Phase Separation in Polymer Solutions with Annealed Excluded Volume Interactions

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ABSTRACT: On the basis of an analytical mean-field model, we consider phase separation and coil−globule transitions in solutions of polymer chains with annealed excluded-volume interactions. In our model, the chain monomers are able to reversibly change their state from a hydrophilic to a hydrophobic one. This may mimic the behavior of polymers in solutions that contain amphiphilic molecules, e.g., globular proteins or surfactants, that are capable of cooperative association with the polymer chains. While the bare polymer chains are either hydrophobic or weakly hydrophilic, the formation of polymer/surfactant or polymer/protein complexes may strongly enhance the solubility of the polymers in water. We predict different phase behavior for solutions of originally hydrophilic or hydrophobic polymers mixed with amphiphiles. In the former case, the solution remains homogeneous at low concentrations of amphiphiles, whereas in the latter case it separates into a dilute and concentrated phase. The Θ-transition of the complexed polymers may be induced by variation either of the concentration of amphiphiles, of the temperature, or of the ionic strength of the solution. At low ionic strength the collapse of an individual, complexed chain with decreasing solvent strength or decreasing amphiphile concentration acquires the character of a first-order phase transition. At high concentrations of amphiphiles and high ionic strengths, we predict the possibility of the coexistence of two semidilute polymer phases, both for hydrophilic and for hydrophobic chains.

1. Introduction

Although association and complexation in mixtures of neutral (nonionic) polymers with small amphiphiles, such as surfactants or small globular proteins, has been observed in numerous experimental systems, the theoretical understanding of these phenomena is still incomplete. The effect of the polymer−protein and polymer−surfactant interactions on the structure and rheological properties of multicomponent polymer solutions is of great importance for various industrial applications (e.g., cosmetics, detergents).[1,2] Moreover, the self-assembly in polymer/protein and polymer/surfactant mixtures can serve as a model for certain stages of a prebiological evolution.[3,4]

There is an important distinction between association of polymers with proteins on one hand and polymers with surfactants on the other. In water-soluble globular proteins, the majority of the hydrophobic groups are usually hidden in the interior of the globule (their attraction leads to the formation of a dense globule with well-defined spatial structure), whereas at the globule−water interface the hydrophilic groups are exposed to water and thus provide the solubility of the globules. However, hydrophobic patches occupy a certain fraction of the globule interface. The attractive (hydrophobic) interaction of such patches with the polymer segments provides the driving force for polymer−protein association. Upon complexation, the spatial (ternary) structure of the protein globule remains generally unperturbed; i.e., only hydrophobic patches on the interface interact with the polymer. Hence, association of proteins occurs (at low degree of loading) noncooperatively. Therefore, no characteristic concentrational threshold for the onset of the association is found. Most studies of complexation of polymers with globular proteins concern oppositely charged[5] or hydrophobically modified water-soluble polymers,[6] although there are some indications of association of proteins with nonionic hydrophilic polymers as well.[7]

In contrast to proteins, surfactants are capable to cooperative formation of aggregates (micelles) complexed with polymer chains. An experimental model system of a water-soluble polymer interacting with an anionic surfactant that has been extensively studied is PEO with SDS,[8−13] although PPO, EDEC, PVA, and PVP with SDS give similar results.[10,14−16] Low solubility of surfactants in water is due to the hydrophobicity of the hydrocarbon "tails" and provides the driving force for polymer−surfactant association. Because of the amphiphilic nature of the surfactant molecules, they self-assemble in aqueous solutions forming finite size aggregates (micelles) at concentrations exceeding a certain critical value (called the critical micelle concentration, cmc).[17,18]

There is convincing experimental evidence of association of ionic surfactants with hydrophilic polymer chains at concentrations below the cmc, but above a certain concentration threshold, usually referred to as the critical association concentration (CAC). This entails that at CAC only individual surfactants but no micelles are present in the solution. The affinity between the hydrophobic tails of surfactants and the polymer units is not strong enough to bind individual surfactants to the chain.[9,12,15] However, weakly attractive interactions may trigger self-assembly of surfactants into micellar-like aggregates complexed with the polymer chain. The driving force of this association is believed to be the

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shielding of the hydrophobic patches at the micellar–water interface by adsorbed polymer units.[19–21] In contrast, the hydrophilic groups of the amphiphiles remain exposed to water. Therefore, complexation may lead to an increased solubility of the polymer–amphiphile complex in water. In other words, water becomes a better solvent for the polymer chain decorated with complexed amphiphiles. This entails an enhancement of intra- and interchain osmotic repulsion in the polymer solution. The experiments indeed show that in dilute solutions the polymer–micelle complexes can be envisioned as "necklaces of pearls" formed by surfactant aggregates bound to the chain.[9,12,15] The osmotic repulsions between adsorbed aggregates results in additional swelling of the necklace with respect to the bare coil size. However, in dilute regime the leading contributions to the free energy of the complex are the free energy of complexation and the translational entropy of adsorbed aggregates along the chain (both proportional to the number of adsorbed micelles). In comparison to these two contribution the osmotic repulsion between adsorbed aggregates is weak. Therefore, the chain conformation is affected by the loading whereas the reverse effect is negligible.[7,22–24] The fact, that the interaction energy between adsorbed aggregates in the long polymer chain is small in comparison to the complexation energy has been confirmed in experiments.[16]

On the contrary, in semidilute solutions, the equilibrium degree of loading of the chains by adsorbed amphiphiles is determined by the balance between the osmotic repulsion and the free energy gain due to complexation. As the strength of the osmotic interactions is not an independent (intrinsic) parameter, but depends on the degree of loading, which, in turn, is determined by the condition of a minimum in the overall free energy, the system can be described in terms of annealed excluded-volume interactions, as proposed in refs 22 and 23. An alternative approach to the description of the polymer/surfactant necklaces based on the analogy with a 1-dimensional liquid has been recently proposed in ref 24.

The aim of the paper is to present systematically the mean-field theory of phase separation in semidilute solutions of polymers with annealed excluded volume interaction in application to associating polymer/surfactant mixtures. The preliminary results of the theory have been already reported in ref 23. The effect of complexation on the phase equilibria and on the conformations of individual chains in solution is studied in a wide range of solvent quality, including the region around the Θ-point, i.e., for hydrophilic or weakly hydrophobic polymers. We focus on the case when the polymer solution contains small amphiphilic molecules (surfactants) at a concentration X smaller than the cmc but larger than the CAC. The generalization of the theory for the case $X \cong X_{\text{cmc}}$, when free micelles appear in the solution, is straightforward. The main results of our analysis can be directly reformulated also for polymer/protein mixtures.

The structure of this paper is as follows. In section 2 our mean-field model is introduced and the phase behavior of polymer solutions containing surfactants capable of cooperative association with polymer chains is considered. In section 3 the conformational transition in individual macromolecules upon complexation is examined in more detail. We also account for finite size (the chain length) effects on the conformational transition. Finally, in section 4 we discuss the results and present our conclusions.

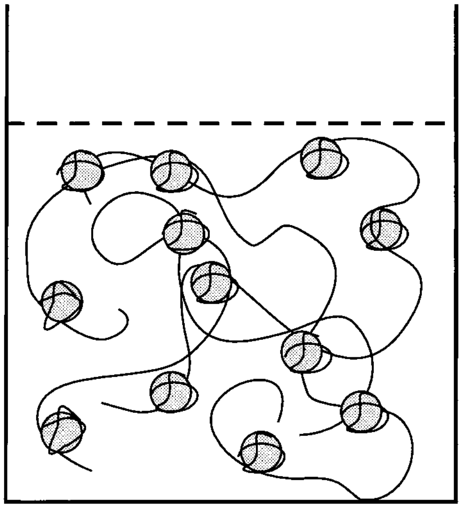

Figure 1. Schematic illustration of a semidilute solution of polymer–micelle complexes.

2. Model and General Formalism

2.1. Coarse-Grained Free Energy. We consider a solution of polymer chains consisting of N monomers immersed in an aqueous phase. The dimensionless concentration (the volume fraction) of monomers in solution is ρ. The chains are flexible; i.e., the Kuhn segment length is equal to the monomer length, which in turn is taken as the unit length in the system.

The quality of the solvent for the monomer units is characterized by the second virial coefficient of monomer–monomer interactions v_0, which in a first approximation is proportional to the relative deviation from the Θ-point, $v_0 \cong (\Theta - T)/T$. We remark that most of hydrophilic polymers like PEO and PNIPAM exhibit an upper Θ-point; i.e., the quality of water as a solvent decreases with increasing temperature.[25] If the temperature T is below the Θ-temperature, water is a good solvent for the polymer whereas above the Θ-temperature water is a poor solvent, and sufficiently long chains collapse and precipitate.[26,27]

As is demonstrated in the following, the hydrophilic/hydrophobic properties of polymer chains can be tuned not only by varying the temperature, but also by addition of small amphiphilic molecules to the solution. The attraction between the hydrophobic groups of the amphiphiles and the polymer chains provides the driving force for their complexation, whereas steric (or electrostatic) repulsion between hydrophilic groups of complexed amphiphiles results in solubilization of the polymer chains. As the binding energies involved are usually of order k_BT (where k_B is the Boltzmann constant and T is temperature) the association is reversible.

We assume that surfactants are associated with polymer chains in the form of spherical aggregates ("micelles"). The resulting polymer–micelle complex has a necklacelike structure, as is illustrated schematically in Figure 1. We assume also that the structure and the size of bound micelles does not vary with increasing degree of loading of the chains, that is apparently the case in many experimental systems.[8–16] Hence, in our approach we neglect the possibility of formation of elongated micelles or lamellar-type structures which may occur at sufficiently high concentrations of polymer and surfactants.

If m micelles are bound to one polymer chain and each micelle occupies a sequence of N_{ad} monomers, the degree of loading of the chain by “adsorbed” aggregates can be defined as

$$\theta = mN_{ad}/N \tag{1}$$

The number of monomers complexed with an amphiphile is assumed to be constant, i.e., N_{ad} is independent of θ. The above equation can be rewritten in terms of local number densities of adsorbed micelles ρ_m and monomer units ρ as

$$\rho_m = \rho\theta/N_{ad} \tag{2}$$

For different systems N_{ad} can vary from ~1 to order 100.[8−10] As we have mentioned above, an increase in the degree of loading of the chains enhances the repulsive osmotic interactions in the solution. Therefore, within our model θ is not an independent variable, but is determined from the condition of minimal free energy of the polymer solution. Following refs 22 and 23, we can write the free energy (per unit volume) as a function of ρ and θ as

$$\frac{f(\rho,\theta)}{k_BT} = \frac{\rho}{N}\ln\rho - \rho\frac{s(\theta)}{k_B} + \rho\theta u + f_{osm}(\rho,\theta)/k_BT \tag{3}$$

The first term in eq 3 accounts for the translational entropy of the polymer chains as a whole and is negligible for large N. The second term in eq 3 is the mixing entropy, which arises from the translational freedom of adsorbed micelles along the polymer chains. Taking into account that each adsorbed micelle occupies a sequence of N_{ad} successive monomers of the chain, we can write the mixing entropy per monomer as[28]

$$-\frac{s(\theta)}{k_B} = \frac{\theta}{N_{ad}}\ln\frac{\theta}{N_{ad}(1-\theta)+\theta} + (1-\theta)\ln\frac{N_{ad}(1-\theta)}{N_{ad}(1-\theta)+\theta} \tag{4}$$

provided that $N/N_{ad} \gg 1$. Note that for $N_{ad} = 1$ eq 4 reduces to the usual expression

$$-s(\theta)_{N_{ad}=1}/k_B = \theta\ln\theta + (1-\theta)\ln(1-\theta) \tag{5}$$

for mixing entropy of loaded and unloaded monomers in the chain.

The third term in eq 3 describes the free energy of formation of adsorbed micelles. This differential free energy, which can also be interpreted as “the adsorption strength”, comprises (i) the translational entropy penalty $-N_sk_BT\ln X$ for immobilization of N_s surfactant molecules in a micelle (we remind the reader that X is the concentration of free surfactants); (ii) the free energy of transfer of N_s surfactant molecules from an aqueous environment into a micelle, $N_s\Delta\mu^0$; and (iii) the energy of complexation of a strand N_{ad} with the micelle, $N_{ad}\Delta E$. It is convenient to express the free energy of complexation not per one micelle, but per monomer in the chain sequence N_{ad} involved in the formation of one micelle−polymer complex. This yields

$$u = \left[\Delta E + (\Delta\mu^0 - k_BT\ln X)\frac{N_s}{N_{ad}}\right]/k_BT \tag{6}$$

Equation 6 can also be rewritten in terms of the critical association concentration, X_{CAC}, as $u = (N_s/N_{ad})\ln(X_{CAC}/X)$, where $X_{CAC} = \exp\{[\Delta\mu^0 + (N_{ad}/N_s)\Delta E]/k_BT\}$.

The explicit calculation of u can be performed on the basis of a particular molecular model for the individual polymer−micelle complex[22,29] and requires calculation of such quantities as ΔE, $\Delta\mu^0$, N_s, and N_{ad}. In our model, we assume that u can be tuned independently of other parameters by variation of the surfactant concentration X, i.e., u decreases logarithmically when X increases.

Complexation of surfactant aggregates changes the osmotic interactions in the polymer solution. Following our earlier mean-field approach, we present the osmotic free energy density as a virial expansion in powers of average densities of all types of particles present in the solution

$$f_{osm}(\{\rho_i\}) = \sum_{ij}\tilde{v}_{ij}\rho_i\rho_j + \sum_{ijl}\tilde{w}_{ijl}\rho_i\rho_j\rho_l + ... \tag{7}$$

where ρ_i is the number density of particles of type i, which are either bare monomers or adsorbed aggregates. The second virial coefficient $\tilde{v}_{ij}$ characterizes binary interactions between the particle of type i and of type j, while the third virial coefficient $\tilde{w}_{ijl}$ is the three-body interaction parameter.

It is convenient to express all terms in the osmotic free energy of the solution in terms of the monomer concentration ρ, using eq 2 for the concentration of adsorbed micelles. The result can be presented as

$$f_{osm}(\rho,\theta) \cong v(\theta)\rho^2 + w\rho^3 \tag{8}$$

where we have introduced an effective second virial coefficient, defined as

$$v(\theta) = v_0(1-\theta)^2 + v_1\theta^2 + 2v_2\theta(1-\theta) \tag{9}$$

and $v_1 = \tilde{v}_1/N_{ad}^2$ and $v_2 = \tilde{v}_2/N_{ad}$ (see below). The renormalized excluded-volume parameters v_1 and v_2 can be interpreted as the second virial coefficients of interaction of two complexed monomers and of a bare and a complexed monomer, respectively. We remark that in the particular case that $v_0 = v_1 = v_2$ the excluded-volume interactions are independent of the degree of loading, i.e., $v(\theta) \equiv v_0$. The effective averaged third virial coefficient $w(\theta)$ correspondingly comprises the normalized virial coefficients of ternary interactions between bare monomers and adsorbed micelles. It is not presented here in an explicit form. Under good solvent conditions for bare polymer the osmotic interactions are dominated by binary repulsions and the contribution of ternary interactions is negligible. On the contrary, when the solvent is poor for the polymer (attractive binary monomer−monomer interactions), the third order-term comes necessarily into play.

As has been discussed above, v_0 is either positive (good solvent) or negative (poor solvent). The monomer−monomer interaction is dominated either by steric repulsion (excluded volume) in the former case or by short-range attraction in the latter case. This attraction provides the driving force for phase separation of noncomplexed polymers above the Θ-point.

The micelle−micelle interaction parameter, denoted by $\tilde{v}_1$, comprises steric and electrostatic contributions, as polymer−micelle complexes generally consist of anionic surfactants.[20] Both contributions are repulsive and provide the main repulsive contribution to the osmotic interactions in the solution. The electrostatic part depends explicitly on the extent of screening of electrostatic interactions, i.e., on the Debye screening parameter κ, which is related to the salt concentration (ionic strength of the solution). At low and moderate ionic strength the micelle−micelle interaction is dominated by the screened Coulombic repulsion. Evidently, $\tilde{v}_1$ decreases with increasing ionic strength of the solution. Hence, variation of the ionic strength of the solution provides a possibility for independent tuning of the second virial coefficient of micelle−micelle interaction. This has recently been demonstrated experimentally by Rosén et al.[30]

Finally, the cross-term in eq 9 describes the contribution of binary contacts between bare monomers and adsorbed micelles and is of particular interest for solutions close to the Θ-temperature. We employ a coarse-grained description in which we consider the interaction of a polymer−micelle complex, comprising the micelle itself and the part of the chain of length N_{ad} adsorbed onto the micelle−water interface, with a bare monomer. We assume that the affinity of the complexed monomers for the micellar surface is relatively large, so that (i) the polymer chain does not make large loops, i.e., the bulk of N_{ad} monomers are localized in the proximity of the micellar surface,[31,32] and (ii) most of the hydrophobic patches on the micellar surface are shielded (saturated) by adsorbed monomers. Then the second virial coefficient of interaction of a monomer with the complexed micelle can be written as

$$\tilde{v}_2 = \frac{2\pi R_{\mathrm{m}}^{\ 3}}{3} + 2\pi \int_{R_{\mathrm{m}}}^{\infty} r^2 (1 - \mathrm{e}^{-U(r)/k_{\mathrm{B}}T})\, \mathrm{d}r \qquad (10)$$

where the first term describes pure steric repulsion (impermeability of the micellar interior region for monomers, R_{m} is the micellar radius), while the second term describes the interaction of a bare monomer with the adsorbed layer around the micelle, formed by N_{ad} monomers. Thus, $U(r)$ is the average potential experienced by the monomer at a distance $r - R_{\mathrm{m}}$ from the micellar surface. The range of the average molecular potential $U(r)$ is proportional to the so-called "adsorption length"[27,33] and gives the effective cutoff length for the integral in eq 10. As the N_{ad} monomers are strongly attracted to the surface the adsorption length is comparable to the monomer size.

The sign of the second term in eq 10 depends on the character of the monomer−monomer interaction, which is repulsive ($U(r) \geq 0$) under good solvent conditions and attractive ($U(r) \leq 0$) under poor solvent conditions. To estimate $U(r)$ we use a mean-field shell approximation, i.e., we assume

$$\frac{U(r)}{k_{\mathrm{B}}T} = \begin{bmatrix} v_0 N_{\mathrm{ad}}/4\pi R_{\mathrm{m}}^{\ 2} & r \leq R_{\mathrm{m}} + 1 \\ 0 & r \geq R_{\mathrm{m}} + 1 \end{bmatrix} \qquad (11)$$

(we remind the reader that the monomer length is taken as the unit length). This leads to $v_2 \cong 2\pi R_{\mathrm{m}}^3/3N_{\mathrm{ad}} + v_0/2$. Hence, under good solvent conditions ($v_0 \geq 0$) the second virial coefficient of binary interaction between bare monomers and complexed micelles is positive, and the main term scales as R_{m}^3. Under poor solvent conditions ($v_0 \leq 0$), however, the balance between steric repulsion (the first term in eq 10) and attraction to the adsorbed layer (the second term in eq 10) significantly reduces v_2.

We remark that even under good solvent condition there is an attractive contribution to v_2 due to the possibility of sharing of one micelle between two separated sequences of monomers within one chain (of those of two different chains). In this case, the micelles work as effective reversible cross-links in the polymer solution. We expect, however, that the number of these cross-links becomes significant only at sufficiently large degrees of loading, when the dominant contribution to the osmotic free energy of the solution is due to micelle−micelle repulsion.

2.2. Phase Equilibrium. The equilibrium degree of loading of polymer chains by adsorbed micelles (at a given monomer concentration ρ and given adsorption strength u, i.e., at fixed chemical potential of free surfactants) can be obtained by minimizing the free energy given by eqs 3 and 8 with respect to θ, i.e.

$$\frac{\partial f(\rho,\theta)}{\partial \theta} = 0 \qquad (12)$$

In a good solvent, all contributions to $v(\theta)$ are positive; i.e., the effective binary interactions in the system are repulsive. Under these conditions, the contribution of ternary interactions in eq 8 can safely be neglected. Below the Θ-point for a bare polymer binary interactions between monomers have attractive character. They are balanced by ternary repulsions that ensures a finite density of the collapsed polymer phase.[27] As is demonstrated in the following, the degree of loading in a dense (collapsed) phase is close to zero so that the third-order term in the osmotic free energy, eq 8, is dominated by ternary interactions between bare monomers. Therefore, eq 12 can be rewritten in an explicit form as

$$\rho(\theta) = -\frac{k_{\mathrm{B}}}{v'(\theta)}(s'(\theta_{\mathrm{b}}) - s'(\theta)) \qquad (13)$$

where

$$-s'(\theta) \equiv -\frac{\mathrm{d}s(\theta)}{\mathrm{d}\theta} = k_{\mathrm{B}}\left[\frac{1}{N_{\mathrm{ad}}} \ln \frac{\theta}{N_{\mathrm{ad}}(1-\theta)+\theta} - \ln \frac{N_{\mathrm{ad}}(1-\theta)}{N_{\mathrm{ad}}(1-\theta)+\theta}\right] \qquad (14)$$

and we have introduced the notation $v' \equiv \mathrm{d}v(\theta)/\mathrm{d}\theta$. We denote the maximum (bulk) degree of loading of a polymer in a dilute solution, $\rho \approx 0$, as θ_{b}. The value of θ_{b} depends solely on the adsorption strength $-u$ (i.e., on the surfactant concentration), and N_{ad} and can be found from the equation

$$\ln \frac{N_{\mathrm{ad}}(1-\theta_{\mathrm{b}})}{N_{\mathrm{ad}}(1-\theta_{\mathrm{b}})+\theta_{\mathrm{b}}} - \frac{1}{N_{\mathrm{ad}}} \ln \frac{\theta_{\mathrm{b}}}{N_{\mathrm{ad}}(1-\theta_{\mathrm{b}})+\theta_{\mathrm{b}}} = u \qquad (15)$$

Equation 15 describes also an equilibrium loading of a

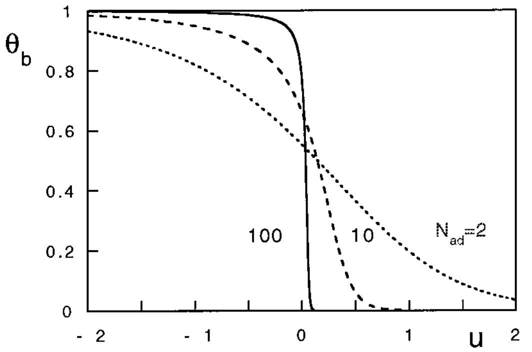

Figure 2. Bulk degree of loading θ_b as a function of u for three values of N_{ad}, indicated in graph.

swollen polymer coil (for $N \rightarrow \infty$ the intrachain concentration of monomers vanishes) as a function of $u \sim \ln(X_{CAC}/X)$. In Figure 2 the bulk degree of loading θ_b is plotted as a function of u for several values of N_{ad}. As one can see from the figure, the bulk degree of loading θ_b is a monotonically increasing function of $-u$, i.e., of the surfactant concentration X. It depends, generally speaking, also on the temperature and on the ionic strength of the solution. The latter affects the interaction between charged headgroups at the micelle–water interface, and as a result, the equilibrium aggregation number and the association energy per amphiphile.[34] We remark that for $N_{ad} = 1$ the term $\exp(-u)$ can be interpreted as the equilibrium constant of conversion from an unloaded to a loaded state for a monomer in the bulk of the solution. For large values of N_{ad}, corresponding to large number of adsorbed monomers and surfactants per aggregate the loading of the chain increases sharply from 0 up to 1 (corresponding to saturation of the chain by adsorbed micelles) when $u \cong 0$, that is $X \cong X_{CAC}$. Hence, for N_{ad}, $N_s \gg 1$ association of surfactants with the chain occurs as a highly cooperative transition, in which translation entropy of individual surfactants and binding enthalpy play the major role, while the mixing entropy of loaded and bare sequences in the chain is negligible. In contrast, for small values of $N_{ad} \sim N_s \sim 1$ the mixing entropy plays an important role providing more gradual increase in the degree of loading with increasing surfactant concentration X.

The condition $v'(\theta) \geq 0$, which simply states that upon loading at a given polymer concentration the strength of the osmotic interactions in solution increase, ensures that $\theta \leq \theta_b$ for $\rho > 0$. Obviously, if the derivative $v'(\theta)$ vanishes (which implies that the osmotic interactions do not depend on the degree of loading), then the equilibrium degree of loading θ is equal to the bulk value θ_b irrespectively of the polymer concentration. This follows clearly from eq 13. The condition $d\rho/d\theta \leq 0$ ensures that the degree of loading, given by eq 13, corresponds to the minimum of the free energy ($\partial^2 f(\rho,\theta)/\partial\theta^2 > 0$) at a given ρ. Moreover, under this condition θ, defined by eq 13, is a single valued function of ρ. As the monomer density in the solution increases, the degree of loading monotonically decreases due to the enhanced osmotic repulsions. This decrease is the strongest for the strongest micelle–micelle interactions, i.e., the largest value of v_1.

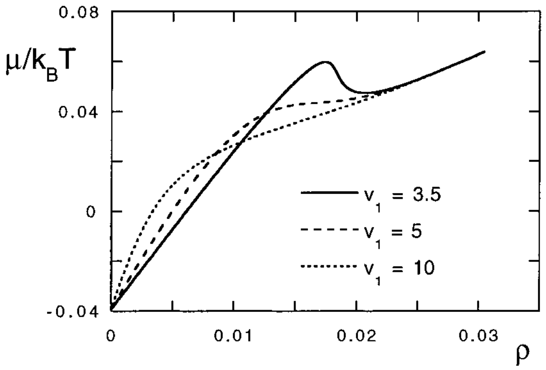

Figure 3. Monomer chemical potential $\mu(\rho)$ for three values of v_1, $v_0 = 1$, $v_2 = 3$, and $N_{ad} = 100$.

To describe phase equilibrium in a polymer–surfactant system at fixed chemical potential of the surfactants we have to analyze of the behavior of the free energy f, or that of the equilibrium monomeric chemical potential

$$\frac{\mu(\rho(\theta))}{k_BT} = \frac{\partial f(\rho,\theta)/k_BT}{\partial\rho} \tag{16}$$

as a function of the monomer concentration ρ using eqs 3 and 13. These equations contain four parameters, namely v_0, v_1, v_2, and θ_b, which depend on the temperature, on the ionic strength of the solution (except v_0), and on the surfactant concentration. In our subsequent analysis, we chose θ_b, v_1, and v_0 as three "independently tuned" (by variation of the surfactant concentration, ionic strength of the solution and temperature, respectively) parameters. The bulk degree of loading θ_b is varied in the range from 0 to 1, although when θ_b approaches the limiting value of 1, it is necessary to go beyond the mean-field model in order to describe interactions between neighboring micelles. The second virial coefficient of bare monomers, v_0, is varied from $v_0 = 1$ corresponding to the athermal solvent conditions up to the value $v_0 = -1$, which corresponds to limiting poor solvent conditions. (We remind the reader that the second virial coefficients are normalized by the third power of the monomer size, which is taken as a unity length in our analysis.) Again, the mean-field approach is not applicable at very high polymer density, i.e., at $v_0 \cong -1$. We return to this point in the discussion. Finally, the renormalized second virial coefficient of micelle–micelle interaction v_1 is chosen larger than unity, that reflects increasing osmotic repulsion upon loading of the chain by micelles.

We start the analysis of the behavior of the chemical potential μ of a monomer as a function of the monomer concentration ρ in the case that water is a good solvent for bare monomers, i.e $v_0 \geq 0$. In Figure 3 the chemical potential of a monomer μ is plotted vs ρ according to eqs 13 and 16 for three values of v_1 at constant v_0, v_2 and θ_b. As mentioned, a decrease in v_1 can be achieved by increasing the ionic strength of the solution. As follows from the figure, for sufficiently large v_1, the chemical potential increases monotonically with increasing concentration in the whole range of ρ. The osmotic interactions are dominated either by monomer–monomer repulsion at large ρ or by micelle–micelle repulsion at small ρ or by their combination in the intermediate region. However, with decreasing v_1, the $\mu(\rho)$ dependence flattens in the intermediate range of concentrations, as the monomer-micelle repulsion (described by the term proportional to v_2 in eq 9) becomes increasingly important. If v_1 is smaller than a certain critical value v_1^{crit}, the chemical potential $\mu(\rho)$ is a nonmonotonic function of ρ in the intermediate range of monomer concentrations. This nonmonotonic behavior of $\mu(\rho)$ indicates phase separation into two coexisting phases, which differ with respect to both the polymer concentration and the degree of loading of the chains by adsorbed micelles. The instability of the one-phase solution and the trend to the phase separation can be also indicated by the nonmonotonic behavior of the chemical potential of the monomer as a function of the degree of loading θ. The latter dependence can be obtained by combining eqs 16 and 13 and may be used equivalently for the analysis of the phase equilibrium in the system. The critical value v_1^{crit} can be obtained from the conditions

$$\frac{\mathrm{d}\mu}{\mathrm{d}\rho} = \frac{\mathrm{d}^2\mu}{\mathrm{d}\rho^2} = 0 \tag{17}$$

Analysis of eq 17 shows that v_1^{crit} is a monotonically increasing function of v_2 and θ_{b}. This implies that the possibility of phase separation is enhanced by increasing the surfactant concentration and the ionic strength of the solution. (We remind the reader that the latter results in weaker repulsion between adsorbed micelles and thus in a smaller value of v_1.)

The polymer concentrations ρ_1 and ρ_2 in the coexisting phases are obtained using the standard Maxwell equal area construction

$$\int_{\rho_1}^{\rho_2} (\mu(\rho) - \mu(\rho_{1,2}))\, \mathrm{d}\rho = 0 \tag{18}$$

while the corresponding degree of loading is found using eq 13. In the critical point, $v_1 = v_1^{\mathrm{crit}}$ we have $\rho_1 = \rho_2$. With decreasing v_1, corresponding with an increasing ionic strength of the solution, the difference in concentrations $\Delta\rho = \rho_2 - \rho_1$ and, correspondingly, the difference in the degrees of loading $\Delta\theta = \theta_1 - \theta_2$, in the coexisting phases increases.

The appearance of the nonmonotonic dependence of $\mu(\rho)$, which indicates the possibility of phase separation, is also evoked by an increase in the concentration of the surfactants (increasing θ_{b}) at constant v_1 and v_2. With decreasing v_1 (increasing ionic strength) the two-phase region, $\rho_1 \leq \rho \leq \rho_2$ in the $(\rho,\theta_{\mathrm{b}})$ plane is extended. Hence, the solution of hydrophilic polymers can be driven toward phase separation into two semidilute phases by an increase in the surfactant concentration and/or an increase in the ionic strength of the solution.

We focus now on the case of poor solvent conditions for bare polymers, $v_0 \leq 0$, when the short-range attraction between monomers dominates over the steric repulsion. In a surfactant-free solution this attraction results in the precipitation of polymers and formation of a dense (collapsed) phase coexisting with a dilute one. The dilute phase contains individual collapsed globules. The concentration of the globules in the dilute phase decreases exponentially with N and vanishes for infinitely long $N \to \infty$, chains.[26,27] The coexistence of a concentrated and dilute phase is reflected in the shape of the chemical potential $\mu(\rho)$, which exhibits a single minimum in the range $\rho > 0$. The equilibrium density in the collapsed phase ρ_{glob} is determined by the balance between attractive binary and repulsive ternary interactions between monomers. It can be determined using the same Maxwell construction, eq 18 with $\rho_1 = 0$, or by applying the condition of vanishing osmotic pressure in the collapsed phase

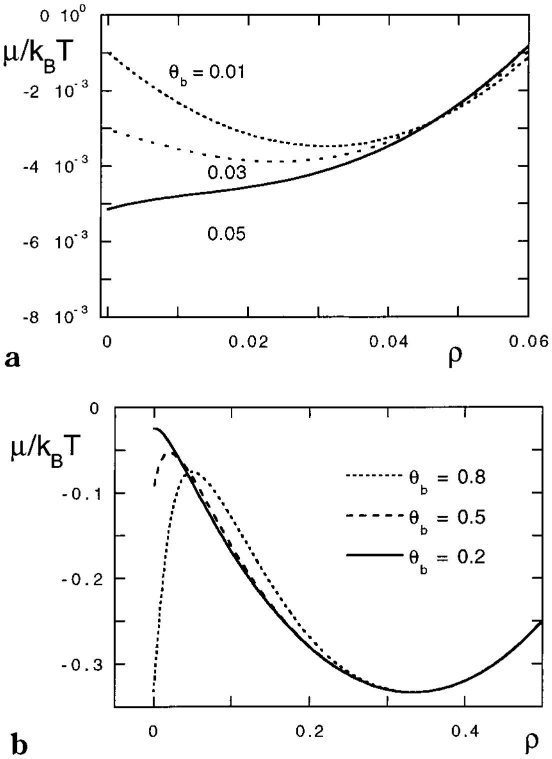

Figure 4. Monomer chemical potential $\mu(\rho)$ for (a) three values of θ_{b}, $v_0 = -0.1$, $v_1 = 10$, $N_{\mathrm{ad}} = 10$, $v_2 = 1$, and $w = 1$ and (b) $v_0 = -1$.

$$\frac{\partial}{\partial\rho}\frac{f(\rho,\theta)}{\rho} = 0 \tag{19}$$

which leads to $\rho_{\mathrm{glob}} = -v_0/2w$. Hence, with decreasing T the density of the collapsed phase progressively decreases and smoothly vanishes in the Θ-point, as $v_0 \sim (\Theta - T)/T$. As T approaches Θ, the minimum in the $\mu(\rho)$ curve progressively becomes more shallow and eventually disappears at $T = \Theta$; at $T \leq \Theta$ (good solvent conditions), the chemical potential is a monotonically increasing function of ρ.

As we shall demonstrate below, even under poor solvent conditions, $v_0 \leq 0$, the collapsed polymers can be resolubilized; i.e., the solution is driven to the one-phase regime by addition of surfactants. The evolution of the shape of $\mu(\rho)$ curves with increasing surfactant concentration (increasing θ_{b}) in the vicinity of the Θ-point, $v_0 \leq 0$, is illustrated in Figure 4a. In this case the density of the collapsed phase is comparatively low even in the absence of surfactants. The degree of loading in the dilute, $\rho = 0$, phase is equal to θ_{b} and, therefore, the chemical potential of the dilute phase

$$\mu(0) \equiv \mu(\rho = 0) = \ln\left(\frac{N_{\mathrm{ad}}(1 - \theta_{\mathrm{b}})}{N_{\mathrm{ad}}(1 - \theta_{\mathrm{b}}) + \theta_{\mathrm{b}}}\right) \tag{20}$$

monotonically decreases with increasing θ_{b}.

The density and the degree of loading in the collapsed phase can be found by either applying the Maxwell construction to $\mu(\rho)$, or, equivalently, by applying eq 19. This leads to

$$\rho_{\mathrm{glob}} = -v(\theta)/2w \tag{21}$$

In combination with eq 13, a closed equation is found for the degree of loading in the collapsed phase for a given set of $(v_0, v_1, v_2, \theta_b)$

$$\frac{k_B v(\theta) v'(\theta)}{2w} = s'(\theta_b) - s'(\theta) \qquad (22)$$

With increasing θ_b, the degree of loading θ of the chains in the collapsed phase progressively increases, approaching θ_b that leads to an increasing effective second virial coefficient $v(\theta)$. As a result, the density of the collapsed phase decreases according to eq 21. The position of the minimum in the $\mu(\rho)$ curve is displaced toward $\rho = 0$ with increasing θ_b, while its depth progressively decreases. The minimum disappears continuously in the *apparent* Θ-point, $\theta_b = \theta^*$, where θ^* is defined by the condition $v(\theta^*) = 0$, i.e.

$$\theta^* = [v_0 - v_2 + \sqrt{v_2^2 - v_0 v_1}]/(v_0 + v_1 - 2v_2) \qquad (23)$$

Simultaneously, the degree of loading in the collapsed phase becomes equal to θ_b. For $\theta_b \geq \theta^*$, μ is a monotonically increasing function of ρ. Hence, close to the Θ-temperature, the Θ-transition induced by increasing surfactant concentration occurs similarly to the conventional Θ-transition induced by increasing temperature in a "bare" polymer solution.

The situation is markedly different when the solvent is sufficiently poor, i.e., far from the Θ-point for the bare polymer, Figure 4b. In this case the density of the collapsed polymer phase is sufficiently high. The shape of $\mu(\rho)$ curves at small θ_b (low surfactant concentration) is qualitatively the same as in the surfactant-free solution; i.e., only one minimum corresponding to the collapsed phase is present. The shape and position of this minimum (i.e., the density of the collapsed phase) are roughly determined by the balance between binary attraction and ternary repulsion of bare monomers and are relatively insensitive to the variation of surfactant concentration. This implies that the degree of loading in the collapsed phase is small.

An increase in θ_b affects mostly the shape of $\mu(\rho)$ in the range of small polymer concentrations (where the degree of loading is close to θ_b). The initial slope of $\mu(\rho)$ curve is determined by the value of $v(\theta_b)$ and is negative at $\theta_b \leq \theta^*$ and positive at $\theta_b \geq \theta^*$ and vanishes in the apparent Θ-point.

Therefore, at $\theta_b \geq \theta^*$ in addition to the "globular" minimum in the $\mu(\rho)$ curves another edge minimum at $\rho = 0$ appears, together with a maximum that separates both minima. The density $\rho_{\max}$ of this maximum shifts toward larger ρ with increasing θ_b, as seen in Figure 4b. Simultaneously, the equilibrium concentration of the dense phase decreases weakly. This reflects a progressive but weak increase in the degree of loading in the dense phase with increasing surfactant concentration (see eq 13).

We now define $\bar{\theta} \geq \theta^*$ such that at $\theta_b \geq \bar{\theta}^*$ we have $\mu(0) \leq \mu(\rho_{\text{glob}})$, where ρ_{glob} is the density of the collapsed phase. This density is found as $\rho_{\text{glob}} = -v(\underline{\theta})/2w$ where θ is determined by eq 22. Hence, at $\theta_b \leq \bar{\theta}$ the dense (collapsed) phase coexists with a dilute one, while for $\theta_b > \bar{\theta}$ the highly loaded dilute phase is thermodynamically more favorable than the collapsed one. Thus, for $\theta_b \leq \bar{\theta}$ the polymer solution with amphiphiles resembles a pure polymer solution below the Θ-point, whereas for $\theta_b > \bar{\theta}$ the coexistence of a collapsed (virtually unloaded) and a *semidilute* (loaded) phase may be expected, which is similar to the $v_0 \geq 0$ case discussed above.

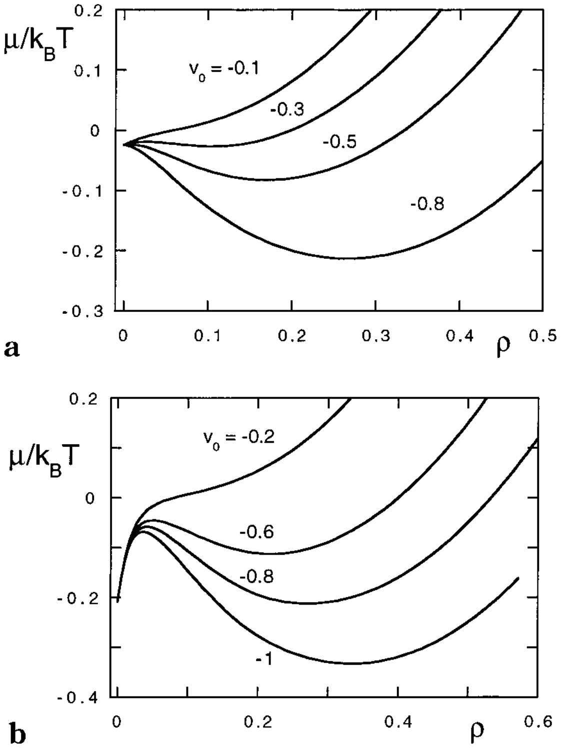

Figure 5. Monomer chemical potential $\mu(\rho)$ for several values of v_0 for (a) $\theta_b = 0.2$, $v_1 = 10$, $N_{\text{ad}} = 10$, $v_2 = 1$, and $w = 1$ and (b) $v_1 = 2$, $\theta_b = 0.7$.

It is also instructive to analyze the shape of the $\mu(\rho)$ curves at constant θ_b, but variable solvent strength v_0. Obviously, an increase in the solvent strength affects the position and the depth of the minimum in the $\mu(\rho)$ curves corresponding to the collapsed phase and the initial slope, $(d\mu/d\rho)_{\rho=0} = 2v(\theta_b)$, while the value of chemical potential in the dilute phase, $\mu(0)$, remains unaffected.

At low surfactant concentration (and high ionic strength of the solution, i.e., small v_1) $(d\mu/d\rho)_{\rho=0} \leq 0$, and the $\mu(\rho)$ curves exhibit only one minimum, when the solvent is sufficiently poor, Figure 5a. With increasing v_0 the initial slope $(d\mu/d\rho)_{\rho=0}$ gradually increases, while the depth of the minimum progressively decreases and its position gets displaced to smaller ρ. Therefore, the evolution of the $\mu(\rho)$ curves with increasing v_0 is similar to that in the surfactant-free case. The minimum in the $\mu(\rho)$ curve disappears when v_0 reaches a certain value, which is still above the Θ-temperature (i.e. at $v_0 < 0$) for the bare polymer. Hence, the presence of small amount of surfactant simply shifts the Θ-point to the poorer solvent conditions, while the character of the Θ-transition induced by the variation of temperature remains the same as in the surfactant-free polymer solution. This shift becomes more pronounced with increasing surfactant concentration or/and decreasing ionic strength.

On the contrary, if v_1 and θ_b are sufficiently large (i.e., at low ionic strength of the solution and high surfactant concentration) then the initial slope of the $\mu(\rho)$ curve is positive, $(d\mu/d\rho)_{\rho=0} \geq 0$, even under very poor solvent conditions. As a result, the $\mu(\rho)$ curve exhibits a deep minimum corresponding to the dense (collapsed) phase and another comparatively shallow edge minimum at $\rho = 0$, as shown in Figure 5b. This situation corresponds

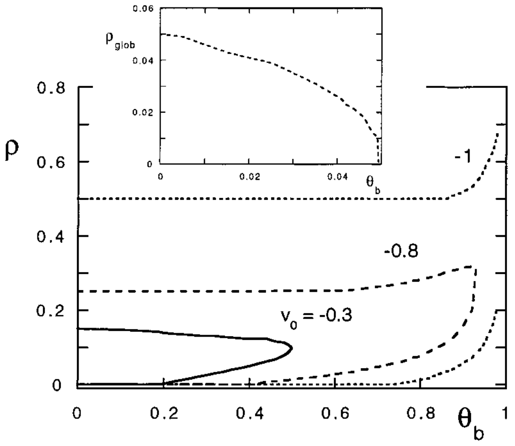

Figure 6. Monomer densities ρ in coexisting phases as a function of θ_b for four values of v_0. In the inset $v_0 = -0.1$ and $v_1 = 3$ is shown, in the figure $v_0 = -0.3, -0.5$ and -1, $v_1 = 5$, and other parameters are those of Figure 5a,b.

to the coexistence of a dilute and dense or that of two semiphases in the solution, depending on the solvent strength. Remarkably, with increasing solvent strength, the minimum corresponding to the collapsed phase disappears and the solution is brought into the one-phase regime above the Θ-temperature for the bare polymer.

In Figure 6, the phase diagram for the polymer solution below the Θ-point in the (θ_b,ρ) plane is shown; i.e., the dependence of the densities of coexisting phases on θ_b are presented for four different values of v_0. As follows from Figure 6, the phase diagrams may have very different shapes, depending on the deviation from the Θ-point measured by v_0.

In the vicinity of the Θ-temperature ($v_0^{\rm tr} < v_0 < 0$, where the value of $v_0^{\rm tr}$ will be specified below) only the coexistence of a dilute and collapsed phases is possible. As discussed above, the density of the collapsed phase smoothly vanishes at $\theta_b = \theta^*$. This is shown in the inset of Figure 6. In contrast, far from the Θ-temperature (below $v_0^{\rm tr}$) the collapsed phase coexists with a dilute one for $\theta_b \le \bar{\theta}$, while for $\theta_b > \bar{\theta}$ coexistence between two semidilute phases occurs. Remarkably, the particular shape of the phase diagram in the range $\theta_b > \bar{\theta}$ depends on the solvent strength.

If v_0 is only slightly below $v_0^{\rm tr}$, then the density of the collapsed phase *decreases* with increasing θ_b, while the density of the coexisting loaded phase simultaneously *increases*. As a result, the boundaries of the two-phase region merge at $\theta_b = \theta_b^{\rm crit}$, which is a critical point of the phase diagram. At $\theta_b \ge \theta_b^{\rm crit}$, the solution is homogeneous in the whole range of the polymer concentrations. At smaller v_0 (e.g., $v_0 = -0.5$), the phase diagram still exhibits a critical point, $\theta_b^{\rm crit}$, but in contrast to the previous case, the densities of both coexisting semidilute phases *increase* with increasing θ_b in the range $\bar{\theta}_b \le \theta_b \le \theta_b^{\rm crit}$.

At very low solvent strength ($v_0 \cong -1$, that corresponds to limiting high polymer density in the collapsed phase), the two-phase region occupies the whole range of θ_b without a critical point. Below $\bar{\theta}_b$ (coexistence between dense and dilute phases) the density in the dense phase is weakly *decreasing* function of θ_b while above $\bar{\theta}$ (coexistence of two semidilute phases) it is an *increasing* function of θ_b. This entails that, provided the polymer density in solution is high enough, the two-phase region corresponding to separation into a bare, collapsed phase and a relatively loaded, semidilute phase is present in the diagram for arbitrary high surfactant concentration.

3. The Coil-to-Globule Transition

3.1. Volume Approximation. The arguments presented in the previous section concern the coexistence of collapsed and dilute phases in a solution of polymers associating with amphiphiles in a poor solvent. These arguments can also be applied for the analysis of the collapse-swelling transition induced by the variation of external parameters (solvent strength, concentration of surfactants or ionic strength of the solution) in an individual long polymer chain, that is, $N \to \infty$. This is known as the "volume approximation" in the theory of the coil–globule transitions.[35] In this approximation, only the leading terms in the free energy of a collapsed globule are retained, i.e., terms $\sim N$, while lower order terms in N are neglected. Such terms are, for instance, the conformational entropy of the chain or the excess free energy of the globule/solvent interface. The collapsed (globular) state of the polymer chain is characterized by the finite density $\rho_{\rm glob} = -v/2w$, which is determined by the local balance of binary attraction and ternary repulsion between monomers and is independent of N. In contrast, a polymer coil in a good solvent is characterized by strong density fluctuations on the scale of the coil as a whole, and the average density in the coil vanishes as $N \to \infty$. Therefore, in the framework of the volume approximation, the coil conformation is associated with an infinitely dilute phase ($\rho = 0$), corresponding to zero osmotic pressure.

As follows from our previous discussion, the transition from a collapsed to a swollen conformation of individual chains in a dilute solution can be induced by (i) increasing the concentration of surfactants, i.e. increasing θ_b; (ii) decreasing the ionic strength of the solution, i.e., increasing v_1; and (iii) increasing the solvent strength, i.e., increasing v_0. All these variations enhance intrachain repulsive interactions. Analysis of the $\mu(\rho)$ curves enables to localize the position of the collapse-swelling transition and to determine its character.

With increasing θ_b (at fixed v_1 and v_0), the chemical potential of the monomer in the dilute phase, $\rho = 0$, corresponding to the coiled conformation, decreases (see eq 20), while that in the collapsed phase is virtually unaffected by θ_b. This trend reflects the increasing favorability of the dilute and highly loaded state with respect to the dense and unloaded. The transition from a collapsed to a swollen conformation occurs when $\mu(0) = \mu(\rho_{\rm glob})$. This transition may occur either as a continuous second-order phase transition at $\theta_b = \theta^*$, similar to the conventional Θ-transition in polymers, or with a finite jump in the concentration between the collapsed and swollen phase at $\theta_b = \bar{\theta}$. In the latter case, the swelling transition acquires the character of the first-order phase transition. Experimentally, this should correspond to the coexistence of collapsed and swollen coils in solution within a narrow range of θ_b. Whether the transition is continuous or discontinuous is determined by the difference between the collapsed (unloaded) and swollen (loaded) state of the chain in the apparent Θ-point.

In Figure 7, the phase diagram for the infinitely long polymer chain is plotted in the (θ_b, v_0)-plane for two

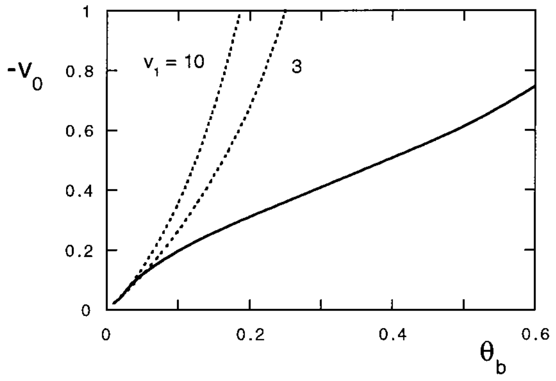

Figure 7. θ^* (dotted line) and $\bar{\theta}$ (solid line) as a function of v_0 for two different values of v_1 (indicated in the graph).

values of v_1. The solid lines denote $\bar{\theta}$ as a function of v_0, and the dashed lines correspond to θ^* (we remind the reader that θ^* corresponds to the apparent Θ-point, i.e., $v(\theta^*) = 0$, while $\theta_b = \bar{\theta}$ corresponds to the surfactant concentration in the bulk at which $\mu(0) = \mu_{\rm glob}$).

At large $-v_0$ and v_1 we find $\bar{\theta} > \theta^*$. As v_0 increases, the difference in $\bar{\theta}$ and θ^* decreases and eventually vanishes at $v_0 = v_0^{\rm tr}$, when the lines $\bar{\theta}(v_0)$ and $\theta^*(v_0)$ cross each other. This entails that, with increasing θ_b, the swelling transition occurs abruptly as a first-order phase transition at $\theta_b = \bar{\theta}$, if $v_0 < v_0^{\rm tr}$, or continuously as a second-order phase transition at $\theta_b = \theta^*$, if $v_0 \geq v_0^{\rm tr}$. Hence, $(v_0^{\rm tr},\theta_b^{\rm tr})$ defined by the condition $\theta_b = \theta^*(v_0) = \bar{\theta}(v_0)$ is the tricritical point in which the line of the first-order phase transitions crosses the line of the second-order phase transitions.

Similarly, a variation of temperature at given surfactant concentration results either in continuous (if $\theta_b \leq \theta_b^{\rm tr}$) or abrupt (if $\theta_b \geq \theta_b^{\rm tr}$) coil-to-globule transition in a polymer chain. It is seen in Figure 7 that the tricritical point $(v_0^{\rm tr},\theta_b^{\rm tr})$ is shifted to slightly higher values of v_0 (to lower temperatures) and smaller bulk degree of loading θ_b (smaller surfactant concentration) with increasing v_1. Thus, for temperatures close to the Θ-temperature our model predicts the coil−globule transition induced by the variation of surfactant concentration to be continuous at high ionic strengths and abrupt at low.

3.2. Finite Size Effects: Conformations of Individual Chains. The volume approximation is exact for description of the coil−globule transition of infinitely long chains ($N \to \infty$). However, for the analysis of conformational transitions induced by variation of the solvent strength or concentration of amphiphiles in an individual chain of finite length we can extend our approach utilized in refs 7 and 22 for the good solvent case to poor solvent conditions. This approach is based on the standard Flory-type arguments, and has been applied for the description of the collapse-swelling transition in polymer chains by several authors.[36,37] According to this approach, the free energy of a polymer−micelle complex can be presented as

$$F = F_{\rm osm} + F_{\rm el} + F_{\rm ad} \qquad (24)$$

and comprises three contributions, namely intramolecular osmotic interactions, the conformational entropy of the coil as a whole, and both enthalpic and entropic contributions from polymer−micelle binding, respectively.

The osmotic contribution to the free energy of a chain can be obtained by integration of $f_{\rm osm}(\rho,\theta)$ given by eq 8 over the volume occupied by the chain, and reads

$$F_{\rm osm}/k_BT = N\rho v(\theta) + N\rho^2 w \qquad (25)$$

where $\rho \cong N/R^3$ is the average density of monomers inside the coil and R is its characteristic dimension (the gyration radius).

The second contribution to the free energy in eq 24 is the conformational entropy of a swollen or collapsed chain as a whole. We estimate this entropy in a Gaussian approximation. If $m = \theta N_{\rm ad}/N$ micelles are complexed with the polymer, the unperturbed Gaussian dimension of the "mixed" chain, consisting of $N(1 - \theta)$ bare monomers and m micelles of size $R_{\rm m}$, can be written as

$$R_G^{\ 2} = N(1 - \theta) + m(2R_{\rm m})^2 = N(1 + \beta\theta) \qquad (26)$$

A correction parameter $\beta \equiv 4R_{\rm m}^{\ 2} N_{\rm ad}^{\ -1} - 1$ is introduced, that renormalizes the Gaussian chain dimensions for micelle adsorption and accounts for the wrapping of the chain around bound micelles.

Both swelling and collapse of the complexed chains with respect to its Gaussian size R_G, given by eq 26, are entropically unfavorable. It is convenient to define an expansion parameter $\alpha \equiv R/R_G$, where R is the radius of gyration of the complexed chain. Then, following refs 37 and 38 we can present the conformational entropy penalty for swelling ($\alpha \geq 1$) and for collapse ($\alpha \leq 1$) as

$$F_{\rm el}/k_BT = \begin{bmatrix} \alpha^2 - \log(\alpha^2) & \alpha \geq 1 \\ \alpha^{-2} - \log(\alpha^2) & \alpha \leq 1 \end{bmatrix} \qquad (27)$$

Note that both the elastic free energy, given by eq 27, and its derivative $\partial F_{\rm el}/\partial\alpha$, which determines the restoring force in a deformed coil, vanish at $\alpha = 1$. Thus, eq 27 describes the conformational free energy of a chain as a continuous and smooth function of $\alpha = R/R_G$ in the whole range of deformation, i.e., $\alpha \leq,\geq 1$.

The translational entropy of the bound micelles along the chain together with the complexation energy per chain are given by

$$F_{\rm ad}/k_BT = N\theta u - Ns(\theta)/k_B \qquad (28)$$

where $s(\theta)$ is defined by eq 4. We again remind the reader that the above expression for the "mixing" entropy is valid only for sufficiently long chains, $NN_{\rm ad}^{\ -1} \gg 1$.

The equilibrium degree of loading of the chain by adsorbed micelles and the equilibrium chain dimension are found by minimizing of the total free energy F with respect to the coil size and the number of adsorbed micelles

$$\frac{\partial F}{\partial R} = 0, \text{ and } \frac{\partial F}{\partial \theta} = 0 \qquad (29)$$

at constant temperature (solvent quality) and chemical potential of the surfactants. The first equilibrium condition, expressed in terms of α, yields

$$\frac{3}{2}N^{1/2}v(\theta)(1 + \beta\theta)^{-3/2} + 3w\alpha^{-3}(1 + \beta\theta)^{-3} = \begin{Bmatrix} \alpha^5 - \alpha^3 \\ \alpha^3 - \alpha \end{Bmatrix} \qquad (30)$$

where the upper expression refers to swollen chains α

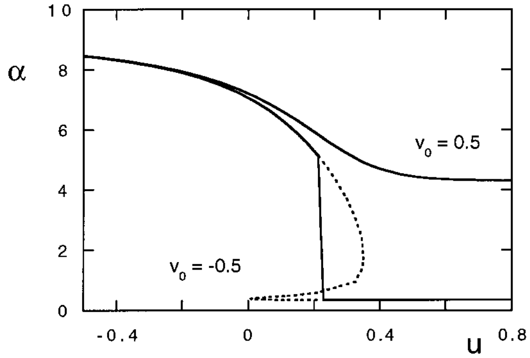

Figure 8. α as a function of u for $v_0 = 0.5$ (solid line) and $v_0 = -0.5$, $v_1 = 5$, $\beta = 0$, $N_{ad} = 5$, and $N = 10000$. The van der Waals loop is indicated by a dashed line.

≥ 1, whereas the lower expression refers to collapsed chains $\alpha \le 1$, respectively. We remark that eq 30 is similar to the equation for the swelling coefficient of the polymer chain in the usual theory of the coil−globule transition[37] and reduces to it if $v(\theta) = \text{constant}(\theta)$ and $\beta = 0$. The second condition in eq 29 gives

$$\frac{N^{1/2}v'(\theta)}{\alpha^3(1+\beta\theta)^{3/2}} + \frac{w'(\theta)}{\alpha^6(1+\beta\theta)^3} + N[s'(\theta_b) - s'(\theta)] - \frac{\beta}{1+\beta\theta}\begin{Bmatrix}\alpha^2 - 1\\ 1 - \alpha^2\end{Bmatrix} = 0 \tag{31}$$

where again the upper and the lower expressions are valid for swollen chains ($\alpha \ge 1$) and collapsed chains ($\alpha \le 1$), respectively. We remark, however, that for long, swollen chains ($\alpha \gg 1$), the term $\sim N$ in eq 31 is the dominant one, and the above condition reduces to $\theta = \theta_b$ with a Langmuir-like dependence of loading on u (see Figure 2). In this regime the loading does not depend on excluded-volume interactions.

We start with the examination of the dimension (the gyration radius) of a long chain, $N = 10^4$, as a function of the surfactant concentration. In Figure 8 the swelling ratio $\alpha = R/R_G$ is plotted as a function of $u \sim \ln(X_{CAC}/X)$ for $\beta = 0$ both for good ($v_0 = 0.5$) and poor ($v_0 = -0.5$) solvent conditions. In the latter case, v_0 is chosen smaller than its value in the tricritical point for the corresponding set of v_1, v_2. In the good solvent case, the renormalized micelle−micelle excluded-volume parameter is chosen larger than the monomer−monomer, $v_1 > v_0$, so that the size of the loaded chain is larger than that of the bare coil. In a good solvent the coil swells continuously with increasing surfactant concentration, whereas in a bad solvent a jump from a collapsed globule to a swollen coil conformation is observed. The value of θ_b at which this jump occurs is found by equating the total free energy of a collapsed globule with that of a swollen coil. The van der Waals loop in Figure 8 for $v_0 = -0.5$ is shown as a dashed line; the equilibrium conformation is shown with a solid one. The degree of loading of the chain by micelles increases continuously with increasing surfactant concentration under good solvent conditions but exhibits a jump in a poor solvent. This jump in θ corresponds obviously to the discontinuity in the α vs u curve presented in Figure 8. At high concentration of surfactants, the degree of loading in good and bad solvents merge. This agrees with the above-mentioned result that in the case of swollen coils θ does not depend on the strength of the excluded-volume interactions.

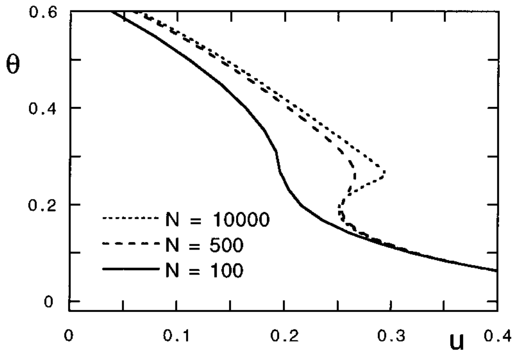

Figure 9. θ as a function of u for $N = 100$, 500, and 10000, $v_0 = -0.35$, $v_1 = 3$, $v_2 = 0$, and $N_{ad} = 10$.

We thus find that the conformational changes occurring in a chain of considerable length upon complexation can be interpreted on the basis of the results obtained in section 3.1 for infinitely long chains. However, in section 3.1 the contribution of the conformational entropy of the chain, eq 27, which, in contrast to other terms in the free energy, scales sublinearly to N, is completely neglected. It is therefore interesting to examine how this entropy affects the character of the collapse-swelling transition in a complexed chain under poor solvent conditions for finite N. In Figure 9 the degree of loading θ is plotted as a function of u at $v_0 < v_0^{tr}$ for three values of N (we keep in mind that $NN_{ad}^{-1} \gg 1$). It is seen that the transition from a collapsed globule to a swollen coil is continuous for the shortest chain whereas it is discontinuous for the longer chains. Moreover, the magnitude of the van der Waals loop increases with increasing N and the $\theta(u)$ dependence approaches that of the infinitely long chain. The reason for smoothening of the collapse-swelling transition in short chains with respect to that in long ones is of course the conformational entropy penalty both the collapsed and swollen state, below and above the transition point, respectively. With increasing chain length the relative contribution of the conformational entropy to the overall free energy gets less and less important. As a result the collapse-swelling transition becomes sharper and gets displaced to higher temperature (or, equivalently, to lower surfactant concentration).

We can thus conclude that the results obtained in frame of the Flory-type model approach those of the volume approximation for large values of N, but can differ in the case of short chains. This dependence of the character of the globule−coil transition on the chain length should also be observed experimentally.

Figure 10, finally, illustrates the effect of local conformational restrictions imposed by the wrapping of the chain segments of length N_{ad} around the micelles on the dimensions of the chain as a function of the surfactant concentration (via θ_b). As one can see from the figure, a decrease in β corresponding-to-increasing ratio N_{ad}/R_m^2 leads to progressive decrease in the size of the swollen coil. The effect gets stronger with increasing degree of loading. In contrast, the dimensions of the chain in the collapsed (globular) state as well as the position of the globule-to-coil transition are virtually unaffected by the variation of β because of the very low degree of loading of the chain in the collapsed state. Remarkably, for small values of β (large number of monomers in a sequence wrapped onto a micelle) an increase in the surfactant concentration and corresponding increase in the degree of loading results in nonmonotonic variation

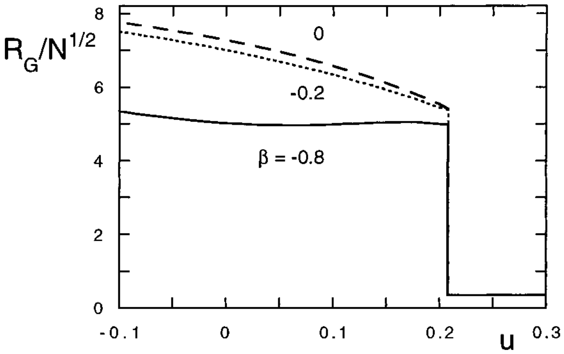

Figure 10. $R_G/N^{1/2}$ as a function of u for $\beta = 0$, -0.2 and -0.8, $N = 10000$, $v_0 = -0.5$, $v_1 = 5$, $v_1 = 0$, and $N_{ad} = 10$.

of the coil size (which decreases at large θ_b due to immobilization of a large number of monomers in adsorbed sequences).

4. Discussion and Conclusions

We have presented a mean-field model for a polymer solution with annealed excluded-volume interactions that can be used to mimic the behavior of a solution of polymers complexed with surfactants. The osmotic interactions between complexed monomers differ from those of bare monomers due to adsorption of the surfactant aggregates. As the degree of complexation is an annealed degree of freedom and is coupled to the polymer conformation via local polymer density, our approach leads to phase behavior quite different from that of the conventional homopolymer solution.

Depending on the quality of the solvent for the bare polymer, i.e., depending on its hydrophilic or hydrophobic nature, we have predicted different types of phase separation to occur in the polymer solution mixed with surfactants. If the polymer is hydrophilic, then the solution is either homogeneous in the whole range of polymer concentrations at low ionic strength and low surfactant concentration, or may phase separate into two semidilute phases at high ionic strength and high surfactant concentration. This behavior is reminiscent of the phase separation in the solution of polymers capable to formation of stable clusters of $n \geq 3$ monomers considered by de Gennes.[39] Remarkably our model predicts coexistence of two semidilute polymer phases even when all interaction between monomers are repulsive.

If, in contrast, the polymer is hydrophobic, the phase behavior of the polymer/surfactant solution is greatly enriched. Depending on the solvent strength (degree of hydrophobicity of the polymer), ionic strength of the solution, overall monomer density and concentration of surfactants we expect stability or instability of the homogeneous solution with respect to separation into coexisting dilute and semidilute or two semidilute phases. The Θ-transition in the solution can be induced by the variation of (i) the solvent strength, (ii) surfactant concentration, or (iii) ionic strength of the solution and may occur continuously or discontinuously. In the former case the concentrations of coexisting dilute and semidilute phases are equal to each other in the apparent Θ-point, while in the latter case the concentration of the semidilute (collapsed) phase remains finite in the renormalized Θ-point.

On the level of an individual chain, the conformational transition from a collapsed (bare) to swollen (loaded) conformation may occur either continuously, as a second-order phase transition, or discontinuously, as a first-order phase transition, with a finite jump in the chain dimensions and in the degree of loading. If the globule–coil transition is induced by an increase in surfactant concentration at low ionic strength of the solution, a discontinuous transition occurs sufficiently far below the Θ-point of the bare polymer. If the transition is initiated by the variation of the solvent strength, then an abrupt transition occurs when the surfactant concentration is high while a continuous transition takes place when the surfactant concentration is low.

We remark that similar conclusions concerning a change of character of the Θ-transition in a polymer with annealed excluded-volume interactions have been made earlier by Berikanov et al.[40] and Jeppesen and Kremer[41] in the context of conformational transitions in PEO. In ref 41, Monte Carlo simulations were performed using a model quite equivalent to that used in our analytical calculations and the jump-wise variation of the chain dimension with the solvent strength was demonstrated. In general, the presence of an annealed degree of freedom in a system capable to undergo a second-order phase transition always makes the transition more abrupt. As a classical example of the similar effect the magnetic transition in compressible Ising model can be recalled.[42]

It is challenging to relate our theoretical predictions to experimental results of Wu et al.[43] and Lee and Cabane[44] for mixtures of PNIPAM with SDS. At temperatures above the LCST (the lower critical solution temperature) of PNIPAM and at intermediate surfactant concentrations two populations of polymers, collapsed (unloaded) and swollen (polymers highly loaded with complexed SDS-micelles) were observed. Clearly, this coexistence results from a competition between the gain in free energy of the chain resulting from collapse (minimizing unfavorable monomer–water contacts) and the gain resulting from the adsorption of micellar aggregates. As two different conformational states may correspond to equally deep local minima in the free energy of the chain at a certain surfactant concentration, a first-order phase transition between these conformations and their subsequent coexistence in solution may be expected.

The same type of arguments can be used for the interpretation of experiments for mixtures of globular proteins with surfactants. It is known that anionic surfactants, such as SDS, denature several common proteins. The stability of a globular conformation of a protein molecule is determined by hydrophobic attractions between monomers; i.e., water is a poor solvent for a certain fraction of (hydrophobic) amino acids that form the interior of the protein globule. Binding of surfactants to the hydrophobic sequences enhances their solubility and thus triggers an abrupt unfolding of the protein globule. However, we have to keep in mind that under experimentally relevant conditions the local polymer concentration in the collapsed polymer (PNIPAM) or protein globules is far above the limit of applicability of our mean-field approach.

At this point, we have to draw the attention of the reader once again to the mean-field character of our model. Only if the number of adsorbed micelles per correlation volume is sufficiently large may it formally be applied; i.e., in this case the excluded-volume parameter can be averaged over loaded and unloaded monomers with respective statistical weights. This condition in turn imposes limitations for the local polymer densities which can be treated by our approach. The limitation becomes especially important in the range of poor solvent conditions, when the local polymer density $\rho \sim |v_0|^{-1}$ may be rather high and the correlation volume $\sim |v_0|^3$ correspondingly small. Therefore, in a formal sense our model is applicable only to polymer solutions in the vicinity of the Θ-point and not to solutions far below the Θ-point. The insights gained from our model, however, may contribute to understanding the phase behavior of the latter solutions.

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Glossary

$f(\rho,\theta)$	free energy density as a function of ρ and θ
m	number of micelles complexed with a chain
N_{ad}	number of monomers complexed with a micelle
R	radius of gyration of a complexed chain,
R_{G}	Gaussian radius of gyration for a complexed chain, eq 26
R_{m}	radius of a bound micelle
$s(\theta)$	mixing entropy in a complexed chain per monomer, eq 4
$s'(\theta)$	derivative of $s(\theta)$ with respect to θ
$v(\theta)$	effective virial coefficient, eq 9
$v'(\theta)$	derivative of $v(\theta)$ with respect to θ
v_0	second virial coefficient of bare monomers,
v_1	renormalized second virial coefficient of complexed micelles
v_2	the same for a bare monomer and a complexed micelle
v_0^{tr}	value v_0 in the tricritical point
v_1^{crit}	critical value of v_1 below which $\mu(\rho)$ is nonmonotonic
u	the "complexation" free energy per monomer
w	third virial coefficient of interaction of bare monomers
α	expansion parameter, defined as R/R_{G}
β	renormalization constant for elasticity, eq 26
θ	fraction of complexed monomers (degree of loading)
θ_{b}	degree of loading in dilute bulk phase
θ^*	"apparent" Θ-point, eq 23
$\bar{\theta}$	the value of θ_{b} at which the chemical potential of a monomer in the collapsed phase $= \mu(0)$
$\theta_{\mathrm{b}}^{\mathrm{tr}}$	value of θ_{b} in the tricritical point
Θ	Θ-temperature, at which $v_0 = 0$
μ	monomeric chemical potential
$\mu(0)$	chemical potential in dilute phase
ρ	monomer density
ρ_{glob}	monomer density in collapsed phase

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