

## Adsorption of Polymer Solutions on Surfactant Monolayers: Global Phase Diagrams.

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**Abstract.** - The phase diagram of insoluble surfactant monolayers at the air/water interface is affected by the addition of polymer in the water subphase. The case of a condensation transition is investigated within the framework of a mean-field theory. The interaction of the polymer with the interface leads to an upward shift of the critical temperature and of the critical concentration (if the monomers are more attracted by the surfactant molecules than by the bare interface). In some situations, the phase diagram can display a triple point.

Many industrial products as well as biological systems involve the presence of *both* macromolecules (polymers, proteins) and amphiphiles (surfactant, fatty acids, phospholipids). In biological systems, for instance, cell membranes are made of phospholipid bilayers on which macromolecular networks are connected (*e.g.*, cytoskeleton) and in which membrane proteins are embedded [1]. In industrial applications, surfactants and polymers are often present in colloidal suspensions and oil-water emulsions [2]. Another example of combined systems involves enhanced drug delivery via micro-encapsulation [3]. In bulk solutions, polymers and surfactants tend to create complex self-assembly structures (connected micelles, gels, networks, etc.) [4-6]. Here we consider another relatively simple situation of an insoluble surfactant monomolecular layer (*Langmuir monolayer*) spread at the *flat* air/water interface and its interaction with a polymer present in the aqueous subphase. Such Langmuir monolayers [7] have many applications (*e.g.*, evaporation control) and are useful as model systems for more complicated fluctuating liquid interfaces (membranes), where curvature effects are of importance.

On a theoretical level, the adsorption (or depletion) of polymers close to an ideal (namely,

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perfectly flat and chemically homogeneous) interface is by now quite well understood [8]. Fewer theoretical works exist for interfaces that are either non-flat (curved, rough) [9, 10] or chemically heterogeneous [11, 12]. Even for a perfectly flat interface, an insoluble surfactant monolayer is an example of a chemically heterogeneous interface whose lateral composition fluctuations are coupled with the process of polymer adsorption [11, 12].

Many surfactant monolayers undergo a complicated series of phase transitions on the air/water interface [7]. In a condensation transition (gas to liquid or liquid-expanded to liquid-condensed), single-phase and two-phase regions in the phase diagram are separated by a coexistence curve. In the two-phase region, condensed and dilute regions of the monolayer coexist. Other more complex phase transitions can also occur, especially in the condensed monolayer states [13].

For simplicity, in this paper we deal only with the condensation transition of the monolayer at the flat air/water interface and address the question of how this two-dimensional phase transition is affected by the presence of polymer adsorption from the subphase. The (dimensionless) free energy  $F$  (rescaled in units of  $k_B T$ ,  $k_B$  is the Boltzmann constant and  $T$  is the temperature) can be separated into three parts: the surfactant contribution  $F_s$ , the polymer contribution  $F_p$ , and the coupling term  $F_{ps}$ :  $F = F_s + F_p + F_{ps}$ .

*The surfactant contribution  $F_s$ :* The monolayer free energy is calculated using a lattice-gas model. Each lattice site is occupied either by a surfactant molecule or by a vacancy. The free energy of a surfactant monolayer is the sum of the enthalpy and entropy of mixing and depends on the monolayer area fraction (or, equivalently, coverage)  $c$  ranging from zero to one. By disregarding linear terms in  $c$ , the surfactant free energy per site  $F_s$ , within a Bragg-Williams (mean-field) theory, is written as

$$F_s = \varepsilon_0 c(1 - c)/(k_B T) + c \log c + (1 - c) \log(1 - c), \quad (1)$$

where  $\varepsilon_0 > 0$  is the interaction parameter of the surfactant on the surface and has units of  $k_B T$ . For temperatures higher than the critical temperature  $T_c = \varepsilon_0/(2k_B)$ , the homogeneous state of the monolayer is stable for all values of  $c$  as shown in fig. 1a) (inset). Note that  $F_s$  and the resulting phase diagrams are symmetric about  $c = 1/2$ . This symmetry will disappear in some of the mixed surfactant-polymer systems considered below.

*The polymer contribution  $F_p$ :* For neutral and flexible polymers solubilized in the subphase, and i) in good-solvent condition and ii) in the semi-dilute concentration regime, a mean-field theory applied to the Edwards density functional is commonly used [14]. After minimization with respect to the polymer profile  $c_p(z)$ , where  $c_p(z)$  is the local monomer concentration ( $z$  being the coordinate in the direction perpendicular to the interface), the free energy  $F_p$  can be expressed as a function of the surface order parameter of the polymer,  $\phi_s$ , defined as  $\phi_s^2 \equiv c_p(z=0)/c_p^\infty$ , where  $c_p^\infty \equiv c_p(z \rightarrow \infty)$ :

$$F_p = \varepsilon_p (\phi_s - 1)^2 (\phi_s + 2)/3; \quad (2)$$

$\varepsilon_p > 0$  is the bulk solvent-polymer interaction parameter in good-solvent conditions<sup>(1)</sup>. The  $F_p$  term has a minimum when the polymer solution is homogeneous ( $\phi_s = 1$ ) because all surface interactions, including the interaction with the bare surface, are taken into account separately in the following coupling term,  $F_{ps}$ . The relevant experimental quantity for measuring the interaction between the polymer solution and the interface is the

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<sup>(1)</sup> More precisely,  $\varepsilon_p = A_0 a(c_p^\infty)^{3/2} (v/3)^{1/2}$ , where  $a$  is the monomer size,  $v$  is the excluded-volume parameter and  $A_0$  is the compact area of surfactants at the interface.

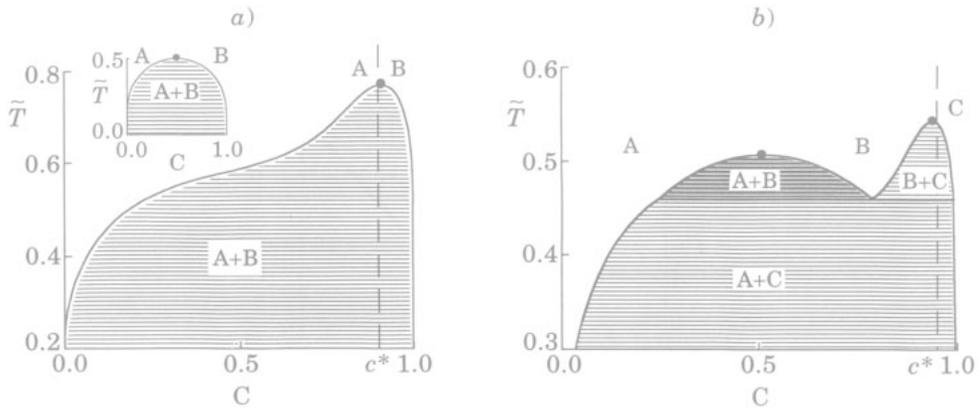


Fig. 1. – We denote  $\tilde{T} \equiv k_B T / \varepsilon_0$ . The phase diagram of the surfactant monolayer is shown for three values of the special transition coverage  $c^*$ . The values of the other parameters are fixed as  $\varepsilon_p = 0.1$  and  $\tilde{T}_{\varepsilon_{ps}} = 1$ . In a)  $c^* = 0.9$ . The monomers are attracted to the interface for high surfactant coverage but repelled for lower values. The critical temperature and the critical coverage are located at  $\tilde{T}_c = 0.77$  and  $c_c = 0.91$  and are shifted upwards with respect to the pure surfactant values (see inset). In the inset  $c^* = \infty$ , corresponding to the limiting case of polymer depletion from the interface (or, equivalently, to the pure surfactant monolayer). The A and B phases are separated by a two-phase coexistence region, A + B. The critical point is located at  $c_c = 0.5$ ,  $\tilde{T}_c = 0.50$ . In b)  $c^* = 0.95$ . The two-phase region labelled BC ends at the critical point:  $\tilde{T}_c = 0.53$ ,  $c_c = 0.94$ . The second AB critical point is located at  $\tilde{T}_c = 0.51$ ,  $c_c = 0.50$ . All three two-phase regions: AB, AC and BC join at a *triple point*:  $\tilde{T} = 0.46$ ,  $c_A = 0.25$ ,  $c_B = 0.79$  and  $c_C = 0.99$ , where all three phases (A, B and C) coexist.

polymer surface excess defined as  $\Gamma \equiv \int_0^\infty [c_p(z) - c_p^\infty] dz$ , and in the mean-field approximation,  $\Gamma \sim \phi_s - 1$ .

*The coupling term  $F_{ps}$* : The simplest phenomenologically but still meaningful expression for the polymer-interface interaction is a coupling term bilinear in the surfactant and monomer concentrations at the interface ( $z = 0$ ). It takes into account only short-ranged interactions between the polymer and the bare interface, and the polymer and the surfactant molecules at the interface:

$$F_{ps} = -\varepsilon_{ps}(c - c^*)\phi_s^2/2; \quad (3)$$

$\varepsilon_{ps}$  describes the affinity of the monomers with the surfactant molecules *relatively* to the bare interface. At  $c = c^*$ ,  $F_{ps}$  changes sign. This is the so-called *special transition* for polymer adsorption and  $c^*$  is the special transition coverage of the monolayer. When  $\varepsilon_{ps} > 0$ , the polymer is depleted (repelled) from the interface for  $c < c^*$  and adsorbed (attracted) for  $c > c^*$ . In the following, we will assume, without loss of generality, that  $\varepsilon_{ps} > 0$ <sup>(2)</sup>.

*The total free energy  $F$* : Combining all three contributions,  $F_s + F_p + F_{ps}$ , eqs. (1)-(3), we obtain the total free energy (per site of the interface). Minimizing it first with respect to the polymer surface order parameter  $\phi_s$ , we obtain

$$\phi_s = (\varepsilon_{ps}(c - c^*) + \sqrt{\varepsilon_{ps}^2(c - c^*)^2 + 4\varepsilon_p^2}) / (2\varepsilon_p). \quad (4)$$

Again, the polymer is depleted from the interface ( $\phi_s < 1$ ,  $\Gamma < 0$ ) for  $c < c^*$  and adsorbed for

<sup>(2)</sup> Indeed, each term of the total free  $F$  is invariant by the transformation  $\varepsilon_{ps} \rightarrow -\varepsilon_{ps}$ ,  $c \rightarrow 1 - c$ ,  $c^* \rightarrow 1 - c^*$ .

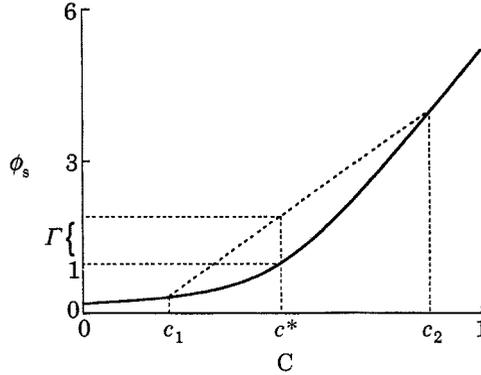


Fig. 2. - The polymer order parameter  $\phi_s$  as a function of the surfactant coverage  $c$  for  $\varepsilon_{ps}/\varepsilon_p = 10$  and  $c^* = 0.5$ . The polymer surface excess,  $\Gamma \sim \phi_s - 1$ , is shown for a surfactant monolayer of average concentration  $c^*$  demixing between coexisting regions of concentration  $c_1$  and  $c_2$ . Due to the convexity of the curve  $\phi_s(c)$ , the surface excess  $\Gamma$  is positive.

$c > c^*$ . If the surfactant monolayer is in the two-phase region, dilute and condensed regions of the surfactant coexist, and the polymer adsorbs differently on those regions because of its different affinity as described by the parameter  $\varepsilon_{ps} \neq 0$ . Note that as the curve  $\phi_s(c)$  is convex (see fig. 2), the polymer surface excess is enhanced when the surfactant monolayer undergoes a phase separation. Qualitatively, the convexity of the curve  $\phi_s(c)$  shows that the concentration fluctuations in the surfactant monolayer increase the polymer surface excess  $\Gamma \sim \phi_s - 1$  [12].

Since we calculated in eq. (4) how the surfactant molecules affect the polymer adsorption, the main remaining task is to understand how the polymer affects the phase diagram of the surfactant monolayer. Using eq. (4),  $\phi_s = \phi_s(c)$ , the total free energy can be written only as a function of the surfactant coverage  $c$ :

$$F(c) = F_s(c) - \varepsilon_p(\phi_s^3 + 3\phi_s - 4)/6. \quad (5)$$

The study of the convexity of the total free energy  $F(c)$  as a function of the only left order parameter  $c$  determines the location of the *modified* spinodal line. Similarly, the full phase diagram can be obtained from a common-tangent construction of  $F(c)$ . This is explained in detail elsewhere [15] and is only summarized here.

As the dependence on temperature of the phenomenological parameters  $\varepsilon_0$ ,  $\varepsilon_p$ ,  $\varepsilon_{ps}$  and  $c^*$  is system dependent and, in general, not very well understood, it is impractical to draw the universal phase diagram in the  $(T, c)$  parameter space. A more complex task is to investigate the phase diagram in the five-dimensional space of these four parameters and the surfactant surface coverage  $c$ . Then, the phase diagram of specific systems can be understood if the temperature dependence of those four parameters can be modelled. However, within simple assumptions on the dependence of  $\varepsilon_0$ ,  $\varepsilon_p$ ,  $\varepsilon_{ps}$  and  $c^*$  on temperature, an interesting insight and some universal features of the global phase diagram can be obtained.

A first general result is that the surfactant phase separation of the interface is enhanced by the presence of the polymer [12], since the monomers induce an effective attractive interaction between the surfactant molecules [11]. In our model, this indirect interaction is represented by the term  $-\varepsilon_p(\phi_s^3 + 3\phi_s)/6$  in the free energy, eq. (5). This coupling term is stronger for larger values of the surfactant coverage  $c$  because  $\phi_s(c)$  is an increasing function

of  $c$ . Consequently, the phase diagram is no longer symmetric about  $c = 1/2$  and is «pushed» towards higher values of  $c$  as can be seen in fig. 1a).

The position of the special transition line  $c = c^*$  plays an important role on the phase diagram. For simplicity, we assume here that  $c^*$  is independent of the temperature and obtain the following results: i) When  $c^* \gg 1$ , the polymer is repelled by the interface and does not modify drastically the position of the coexistence curve of the surfactant monolayer. The inset of fig. 1a) represents the limiting  $c^* \rightarrow \infty$  case. ii) On the other hand, when  $c^* \ll 0$ , the polymer is strongly adsorbed onto the interface resulting in a big increase of the coexistence region in the phase diagram. If  $\varepsilon_0$ ,  $\varepsilon_p$  and  $T\varepsilon_{ps}$  (in addition to  $c^*$ ) are taken as temperature independent [15], one can show that the phase diagram retains its symmetry with respect to  $c = 1/2$  and that the temperature dependence of the spinodal line obeys the scaling law  $T \sim (|c^*|c(1-c))^{1/3}$ . iii) When the special transition line  $c = c^*$  intersects the phase diagram for physical values of the surfactant surface coverage  $c$ ,  $0 < c^* < 1$ , interesting situations can occur. The breaking of the symmetry of the phase diagram about  $c = 1/2$  can become quite pronounced as is shown in fig. 1a). For values of  $c^*$  approaching 1 from below a new type of phase diagram can be obtained and is shown in fig. 1b). The phase behaviour displays a triple point and three two-phase regions between three homogeneous phases: A, B and C. The AB and BC two-phase regions terminate each at a critical point.

In the situation when the special transition coverage  $c^*$  satisfies the inequality  $c_1(T) < c^* < c_2(T)$ , where  $c_1(T)$  and  $c_2(T)$  are the two coexisting values at a given  $T$ , the polymer is adsorbed on the condensed surfactant regions ( $c = c_2$ ) and is depleted from the dilute regions ( $c = c_1$ ) always keeping in mind that  $\varepsilon_{ps} > 0$ . Our results should be compared with a previous work [11] where several phase diagrams for the mixed polymer-surfactant system have been proposed on general grounds. Our specific model predicts phase diagrams which do not directly correspond to the ones proposed in ref. [11]. In addition to the special transition line for the polymer ( $c = c^*$ ) and to the coexistence line for the surfactant molecules, ref. [11] predicted a  $\Theta$  line distinguishing whether the polymer segregates from the surfactant or not (in the case where the polymer is adsorbed). Such a prediction is not obtained in our mean-field model since we have only one minimum of the polymer surface value  $\phi_s$  as a function of surfactant coverage  $c$  (see eq. (4)). It will be interesting to understand in a detailed way this discrepancy, especially for  $0 < c^* < 1$ , where the coupling between the special transition and the surfactant phase diagram is the strongest.

Global phase diagrams of the adsorption of a polymer solution on a surfactant monolayer have been addressed here within a relatively simple model. However, this model has several limitations. The expression for the free energy of the surfactant monolayer  $F_s$  does not describe the important possibility for orientational ordering of the hydrophobic tail. This ordering is responsible for many phase transitions observed recently even for Langmuir monolayers of simple fatty acids [13].

Furthermore, most of neutral polymers are not soluble in water. Because of the strong polarity of water molecules, hydrogen bonds play an important role in water/polymer systems and probably will require more specific models to take into account those interactions. In particular, bulk solutions of polymers in water can exhibit miscibility curves (temperature of solubility for the polymer *vs.* concentration of monomers  $c_p$ ) in the form of closed loops (see [2] for more details). To some degree, we can model it by introducing this complicated temperature dependence in our parameter  $\varepsilon_p$ .

We believe that hydrophobically modified water-soluble polymers (HM-WSP) can be an interesting class of polymers of direct relevance to our predictions [4, 5]. Such copolymers consist of a water-soluble backbone with covalently bound hydrophobic side chains. They are likely to be attracted by the bare interface. If the surfactant is non-ionic, with polar heads

similar to the monomers of the backbone, the monomers are repelled by the surfactant molecules (acting as a polymer «brush» [11] in good-solvent conditions). In our model these assumptions correspond to  $\epsilon_{ps} < 0$  and  $0 < c^* < 1$ , and these two parameters can be further tuned by modifying the length of the hydrophobic side chains. Finally, an extension of our work could deal with interaction of charged polymers (polyelectrolytes) with cationic or anionic surfactant monolayers as it is known that those polymer/surfactant systems depend crucially on those electrostatic interactions [5].

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