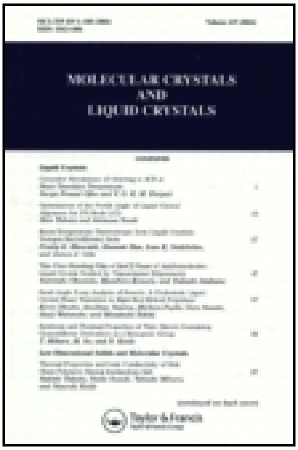

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Dilute Polymer in a Lyotropic Lamellar System without Interaction: A Possible Depletion Flocculation Effect

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Dilute Polymer in a Lyotropic Lamellar System without Interaction: A Possible Depletion Flocculation Effect

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Dedicated to Professor Alfred SAUPE, for his seventieth birthday

It has been observed that a swollen L_α phase (Surfactant: Cetylpyridinium Chloride; Cosurfactant: Hexanol; Solvent: Brine) keeps (at least) metastable under the addition of a *Dilute* quantity of a neutral, flexible polymer (Polyacrylamide) in brine in a large domain of concentration (Ref. 3a), however the periodicity of the lamellar phase suffers a strong decrease. We explain this phenomenon by a privileged swelling of the polymer coils, under the effect of an osmotic pressure localized in the coil region.

Keywords: Swollen surfactants; diluted polymer; compatibility polymer-surfactant; lamellar systems

There are now numerous situations where one has to consider the question of the insertion of particles in a solution of surfactants, whether it concerns magnetic particles, proteins, or polymers, and whether the interest is primarily for applications, or for the search of a novel physical behaviour of a fundamental character. The physical properties of these *complex systems* encompass the 'soft matter' organization versatility of the colloidal matrix and the specific characteristics of the dopant, as for example the ferrosmectics which show up remarkable magnetic patterns [1], the polymer-doped phases [2, 3] which find many applications in paints, food, cosmetics or in

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the pharmaceutical industry, mostly in reason of their rheological properties, or the protein-doped lameller phases [4], which could provide us with biological model systems.

We have found that, by introducing a *dilute* solution of a neutral, flexible polymer (polyacrylamide) in brine as the solvent in a mixture of surfactant (cetylpyridinium chloride) and cosurfactant (hexanol), the system still displays a L_α phase stable in a large domain of concentration (ref. 3a; this paper reports on the modification of the phase diagram of the above mixture of surfactants, swollen in brine, in presence of the polymer; the interlamellar thickness ranges from 100Å to 300Å, while the bilayer thickness δ is fairly constant, of the order of 25Å, as shown by neutron studies [5]), with the polymer coils staying inside the layers of solvent; Figure 1 is a freeze-fracture observation of a sample cleaved between the monolayers of surfactant on most of its area; the individual polymer coils deform the bilayer and are therefore visible, although they are not in direct contact with the exterior; the mean distance between coils is measureable in the picture, and could be compared to what is expected from the composition of the sample and the X-ray measurements of the periodicity of the doped L_α phase. The most spectacular result is that *the system experiences a strong*

FIGURE 1 Freeze-fracture observation of a swollen surfactant in the L_α phase, doped with polyacrylamide (Mukta Singh). 1cm = 3000Å.

decrease of the interlamellar spacing of the L_α phase, at practically constant bilayer thickness, (the decrease is, in some parts of the phase diagram, of the order of 20%), without phase separation. There is little reason to believe that a strong adsorption does prevail between the polymers coils and the surfactant: the polyacrylamide coils dissolve indeed very easily in water and should show no electrostatic interaction with the layers, being neutral. All these features led us to the simple model which is pictured Figure 2, which takes into account the fact that the radius of gyration of the polymeric coils is large compared to the brine layer thickness, which could easily deform. Of course this model has some disadvantage, like a clear reduction in entropy of the polymeric coils due to the confinement, as well as reduction in the entropy of fluctuation of the bilayers. The question is therefore to understand whether the situation so pictured corresponds to a minimum of energy, although the polymer coil is somewhat confined. The answer is positive, and our system might well be *mechanically* stabilized by a process which bears some resemblance with the process of *depletion flocculation* [6, 7], advocated to explain the segregation of particles in a solution of non-adsorbed or weakly adsorbed polymers. Whether this is a truly stable phase or a metastable one is an open question.

More precisely, we assume that the monomers generate, in each region of the solvent occupied by a coil (which are well apart one another, the solution being dilute), a high osmotic pressure with respect to the solvent around; it is precisely this osmotic pressure which pumps brine into the region of the coil, hence acting against the forces of confinement, and deforming the bilayer.

The following treatment then holds for a dilute solution of polymer in between two bilayers. As we decrease the interlamellar thickness (by decreasing the solvent concentration), or as we increase the volume fraction of polymer in solvent (ϕ in our treatment), we approach the semi-dilute behavior. Scaling arguments have been already given to describe this semi-dilute regime [8], which will remain outside the present discussion. We also as-

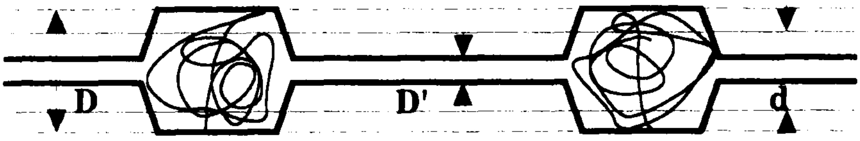

FIGURE 2 Simplified sketch of polymer coils confined in between two membrances.

sume, as already stated, that the coils have no particular interaction with the nearby layers, in the manner of ref. 9, where one talks of the confinement energy of the polymer [9].

Let R_G the Flory radius of the coil in a bulk solution; $R_G \cong aN^{3/5}$, or more precisely: $R_G \cong aN^{3/5}\ (v/a^3)^{1/5}$ (where v is the excluded volume v per monomer, see [10]; $v/a = 1 - 2\chi$, χ being the Flory parameter; since water is a good solvent for polyacrylamide, we assume that $0 < v/a^3 < 1$). According to Daoud *et al.* [9], a polymer coil confined between two parallel separated a distance $D < R_G$ takes a disk-like shape of radius $R \cong aN^{3/4}\ (a/D)^{1/4}(v/a^3)^{1/4}$, energy of confinement $U_{\text{conf}} \cong k_BTN\ (a/D)^{5/3}$- again, taking into account the excluded volume, we shall rather use $U_{\text{conf}} \cong k_BTN\ (a/D)^{5/3}(v/a^3)^{1/3}$. The condition of independence of the coils from one another is: $u \equiv (\pi n_\Sigma R^2)^{-1} \gg 1$, where $n_\Sigma = d \times \phi/Na^3$ is the density of coils per unit area, and d the average thickness of the layer of solvent (Fig. 2) in the polymer doped phase. We assume that this condition is fulfilled.

The contributions to the energy U_{coil} of a confined coil are as follows:

a) the energy of confinement itself

$$U_{\text{conf}} \cong k_BTN(a/D)^{5/3}(v/a^3)^{1/3}, \tag{1}$$

b) the energy of curvature

$$U_{\text{curv}} \approx 2\kappa \tag{2}$$

where κ is the rigidity modulus of the bilayer; this term describes the elastic deformation.

c) the energy U_{dec} associated with decrumpling of the membranes requires some discussion. If $R_G \gg d$, we would expect all the degrees of freedom of the membrane quenched by the presence of the coils; i.e., in this limit, we find $U_{\text{dec}} \cong k_BT/n_\Sigma\ a^2 \approx k_BT \times a/d \times N/\phi$ for each coil, a considerable energy which would be the dominant term in U_{coil}, and would probably forbid the polymer to enter the L_α phase. Therefore we assume that the coil does not strongly 'stick' to the membrane, which is justified when the De Gennes-Taupin correlation length [11] $\xi \approx a \times \exp\ \alpha\kappa/k_BT$ (α a numerical constant) is large compared to R. Furthermore, there is another characteristic distance in play, viz. the length scale $L \cong d \times (\kappa/k_BT)^{1/2}$ typical of thermal fluctuations [12], which is smaller than ξ. These fluctuations are therefore of a rather small amplitude compared to their size, and consequently easily damped in the region in contact with the coil; hence

$$U_{\text{dec}} \cong k_B T \times R^2/L^2 \cong k_B T(k_B T/\kappa) N^{3/2}(a/d)^2(a/D)^{1/2}(v/a^3)^{1/2} \tag{3}$$

is probably a good estimation of the effect of decrumpling.

d) the elastic energy U_{str} due to the additional tension in the membrane resulting from the pressure exerted on it. U_{str} will be shown below to be small enough, not affecting much the treatment that we present here, but rather renormalizing it.

In the sequel, we assume that U_{dec}, U_{curv} and U_{conf} are the only relevant terms in the free energy of a coil. The values of these terms will be estimated and compared farther on. We write $U_{\text{coil}} = U_{\text{curv}} + U_{\text{conf}} + U_{\text{dec}}$. More generally we shall write $U_{\text{coil}} = U_{\text{curv}} + \Sigma U'_{\text{coil}}$, where U'_{coil} stands for U_{conf} or U_{dec} and Σ stands for a sum over the two contributions.

Let then D' be the thickness of the solvent layer outside the bumps created by the coils. We have:

$$\Delta \equiv (1 - \pi n_\Sigma R^2)D' + \pi n_\Sigma R^2 D - d = 0 \tag{4}$$

This equation insures that the density of coils has volume fraction ϕ. We estimate now the pressure ϖ which is at the origin of the 'flocculation' of the layers as follows:

The free energy of the lamellar phase $F = F(w, d, T)$ at constant volume per coil $w = \pi R^2 D$ *is* $F = U_{\text{coil}}\, n_\Sigma \Sigma$, where Σ is the total membrane area, i.e. a constant. Let ϖ be the osmotic pressure inside the volume w occupied by the coil. The relevant thermodynamic function $G = G(\varpi, d)$ is

$$G = G(\varpi, d, T) = F(w, d, T) + \varpi w n_\Sigma \Sigma \tag{5}$$

This gives, per unit membrane area,:

$$g(\varpi, d, T) = G(\varpi, d, T)/\Sigma = U_{\text{coil}} n_\Sigma + \varpi w n_\Sigma \tag{6}$$

The osmotic pressure obtains form $\partial g(\varpi,d,T)/\partial w \equiv 0$:

$$\varpi = -\partial U_{\text{coil}}/\partial w \tag{7}$$

Let p be the scaling exponent of D^{-1} in $U'_{\mathrm{coil}}(p=5/3$ for U_{conf}, $p=1/2$ for $U_{\mathrm{dec}})$;we have:

$$\varpi = -\partial U_{\mathrm{coil}}/\partial w = -2D/w \times \partial U'_{\mathrm{coil}}/\partial D = 2/w \times \Sigma\, pU'_{\mathrm{coil}} \tag{8}$$

i.e., with:$\varpi = \varpi_{\mathrm{conf}} + \varpi_{\mathrm{dec}}$

$$\varpi_{\mathrm{conf}} = 10/3 \times k_B T/\pi a^3 \times N^{-12}(a/D)^{13/6}(v/a^3)^{-1/6} \tag{9a}$$

$$\varpi_{\mathrm{dec}} = k_B T/\kappa \times k_B T/\pi a^3 \times (a/d)^2(a/D) \tag{9b}$$

Hence:

$$g(\varpi,d,T) = U_{\mathrm{coil}} + 2n_\Sigma \times \Sigma\, pU'_{\mathrm{coil}} \tag{10}$$

ϖ is a *local* pressure which acts in the region of the coil (solvent + solute), not in the layer of pure solvent located in its near vicinity; the central argument of this paper is that thermodynamic methods can be safely used at the scale of this domain because the number of monomers N is intrinsically large, although it keeps small compared to the total number of sites $N_t \cong \pi R^2 D/a^3 \cong \pi N^{3/2}(a/D)^{-1/2}(v/a^3)^{1/2}$. The quantity ϖ is indeed here a spatial pressure fluctuation, which exists also in a $3D$ solution, but on much smaller times since it is blurred by the rapid Brownian movement. Here, we expect the Brownian movement to be of a much milder nature, since the motion of the coils has to suffer not only the classical friction on the solvent, but also a probably dominant friction with the layers of surfactant. The phenomenon of flocculation has time to build if the typical relaxation time $\tau_r \approx \eta R^2 D/k_B T$ of the spatial fluctuations of the coils is larger than the typical relaxation time τ_1 of the layers $(\tau_1 \approx \eta/\kappa k^3)$, where η is a viscosity and $k \approx n_\Sigma^{1/2}$ the inverse of a typical distance between coils. This condition reads:

$$\kappa/k_B T \times \phi N^{1/2}(D/a)^{1/2} > 1 \tag{11}$$

It is interesting to compare the value of ϖ which is derived in eq. (9) with the mean field value deduced from a Flory-Huggins model for the microdomains in presence (the coil and the surrounding pure solvent). The FH model yields a free energy for the coil in solvent

$$U_{\mathrm{coil\ FH}} \cong k_B T\{\chi N N_s/N_t + \ln N/N_t + N_s \ln N_s/N\} \tag{12}$$

(here $N_s = N_t - N$ is the number of sites occupied by the solvent in the coil region). U_{coilFH} contributes to the osmotic pressure by a term ϖ_{FH}:

$$\varpi_{FH} \cong -1/a^3 \times \partial U_{\mathrm{coilFH}}/\partial N_t|_N \cong 2(1-2\chi)k_BTa^3 \times N^2/N_t^2 \tag{13}$$

There is no term linear in the fraction of sites occupied by the monomers $\Psi = N/N_t$ in contrast with the usual theory (there is only one chain, so that this term is negligible). The ratio of the two contributions to the global and local osmotic pressures ϖ_{conf} (say) and ϖ_{FH} is:

$$\varpi_{FH}/\varpi_{\mathrm{conf}} \approx N^{-1/2}(D/a)^{7/6}(v/a^3)^{1/6} \tag{14}$$

Note that the worse the solvent, the smaller the ratio, as expected.

We now speculate on the thermodynamical meaning of equations (8) and (10):

a) first note that $\partial\varpi/\partial w = -2p/w(U'_{\mathrm{coil}}/w + \varpi)$ is always negative;

$$\partial\varpi/\partial w < 0 \tag{15}$$

this inequality insures that *the system is at least metastable*, since the (osmotic) pressure increases when the volume decreases;

b) next, the derivative of g with respect to d reads:

$$\partial g/\partial d = (1+2p_{\mathrm{dec}})n_\Sigma \times \partial U_{\mathrm{dec}}/\partial d + [U_{\mathrm{coil}} + 2\sum pU'_{\mathrm{coil}}] \times \phi/Na^3 \tag{16}$$

Let q be the scaling exponent of d^{-1} in U'_{coil} ($q_{\mathrm{conf}} = 0, q_{\mathrm{dec}} = 2$); we note that the contribution of U_{conf} to $\partial g/\partial d$ is a positive constant, indicating that ,the membranes tend to collapse under this effect; it is the decrumpling term which limits this tendency, yielding a value of d which minimizes the energy per unit area g, viz.:

$$\partial g/\partial d \equiv n_\Sigma/d \times (\kappa + 13/3 \times U_{\mathrm{conf}} - 2U_{\mathrm{dec}}) = 0 \tag{17}$$

Note that the second derivative $\partial^2 g/\partial d^2$ is positive for any value of d, so that the solution, if it exists, is stable.

We introduce at this stage some orders of magnitude: with $N \approx 3000$, $\kappa/k_BT = 1.5$-according to Bassereau[13], $v/a^3 = 1/2$, assuming that all the terms are of the same order of magnitude in equ. 17, we find $D/a \approx 120 \approx 2$

d/a. Taking $a \approx 3$Å, we get $d \approx 180$Å and ξ at least of the order of 1000 Å, $L \approx 220$Å, i.e. comparable to $R \approx 310$Å. Inequality (11) is satisfied by these numerical values, while the condition $u > 1$ is only marginally satisfied.

Before further proceeding, let us check that the energy of stretching is small. In the region of the bump, which is of radius R, the surface tension is of the order of $\gamma = \varpi R$, and is proportional to the $2D$ strain in the bilayer, viz. $\gamma = \lambda\ \varepsilon$, where, on the basis of dimensional arguments, we expect the elastic coefficient λ to be of the order of κ/a^2. Hence the elastic energy stored in the stretching of one bump is of the order of $U_{str} \approx 2\pi/2 \times \varepsilon\gamma R^2 = \pi a_0^2/2\kappa \times \gamma^2 R^2$. Using the values obtained above for the different terms in this expression, we find:

$$U_{str} \approx 100\pi/9 \times (k_BT)^2/\kappa \times (a_0/a)^2(a^4/Dv)^{1/3}(R/D)^4N^{-1} \tag{18}$$

which yields a much smaller term than the term U_{conf}, say. The ratio:$U_{str}/U_{conf} = 400\pi/9 \times k_BT/\kappa \times (a_0/a)^2\ (v/a^3)^{1/3}\ (a/D)^{11/3}\ N$ has indeed scaling behaviour ruled by the terms $(a/D)^{11/3}N$; inserting numerical values as above, we find $(a/D)^{11/3}N \approx 0.7 \times 10^{-4}$, i.e. a very small value. Note however that the strain itself in not entirely negligible: the area in contact with a coil, viz. $2\pi R^2$, is strained to an area $2\pi R^2(1 + 2\varepsilon)$; therefore area A, with there are An_s coils, becomes $A(1 + 4\pi n_\Sigma \varepsilon R^2)$, where:

$$4\pi n_\Sigma \varepsilon R^2 \cong 40\pi/3 \times k_BT/\kappa \times \phi N^{3/4}(d/a)(v/a^3)^{7/12}(a/D)^{35/12}. \tag{19}$$

Using the above numerical values, this is of the order of $A\ \phi$, with A of the order of unity.

The analysis above makes use of 3 unknowns, D, D', and d, with only 2 relations between them (eq. 4 and 17); the third one is obtained through an analysis of the undulations before and after introduction of the polymer. These undulations are of two origins, the thermal fluctuations, and those due to the presence of the coils. Let $k^2 = A^{pr}/A$ a 'crumpling' parameter which takes into account this effect; we have: $\phi_1 d_0/\delta = k^{-2}$, where A^{pr} is the projected area and A is the real area; δ is the thickness of the bilayer, and d_0 is the interlamellar distance in lamellar systems with no polymer; d_p(formerly noted d) is the same distance in lamellar systems with polymer; ϕ_1 is the volume fraction of the surfactant. We have, with self-speaking notations:

$$k_p^2 d_p = k_0^2 d_0 \tag{20}$$

so that, since $d_p < d_0$, the undulations of the system with polymer must be smaller than those of the system without.

Golubovic and Lubensky [12] have given the form of k^2 when the crumpling is due to thermal fluctuations:

$$k_0^2 \cong 1 + k_B T/4\pi\kappa \times \ln[d_0/d_{ph} \times (\kappa/k_B T)^{1/2}(\pi/4a_0)^{1/2}]$$

$$\equiv 1 + 2(\Delta k_0)_{\text{thermic}} \tag{21}$$

here d_{ph}^2 is the area of each polar head of the surfactant and a_0 is a numerical coefficient in Helfrich's relation for steric repulsive interaction [14].

The change in area of the bilayers in the presence of polymer dominates the contribution due to the thermal fluctuations, as can be readily seen. Assume further that no stretching of the bilayer is necessary to accommodate the coils. Hence:

$$k_p^2 \equiv 1 + 2(\Delta k_p)_{\text{thermic}} + (\Delta k_p)_{\text{conf}} \approx (\Delta k_p)_{\text{conf}} = (1 - \pi n_\Sigma R^2) + 4\pi n_\Sigma R^2 \tag{22}$$

$(\Delta k_0)_{\text{thermic}}$ and $(\Delta k_p)_{\text{thermic}}$ are both comparable and also much smaller than the term $(\Delta k_p)_{\text{conf}}$. Therefore, for two lamellar samples, with and without polymer, but with the same ϕ_1, eq. 20 gives:

$$(1 + 2(\Delta k_0)_{\text{thermic}})/d_p = k_p^2/d_0$$

which simplifies to:

$$1/d_p - 1/d_0 \approx 3\pi n_\Sigma R^2/d_p \tag{23}$$

since the thermal fluctuations are much smaller than the geometrical undulations due to the coils.

This relation has been checked versus the experimental data in ref. 3b and ref. 15, with a relatively good agreement. The discrepancies are most probably due to the neglect of the stretching contribution, especially in the region of the smaller d_0 values, and of the thermal fluctuations, especially in the region of the larger d_0 values [15].

To conclude, the theory above presents a simple model of confinement of dilute polymer coils in a swollen lameller phase, based on the idea of a privileged swelling in the region of the coils, in order to increase the entropy of configuration. The same type of arguments has been used to explain flocculation, or suggested to understand the passage of polymer coils through narrow pores [16]. The main conclusion of our analysis is the possibility of a metastable lamellar phase doped with polymers, even if those polymers have size $R_G > d$. A more detailed calculation remains to be done, and the present work does not aim at more than a rough estimate of the magnitude of the quantities in play.

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