.M.; Haak J.R.; Rupert L.A.M. *Physico-chemical properties of selected anionic, cationic, and nonionic surfactants*; Elsevier, 1993.

[26] Bell C. G.; Breward C. J. W.; Howell P. D.; Penfold J.; Thomas R. K. **2007**, In preparation.

[27] Penfold J.; Tucker I.; Thomas R.K.; Taylor D.J.F.; Zhang X.L.; Bell C.G.; Breward C.J.W.; Howell P.D. *Langmuir* **2007**, Web alert DOI: 10.1021/la063016x.

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Macroscopic modelling of the surface tension of polymer-surfactant systems

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