

Onset of self-assembly in polymer-surfactant systems

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Abstract. – The onset of self-assembly in a dilute aqueous solution containing a flexible polymer and surfactant is theoretically studied. Focusing on the effect of the surfactant on polymer conformation and using a conjecture of partial collapse of the polymer at the onset of self-assembly, we obtain results which agree with known experimental observations: i) polymer-surfactant self-assembly always starts at a lower concentration (cac) than the one required for surfactant-surfactant self-assembly (cmc); ii) in charged systems the cac increases with salt concentration and is almost independent of polymer charge; iii) in weakly interacting systems the cac remains roughly proportional to the cmc over a wide range of cmc values. The special case of amphiphilic side-chain polymers strongly supports our basic conjecture. A similarity is found between the partial collapse induced by the surfactant and general results concerning the effect of impurities on critical phenomena.

Aqueous solutions containing polymers and surfactants have been the subject of extensive research in the past few decades [1, 2]. The possibility to achieve polymer-surfactant aggregation at very low surfactant concentration offers a delicate control over the properties of the mixture, a feature being used in numerous applications [3].

The joint self-assembly of polymers and surfactants usually starts at a well-defined surfactant concentration, the “critical aggregation concentration” (cac). One of the most consistent experimental observations in polymer-surfactant systems is that the cac is found to be lower than the “critical micellar concentration” (cmc) of the polymer-free surfactant solution. Consequently, polymer-surfactant systems are commonly divided into two categories [4]: i) polyelectrolyte and oppositely charged ionic surfactant, where the cac can become several orders of magnitude lower than the cmc ; ii) neutral polymer and ionic surfactant, where the cac is lower than, but comparable to the cmc . Less common are systems containing a polyelectrolyte and a non-ionic surfactant [5], which can be included in the second category as their cac is comparable to the cmc . Systems where both species are neutral exhibit a very weak effect [6, 7].

Several theories have been suggested for polymer-surfactant aggregation [8-13]. They include various generalisations of micellisation theories [14] in the presence of a polymer. However, most of those models do not explicitly treat intra-chain features of the polymer.

This approach may be justified for rigid polymers such as DNA or strong polyelectrolytes in the absence of salt. It is somewhat more questionable in view of the strong conformational changes observed in flexible polymers upon self-assembly [6].

This letter takes a different point of view. Instead of examining the effect of added polymer on surfactant micellisation, we rather focus on the effect of the surfactant on the statistics of a flexible polymer below and at the onset of self-assembly. Details of the joint self-assembly above the cac (*e.g.*, morphology of aggregates and their arrangement along the chain) probably depend on various molecular parameters. We suggest, however, that the *onset* of self-assembly in such systems may be accounted for by more general considerations related to dilute mixtures of polymers and smaller, interacting molecules. We conjecture that in a flexible polymer-surfactant system the cac is associated with a considerable change in polymer statistics, *i.e.*, local instability of the polymer chain. This description is reminiscent of de Gennes' and Brochard's treatment of a polymer in a binary mixture of good solvents close to its critical point [15]. Similar to the latter scenario, the polymer is predicted to undergo *partial collapse* [15] at the cac, which marks the onset of aggregation. This approach allows us to distinguish and explain some common, "universal" features in the vast experimental literature which has accumulated on polymer-surfactant systems. (See, *e.g.*, ref. [13] for a more microscopic approach.)

The free energy of the polymer solution is assumed to be characterised by a single interaction parameter (2nd virial coefficient). Thus, the theory is applicable to a dilute as well as semi-dilute polymer regime. The theory is restricted, however, to the onset of binding (cac) and its vicinity. Issues of morphology, phase behaviour and rheology, especially in more concentrated polymer-surfactant systems, are very interesting and important [6], but lie outside the scope of the current letter.

Consider a dilute solution of polymer and surfactant whose local concentrations are denoted by c and φ , respectively. The polymer is assumed to be flexible and in a good solvent. The surfactant is both below its cmc and cac. The free-energy density can be divided into three terms accounting for the polymer contribution, the surfactant one, and the polymer-surfactant interaction,

$$f(c, \varphi) = f_p(c) + f_s(\varphi) + f_{ps}(c, \varphi). \quad (1)$$

Since the concentrations of both species are low and we are interested only in the onset of binding, we restrict to two-body interactions between monomers and surfactants. Thus, the leading quadratic term in the expansion of $f_{ps}(c, \varphi)$ is sufficient, $f_{ps}(c, \varphi) = -wc\varphi$, where $w \equiv -\partial^2 f_{ps}/\partial c \partial \varphi$ is a parameter characterising the attraction strength.

In the absence of polymer the surfactant concentration has a homogeneous value, $\varphi \equiv \varphi_b$, corresponding to the minimum of the grand-canonical free energy of the surfactant, $f_s(\varphi) = h(\varphi) - \mu\varphi$, where h denotes the canonical free energy and μ is the surfactant chemical potential. Consider a small perturbation in local surfactant concentration, $\varphi = \varphi_b + \delta\varphi$. Since the solution is both below its cac and cmc, f can be expanded in small $\delta\varphi$ to yield

$$f = f_p(c) + f_s(\varphi_b) - wc\varphi_b - wc\delta\varphi + \frac{1}{2}f_s''(\varphi_b)\delta\varphi^2, \quad (2)$$

where $f_s''(\varphi) \equiv \partial^2 f_s/\partial \varphi^2$. We identify the cmc as the value of φ at which, for $c = 0$, the surfactant solution becomes unstable to small perturbations, *i.e.*, $f_s''(\varphi_{cmc}) = 0$. This simplification neglects various surfactant features, assuming that surfactants can be considered for $\varphi < \varphi_{cac}$ merely as interacting small molecules, and their specific features be incorporated in the phenomenological parameter φ_{cmc} .

Let $F(x)$ be a dimensionless function such that $\varphi = \varphi_{cmc}F(x)$ solves the equation

$\varphi_{\text{cmc}} f_s''(\varphi) = 1/x$. Obviously, for $x \rightarrow \infty$ the solution is $\varphi = \varphi_{\text{cmc}}$, *i.e.*, $F(x \gg 1) \simeq 1$. In the other limit, $x \rightarrow 0$ and $f_s''(\varphi) \rightarrow \infty$, the solution for φ must tend to zero independently of φ_{cmc} . Hence, $F(x \ll 1) \sim x$. This asymptotic behaviour is also obtained by calculating explicit expressions for $F(x)$ in more specific models [16]. (For example, taking the simplest expression, $f_s = \varphi(\ln \varphi - 1) - u\varphi^2/2$, gives $F(x) = (1 + 1/x)^{-1}$.)

In the presence of the polymer, minimisation of eq. (2) with respect to $\delta\varphi$ gives $\delta\varphi = [w/f_s''(\varphi_b)]c$, and $f = f_s(\varphi_b) + f_p(c) - wc\varphi_b - w^2/[2f_s''(\varphi_b)]c^2$. Thus, the interaction with the surfactant leads to an effective reduction in the 2nd virial coefficient of the polymer [17],

$$v_{\text{eff}} = v - v_{\text{ps}}, \quad v_{\text{ps}} \equiv w^2/f_s''(\varphi_b), \quad (3)$$

where v is the bare 2nd virial coefficient. The chain becomes unstable when $v_{\text{eff}} = 0$. At this point the local polymer concentration, c , is expected to increase significantly (due to contraction of chain conformation), leading to a sharp increase in $\delta\varphi$ as well. We identify this instability, therefore, as the cac. Using eq. (3) and the function $F(x)$ defined above, the following scaling expression for the cac is found:

$$\varphi_{\text{cac}} = \varphi_{\text{cmc}} F[v/(w^2\varphi_{\text{cmc}})] < \varphi_{\text{cmc}}, \quad (4)$$

where $F(x) \sim x$ for $x \ll 1$ and tends to unity for $x \gg 1$. This simple model demonstrates the physics governing the flexible polymer-surfactant system: polymer-surfactant affinity induces attractive correlations between monomers, which compete with the bare intra-chain repulsion. The correlations become stronger as the cmc is approached, and *they are bound to win before reaching the cmc, i.e.*, $\varphi_{\text{cac}} < \varphi_{\text{cmc}}$. The fact that the cac is lower than the cmc has been established by numerous experiments [1, 2]. The argument $x = v/(w^2\varphi_{\text{cmc}})$ in eq. (4) determines the strength of the *effective* polymer-surfactant interaction. Two limiting cases arise: i) strong polymer-surfactant interaction ($x \ll 1$), where $\varphi_{\text{cac}} \ll \varphi_{\text{cmc}}$; ii) weak interaction ($x \gg 1$), where $\varphi_{\text{cac}} \lesssim \varphi_{\text{cmc}}$. Note that the distinction between strong and weak interaction involves not only the bare polymer-surfactant interaction (w) as compared to the surfactant-surfactant one ($1/\varphi_{\text{cmc}}$), but also the intra-chain interaction (v). This observation was not emphasized sufficiently, in our opinion, in previous studies.

In the case of strong polymer-surfactant interaction, $w^2 \gg v/\varphi_{\text{cmc}}$, the attraction between surfactants in the solution is insignificant and the cac becomes independent of the cmc, $\varphi_{\text{cac}} \sim v/w^2 \ll \varphi_{\text{cmc}}$. Practically, this corresponds to the case of a charged polymer (polyelectrolyte) interacting with an ionic surfactant of the opposite charge [4]. Due to strong electrostatic interactions, the cac in such systems is usually found to be orders of magnitude lower than the cmc. In order for our assumption of polymer flexibility to still hold, the system should contain additional salt so as to screen the electrostatic interactions on the length scale of the induced attractive correlations. Both v and w are expected to be dominated in this case by electrostatics, and thus mainly depend on the polymer ionization degree, I , and salt concentration, c_s .

A surfactant-free polyelectrolyte solution is a complicated system by itself, whose behaviour as function of I and c_s is not completely settled yet [18]. Two observations, however, can be made: i) the monomer-monomer parameter, v , should have a stronger dependence on I than the monomer-surfactant one (the simplest dependence would be $v \sim I^2$ and $w \sim I$); ii) both v and w should have a similar decreasing dependence on c_s . Consequently, $\varphi_{\text{cac}} \sim v/w^2$ should increase with c_s and, somewhat more surprisingly, be independent or weakly dependent on I . The increase of cac with salt concentration was observed in many experiments [4]. A more detailed discussion of the dependence on c_s is postponed to a future paper [16]. The physical reason for the weak dependence on I stems from a competition between a polymer-surfactant effect and an intra-chain one. A vanishing or slightly *increasing* dependence on I was observed

in several systems involving polyelectrolytes and oppositely charged surfactants with added salt [19-21].

In the case of weak polymer-surfactant interaction, $w^2 \ll v/\varphi_{\text{cmc}}$, according to eq. (4), the cac and cmc become comparable, $\varphi_{\text{cac}} = A\varphi_{\text{cmc}}$, where $A \lesssim 1$ is a constant which is not very sensitive to changes in v , w or φ_{cmc} . Practically, this limit applies to systems where at least one of the species is uncharged [5]. The cac is expected to depend in this case on molecular details, but *this complicated dependence should be mostly incorporated in the cmc*. In other words, changing various parameters may lead to considerable changes in the cmc, yet the cac is expected to follow such changes roughly linearly. This simple prediction agrees with various experiments [5, 22], where proportionality between the cac and cmc was observed over a wide range (up to two decades) of cmc values.

The treatment given above for the onset of self-assembly yields a cac which can be described as a “shifted” θ collapse—a sharp transition of polymer conformation occurring when the 2nd virial coefficient changes sign. In practice, however, the binding of surfactants to flexible polymers exhibits a steep, albeit continuous increase at the cac. Due to the different range of competing interactions in this case, the chain undergoes a *partial collapse* [15] into sub-units (“blobs”). The interaction between monomers within each blob is dominated by the short-range repulsion, whereas the interaction between blobs is dominated by the attractive correlations. Binding progresses *continuously* as additional blobs form and the local monomer concentration increases.

The attractive potential induced between the monomers due to surfactant correlations is assumed to have the general form $U(r) = -e^2\psi(r/\xi)$, where e^2 is a coupling constant, ξ a correlation length, and $\psi(x)$ a dimensionless function decaying fast to zero for $x > 1$. The two parameters, e^2 and ξ , are related to our phenomenological interaction parameter, w . Assuming weak correlations, $U < 1$ (in units of $k_{\text{B}}T$), we readily obtain for the effective excluded-volume parameter of the chain, $v_{\text{eff}} = v + \int \text{d}\mathbf{r}U(r) = v - k_1e^2\xi^3$, where k_1 is a dimensionless constant. Comparing to eq. (3) we find $e^2 \sim v_{\text{ps}}/\xi^3$.

Let us now consider blobs of size ξ , each containing g monomers. The potential between blobs, $V(r)$, consists of a hard-core part, $V(r < \xi) \rightarrow \infty$, and an attractive part, $V(r > \xi) \sim g^2U(r)$, coming from the interaction of g^2 pairs of monomers. The resulting excluded-volume parameter for the blobs is $v_{\text{blob}} = \int \text{d}\mathbf{r}[1 - \exp[-V(r)]] \simeq k_2\xi^3 - k_3\xi^3 \exp[k_4g^2e^2]$, where k_2, k_3, k_4 are dimensionless constants. The condition for partial collapse is $v_{\text{blob}} = 0$, *i.e.*, $g^2e^2 = \ln(k_2/k_3)/k_4 = \text{const}$. In addition, the blob size and number of segments are related by a certain power law, $\xi \sim g^\nu$ ($\nu \simeq 0.6$ for a self-avoiding random walk). Substituting this relation and the value of e^2 in the partial-collapse condition, we get

$$g \sim (v/v_{\text{ps}})^{1/\alpha}, \quad \xi \sim (v/v_{\text{ps}})^{\nu/\alpha}, \quad \alpha \equiv 2 - 3\nu. \quad (5)$$

In order for these results to be consistent with the physical picture in mind, g should decrease with v_{ps} (*e.g.*, the entire chain should reduce to a single blob for small enough φ_{b}). The condition for self-consistency is, therefore, $\alpha > 0$, or $\nu < 2/3$. This yields a precise definition for our requirement of polymer flexibility—on the length scale of surfactant correlations the chain statistics should obey $\nu < 2/3$. (In particular, the chain should not be stretched, having $\nu = 1$.) In polyelectrolyte solutions, for example, this condition sets a lower bound for salt concentration, below which the chain is too stretched on the length scale of ξ and the partial-collapse picture becomes invalid.

Repeating the calculation in d dimensions gives the same result as eq. (5) with $\alpha = 2 - \nu d$. Our self-consistency condition is similar to well known results for the critical behaviour of disordered systems. For both annealed and quenched impurities (Fisher renormalisation [23] and the Harris criterion [24], respectively) the critical behaviour of the system is affected by

impurities if $\nu < 2/d$, *i.e.*, $\alpha > 0$ (the “cross-over exponent”). Similarly, surfactants affect the conformational behaviour of a polymer only if $\nu < 2/d$. We note that for self-avoiding walk [$\nu \simeq 3/(d+2)$] this condition is satisfied for $d < 4$, which is consistent with the fact that short-range interactions such as the one induced by the surfactant become irrelevant to polymer statistics for $d \geq 4$.

The onset of association is expected when blobs can form, *i.e.*, when g becomes smaller than a certain number of monomers, n , corresponding to the finite range of surfactant-induced correlations. (Unlike the critical system discussed by de Gennes and Brochard [15], it is the correlation amplitude (e^2), rather than the correlation length (ξ), which becomes large in a surfactant solution approaching the cmc.) Using eqs. (5), (3), and the function $F(x)$, we find

$$\varphi_{cac} = \varphi_{cmc} F[n^{-\alpha} v / (w^2 \varphi_{cmc})]. \quad (6)$$

Comparison to eq. (4) shows that the preceding, less refined analysis of the cac applies to complete collapse ($g \sim 1$) rather than the onset of the actual partial collapse. The similarity to Harris’ results persists: for small $\varphi_{cac}/\varphi_{cmc}$ we find from eq. (6) $n \sim \varphi^{-1/\alpha}$, which is analogous to Harris’ result for the broadening of the critical point by impurities, $\Delta T/T_c \sim \rho^{1/\alpha}$, where $\rho \ll 1$ is the concentration of impurities. (Recall that the number of monomers, n , serves as a conjugate variable to $\Delta T/T_c$ in the regular polymer-magnetism analogy [25].)

Another result of the partial-collapse picture is that *at the cac* the polymer should obey Gaussian statistics as a function of polymerisation degree. This prediction is still to be confirmed experimentally. Some support can be found in light scattering and potentiometric experiments, reporting a surprisingly weak interaction between charged aggregates of ionic surfactants and neutral polymer [26]. Contraction of the polymer at the cac was also observed in several systems [27].

To complete the picture, a third scenario is to be considered. When the number or length

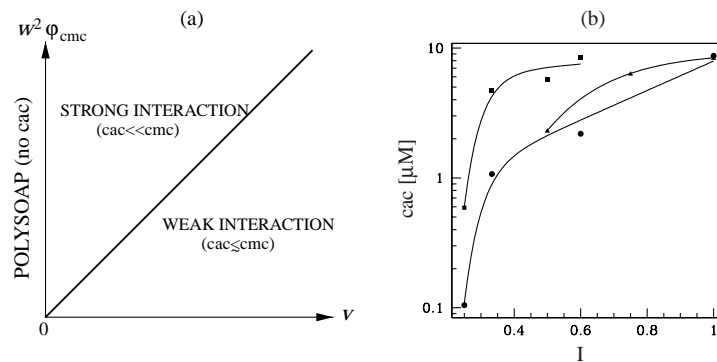


Fig. 1. – (a) Summary of self-assembly regimes: i) a strong-interaction regime ($w^2 \varphi_{cmc} > v$) where $\varphi_{cac} \ll \varphi_{cmc}$, corresponding experimentally to systems containing a polyelectrolyte and an oppositely charged ionic surfactant; ii) a weak-interaction regime ($w^2 \varphi_{cmc} < v$) where $\varphi_{cac} \lesssim \varphi_{cmc}$, corresponding to systems where one of the species is uncharged; iii) a polysoap regime ($v = 0$) where there is gradual binding (no cac), corresponding to polymers which form aggregates in the absence of surfactant. (b) Dependence of cac on polymer charge close to the polysoap regime. Triangles: poly(maleic acid-co-butylvinylether), DTAB, 5 mM KBr (ref. [19]). For $I < 0.5$ this polymer becomes a polysoap. Circles: $(\text{CH}_2)_x(\text{CH}_2)_y$ -ionine bromide, SDS, no salt. Squares: with 20 mM NaBr (ref. [28]). A distance of 3 hydrocarbon groups between charged groups along the backbone has been defined as $I = 1$. The lines are merely guides to the eye.

of hydrophobic side chains attached to a hydrophilic backbone is large enough, the polymer (known as *polysoap*) is already partially collapsed by itself and should not exhibit any further instability upon addition of surfactant. Hence, no sharp onset of binding (cac) is expected; the binding to such a chain should progress gradually as a function of surfactant concentration. This indeed was observed for the interaction of ionic surfactants with hydrophobically modified polyacids [19, 20, 29]. By synthesizing water-soluble polymers with various hydrophobic side-chain lengths and controlling their ionization degree, a cross-over from the polysoap regime (defined above) to the polyelectrolyte regime could be seen. Indeed, it was accompanied by a cross-over from gradual to sharp, co-operative binding [19]. We regard this experimental observation as a strong support for our basic conjecture, associating the cac with a conformational change.

The diagram in fig. 1a summarises the three self-assembly regimes. Note that a cross-over to the polysoap behaviour ($v = 0$) is possible only from the strong-interaction regime ($w^2\varphi_{\text{cmc}} \gg v$). The physical reason is that close to the polysoap regime the stability of the polymer is only marginal, and a small amount of surfactant is sufficient to cause partial collapse. Hence, in this region of $v \gtrsim 0$ intra-chain features, rather than the affinity between the two species, determine the onset of self-assembly. As a result, the cac can be significantly reduced without a significant change in the bare polymer-surfactant interaction, or, moreover, even if the bare affinity becomes *weaker*. There are two available experimental works which demonstrate this surprising result [19, 28], as shown in fig. 1(b).

In conclusion, focussing on the onset of self-assembly (the cac), we have presented a unified description of the interaction between a flexible polymer and surfactant in dilute solution. Apart from the bare interaction between the two species, intra-chain interactions (*i.e.*, the effective excluded-volume parameter of the chain) are shown to have an important role. Utilising a conjecture of partial collapse of the polymer at the onset of binding, simple predictions can be made, which seem to be well supported by experiments. We have pointed out an interesting analogy between the partial collapse induced by the surfactant and the smoothing of critical behaviour by impurities in disordered systems.

Three self-assembly regimes are found, as shown in fig. 1(a). By modifying the polymer, one can observe a cross-over between the regimes without necessarily changing the bare polymer-surfactant interaction. An interesting experiment would be to take a weakly interacting system (*e.g.*, a polyacid like PAA and a non-ionic surfactant such as C_nE_m) and by carefully modifying the polymer gradually shift it to the strong-interaction regime and finally to the polysoap regime: the cac is predicted to decrease from a value close to the cmc to much lower values and finally to disappear.

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