

Self-Assembly in Mixtures of Polymers and Small Associating Molecules

Haim Diamant[†] and David Andelman**School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel**Received June 25, 1999; Revised Manuscript Received June 19, 2000*

ABSTRACT: The interaction between a flexible polymer in a good solvent and smaller associating solute molecules such as amphiphiles (surfactants) is considered theoretically. Attractive correlations, induced in the polymer because of the interaction, compete with intrachain repulsion and eventually drive a joint self-assembly of the two species, accompanied by partial collapse of the chain. Results of the analysis are found to be in good agreement with experiments on the onset of self-assembly in diverse polymer–surfactant systems. The threshold concentration for self-assembly in the mixed system (critical aggregation concentration, cac) is always lower than the one in the polymer-free solution (critical micelle concentration, cmc). Several self-assembly regimes are distinguished, depending on the effective interaction between the two species. For strong interaction, corresponding experimentally to oppositely charged species, the cac is much lower than the cmc. It increases with ionic strength and depends only weakly on polymer charge. For weak interaction, the cac is lower but comparable to the cmc, and the two are roughly proportional over a wide range of cmc values. Association of small molecules with amphiphilic polymers exhibiting intrachain aggregation (polysoaps) is gradual, having no sharp onset.

I. Introduction

Aqueous solutions containing polymers and smaller solute molecules are common in biological systems and industrial applications. In many cases, the small molecules are amphiphilic (surfactants) and may self-assemble with the polymer chains into joint aggregates. Such systems, synthetic as well as biological, have been the subject of extensive research in the past few decades.^{1,2} The possibility to achieve polymer–surfactant aggregation using very low surfactant concentration offers a delicate control over the properties of the solution, a feature being used in numerous applications.³

The current article presents a theory for the onset of self-assembly in such mixed systems.⁴ The theory considers the various interactions in a very general way, not taking into account microscopic details of the small molecules or the polymer. Indeed, the particular structure of a surfactant may affect the details of its aggregation. Nevertheless, we suggest that the *onset* of joint polymer–surfactant self-assembly is mainly determined by simpler, more general considerations.

Self-assembly of polymer–surfactant complexes usually starts at a well-defined surfactant concentration, the “critical aggregation concentration” (cac). One of the most consistent experimental observations in polymer–surfactant systems is that the cac is found to be lower than the “critical micelle concentration” (cmc) of the polymer-free surfactant solution

$$\varphi_{\text{cac}} < \varphi_{\text{cmc}}$$

Consequently, polymer–surfactant systems are commonly divided into two categories: (i) systems whose cac is much lower than the cmc, $\varphi_{\text{cac}} \ll \varphi_{\text{cmc}}$; (ii) systems where the cac is lower than, but comparable to, the cmc, $\varphi_{\text{cac}} \lesssim \varphi_{\text{cmc}}$. Experimentally, the former case corresponds

to systems containing a polyelectrolyte and an oppositely charged ionic surfactant,⁵ e.g., poly(acrylic acid) (PAA) and dodecyltrimethylammonium bromide (DTAB). The strong electrostatic attraction between the two species can cause the cac in such systems to be several orders of magnitude lower than the cmc. The latter case usually corresponds to systems containing a neutral polymer and an ionic surfactant,⁶ e.g., poly(ethylene oxide) (PEO) and sodium dodecyl sulfate (SDS). Somewhat less common are systems containing a polyelectrolyte and a nonionic surfactant,^{7–9} which can be included in the second category as their cac is comparable to the cmc. Systems where both species are neutral exhibit a very weak effect.^{7,10,11}

The cac is usually interpreted in terms of the strength of interaction, or affinity, between the two species. In analogy to regular micellization,¹² $\log(\varphi_{\text{cac}})$ is related to the free energy of transfer (in units of $k_{\text{B}}T$) of a molecule from the aqueous solution to a joint aggregate. Evidently, the affinity should be much stronger for oppositely charged species (the first category above) than for the other cases, resulting in a very low cac in those systems. The difficulty, however, is to correctly identify the various contributions to this free energy. Apart from the bare interactions among the various molecules, there may be additional contributions from conformational changes of the polymer induced by the joint self-assembly. Therefore, construction of a detailed, reliable molecular model for this complex system is a complicated task.

Several theories have been presented for polymer–surfactant aggregation.¹³ Most of the models¹⁴ attempt to add the polymer as another ingredient to the already-established thermodynamic theory of micellization.¹² These models are usually applied to the case of neutral polymers. The prediction of $\varphi_{\text{cac}} < \varphi_{\text{cmc}}$ does not arise naturally from the models but depends on the choice of parameters. Other models,^{15,16} inspired by the Zimm–Bragg theory of coil–helix transition,¹⁷ treat the bound surfactant as an adsorbed one-dimensional lattice gas. Using two fitting parameters, for the affinity between

* To whom correspondence should be addressed.

[†] Current address: The James Franck Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637, USA.

the two species and for “binding cooperativity”, they account for binding isotherms in polyelectrolyte–oppositely charged surfactant solutions. Additional models for polyelectrolyte–ionic surfactant systems attempt to calculate the interaction between the two species focusing on electrostatics^{18,19} and counterion-condensation effects.^{20,21}

The models mentioned above do not explicitly consider internal features of the polymer chain. This approach may be justified for rigid polymers such as DNA or strong polyelectrolytes at low ionic strength, where electrostatic interactions are not screened. It is somewhat more questionable in view of the strong conformational changes observed in flexible polymers upon self-assembly.^{22–25} In fact, most models use various interaction parameters to fit experimental data, which may implicitly contain conformational effects (e.g., the cooperativity parameter in one-dimensional models, whose physical origin is not specified²⁶).

Two recent works²⁷ have treated the polymer chains in more detail, but in a different context. Both assume that spherical surfactant micelles have already bound to the polymer and try to study the additional effect of the adsorbed chain. In another work²⁸ a detailed molecular thermodynamic theory of polymer–surfactant complexes was presented. This model applies to neutral polymers and contains several molecular parameters.

The present work takes a different approach toward the joint self-assembly of polymers and small solute molecules such as surfactants. Instead of starting from a model of surfactant micellization and trying to add the polymer as a further complication, we rather focus on flexible polymers in solution and study the effect of small associating molecules, treated as impurities, on the chain statistics. Unlike surfactant micelles, a flexible polymer can be treated as a thermodynamic, large system. Hence, if the polymer undergoes a significant change of conformation at the onset of self-assembly, then a simple phenomenological approach might be more successful than in pure surfactant solutions. We thus conjecture that in a mixed system of flexible polymers and small molecules the cac is associated with a local instability (partial collapse) of the polymer chain. The instability occurs when attractive correlations induced by the interaction between the species overcome the intrinsic intrachain repulsion. This description is reminiscent of de Gennes’ and Brochard’s treatment of a polymer in a binary mixture of good solvents close to the demixing critical point.²⁹ Similar to the latter scenario, the polymer studied in the current work is predicted to undergo *partial collapse*²⁹ at the cac , which marks the onset of association. The simple criterion of partial collapse leads to several interesting predictions which seem to be well supported by experiments. Furthermore, it allows us to distinguish and explain certain common, “universal” features in the vast experimental literature which has accumulated on polymer–surfactant systems.

The theory presented here is phenomenological in nature and does not consider molecular or structural details. Hence, on one hand, its results are fairly general, relying on a single requirement—that the polymer be flexible enough for its local conformation to play a significant role in the self-assembly. (This assumption is quantified in section III.) Unlike detailed molecular models,²⁸ the number of parameters is reduced to three: one accounting for the affinity between

the two species (w), another accounting for intrachain repulsion (v), and the third is the cmc of the polymer-free solution, (φ_{cmc}). On the other hand, the theory is restricted to the onset of association (cac) and its vicinity. Since we are not interested in the micellization itself, we treat the surfactant solution, as it approaches the cmc, as a dilute solution of small associating molecules approaching phase separation. The theory cannot provide, therefore, a reliable detailed description of aggregation. More molecular approaches can be found in references 14 and 28. Nevertheless, it is worth mentioning that models of a simpler, more general nature were successfully employed in the past for describing the interaction of polymers with surfactant monolayers.³⁰

The free energy of the polymer solution is assumed to be characterized by a single interaction parameter (second virial coefficient). The theory is thus applicable to a dilute as well as a semidilute polymer regime. Issues of morphology, phase behavior, and rheology, especially in semidilute and concentrated polymer–surfactant systems, are very interesting and important,^{10,31} but they lie outside the scope of the current work.

The structure of the article is as follows. In section II a simple thermodynamic model for the onset of self-assembly in the mixed system is presented. The main results of this model, as given in section IIB, can be divided into two limiting cases, corresponding to strong or weak effective interactions between the two species. In section III we present a more refined model, using a scaling approach to treat the partial collapse of the polymer in more detail. We qualitatively discuss in section IV the special case of amphiphilic polymers and polysoaps, which provides experimental support for our assumptions. Finally, in section V, we present some conclusions and future directions. Throughout the paper, we compare our results with available experiments whenever possible and stress points where experimental support is still required. To make the central results as clear as possible, we have put most of the technical calculations in two appendices. Appendix A contains a detailed statistical-mechanical calculation, which is used to verify the general results of section II while allowing for their systematic improvement. Appendix B presents the details of the scaling calculation, leading to the results of section III.

II. Thermodynamic Approach

A. The Model. Consider a solution of polymer and smaller solute molecules whose local concentrations are denoted by c and φ , respectively. The free energy density can be divided into three terms accounting for the polymer contribution, the small solute one, and the coupling between the two

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

(All energies are expressed hereafter in units of the thermal energy $k_B T$, i.e., f has the dimensions of inverse volume.) We treat the repulsion between monomers of the chains using a second-virial term

$$f_p = f_p^0 + \frac{1}{2}vc^2 \quad (\text{II.2})$$

where f_p^0 is the free energy of an ideal polymer solution and $v > 0$ is the second virial coefficient (having dimensions of volume). This treatment is valid for dilute,

as well as semidilute polymer solutions. Since the concentrations of both species are low and we are interested only in the onset of association, the leading quadratic term in the expansion of $f_{ps}(c, \varphi)$ suffices

$$f_{ps} = -w\varphi\varphi \quad (\text{II.3})$$

where $w \equiv -\partial^2 f_{ps}/\partial c\partial\varphi$ is a parameter characterizing the interaction strength and having dimensions of volume. In fact, as will be shown below, this general model is sufficient for obtaining our main qualitative results. However, for the sake of clarity, let us specify an expression for the small solute contribution as well:

$$f_s(\varphi) = \varphi(\log \varphi - 1) - \frac{1}{2}u\varphi^2 - \mu\varphi \quad (\text{II.4})$$

The first term in this expression accounts for the ideal entropy of mixing of the small molecules, the second describes short-range attraction, and the third is due to a contact with a reservoir of small molecules having a chemical potential μ .

In the absence of polymer, the small solute concentration has a bulk value, $\varphi = \varphi_b$, corresponding to the minimum of f_s . Consider a small perturbation in local concentration, $\varphi = \varphi_b + \delta\varphi$. Assuming that the solution is both below its cac and cmc, f can be expanded in small $\delta\varphi$ to yield

$$f = f_p(c) + f_s(\varphi_b) - w\varphi(\varphi_b + \delta\varphi) + \frac{1}{2}f_s''(\varphi_b)\delta\varphi^2 \quad (\text{II.5})$$

where $f_s''(\varphi) \equiv \partial^2 f_s/\partial\varphi^2$. In this work, we identify the cmc as the value of φ at which, for $c = 0$, the solution becomes unstable to small perturbations, i.e.

$$f_s''(\varphi_{\text{cmc}}) = 0 \quad (\text{II.6})$$

Equation II.6 is essentially a (spinodal) phase separation condition. In practice, due to the particular structure of surfactants and the resulting finite-size effects, the cmc does not correspond to a true phase transition, and $f_s''(\varphi_{\text{cmc}})$ is not strictly zero. In the case of aggregation into finite micelles of typical aggregation number n , a rough estimate for $\varphi_{\text{cmc}}f_s''(\varphi_{\text{cmc}})$ is given by φ_1/φ_n , the volume-fraction ratio of single molecules and molecules participating in aggregates. This gives $\varphi_{\text{cmc}}f_s''(\varphi_{\text{cmc}}) \sim n^{-1}e^{-\epsilon}$, where ϵ is the energy per molecule (in units of $k_B T$) gained by aggregation.¹² For typical values of $n \sim 100$ and ϵ of a few $k_B T$, this is a small, yet finite number. Since we are interested in the onset of the joint self-assembly (which is subsequently found to occur at a lower concentration than the polymer-free surfactant micellization), we allow ourselves to ignore these delicate considerations. Using eq II.6, we thus assume that for $\varphi \leq \varphi_{\text{cac}}$ specific features of the surfactant can be incorporated in the phenomenological parameter φ_{cmc} .

In the presence of the polymer, minimization of eq II.5 with respect to $\delta\varphi$ gives

$$f = f_p^0 + f_s(\varphi_b) - w\varphi\varphi_b + \frac{1}{2}\left(v - \frac{w^2}{f_s''(\varphi_b)}\right)c^2 \quad (\text{II.7})$$

The last term in f implies an effective reduction in the second virial coefficient of the polymer

$$v_{\text{eff}} = v - v_{ps}; \quad v_{ps} \equiv \frac{w^2}{f_s''(\varphi_b)} \quad (\text{II.8})$$

Thus, letting the distribution of small molecules, φ , reach equilibrium has led to an effective attraction between chain monomers.³²

The polymer will become unstable when $v_{\text{eff}} = 0$. At this point c is expected to increase significantly (due to contraction of chain conformation), leading to a sharp increase in $\delta\varphi$ as well. We identify this point, therefore, as the cac. Setting $v_{\text{eff}} = 0$ in eq II.8 and using eq II.4 for f_s , we find the following expression for the cac:

$$\varphi_{\text{cac}} = \varphi_{\text{cmc}}F\left(\frac{v}{w^2\varphi_{\text{cmc}}}\right) < \varphi_{\text{cmc}} \quad (\text{II.9})$$

$$F(x) = \frac{1}{1 + 1/x} \approx \begin{cases} x - x^2 & x \ll 1 \\ 1 - 1/x & x \gg 1 \end{cases}$$

This simple calculation demonstrates the physics governing the mixed system: the affinity between the flexible polymer and the small solute induces attractive correlations between monomers, which compete with the bare monomer–monomer repulsion. The correlations become stronger as the cmc is approached, and *they are bound to win before reaching the cmc*, i.e., $\varphi_{\text{cac}} < \varphi_{\text{cmc}}$. The fact that the cac is lower than the cmc has been established by numerous experiments.^{1,2} According to the description given here, this fact is a manifestation of a general effect of equilibrated (annealed) impurities.

It is important to note that the qualitative features of expression II.9, relating the cac and cmc, do not depend on the specific model taken for the small molecules, i.e., the expression for f_s . In Appendix A we present a more detailed statistical-mechanical calculation, yielding eq II.9 as a first order in an expansion. Going beyond this first, mean-field approximation gives the same qualitative relation between φ_{cac} and φ_{cmc} as in eq II.9, with merely a modified function F . This modified function can be written in a closed form using the inverse function $x = F^{-1}(y)$ of $y = F(x)$:

$$F^{-1}(y) = \frac{y(1 - y + y^2)}{(1 - y)^3}$$

$$F(x) \approx \begin{cases} x - 2x^2 & x \ll 1 \\ 1 - 1/x^{1/3} & x \gg 1 \end{cases} \quad (\text{II.10})$$

Both expressions for $F(x)$, eqs II.9 and II.10, have the same limiting behavior, i.e., $F(x) \approx x$ for small x and $F(x) \approx 1$ for large x . The two expressions differ, however, in higher orders. The difference is particularly significant in the asymptotic approach toward saturation ($x \gg 1$). The mean-field calculation gives a x^{-1} dependence, whereas the improved analysis yields a much slower trend toward saturation, of $x^{-1/3}$. The difference is also evident in Figure 1, which shows the two results for $F(x)$. Indeed, large values of the argument x correspond to solute concentrations approaching the cmc, $\varphi_{\text{cac}} \sim \varphi_{\text{cmc}}$, where solute–solute correlations become strong and the mean-field approximation should give poor results.

In fact, the leading asymptotic behavior of the function F , relating the cac and cmc, can be obtained on very general grounds, without specifying an expression for f_s . To this end, we use the following mathematical construction. (The uninterested reader can skip the

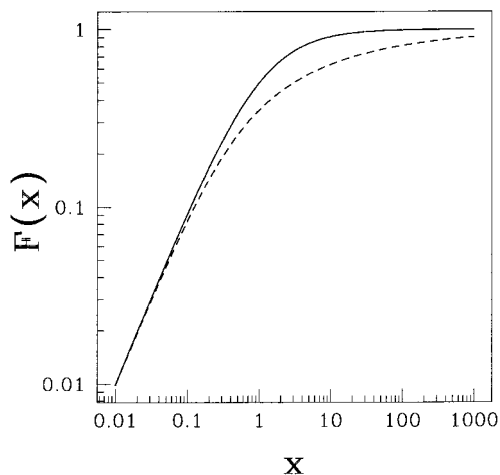


Figure 1. Scaling function $F(x)$: solid line, mean-field calculation (eq II.9); dashed line, beyond mean field (eq II.10).

following derivation and just recall the general result, eq II.11.) Let F be a dimensionless function, such that $\varphi = \varphi_{\text{cmc}} F(x)$ solves the equation $\varphi_{\text{cmc}} f_s''(\varphi) = 1/x$. (x is now merely an unspecified argument.) According to eq II.6, for $x \rightarrow \infty$ the solution to the equation is $\varphi = \varphi_{\text{cmc}}$. Hence we get the asymptotic behavior for large arguments, $F(x \gg 1) \approx 1$. In the other limit one has $x \rightarrow 0$ and $f_s''(\varphi) \rightarrow \infty$. Since $f_s(\varphi)$ is a well-behaved function for $\varphi > 0$, the solution for φ must tend to zero. Hence $F(x \rightarrow 0) \rightarrow 0$. Moreover, in this limit the solution $\varphi \rightarrow 0$ must become independent of the fixed parameter φ_{cmc} , which leads to the asymptotic behavior $F(x \ll 1) \sim x$. The general expression for the cac is thus

$$\varphi_{\text{cac}} = \varphi_{\text{cmc}} F\left(\frac{v}{w^2 \varphi_{\text{cmc}}}\right) < \varphi_{\text{cmc}}$$

$$F(x) \sim \begin{cases} x & x \ll 1 \\ 1 & x \gg 1 \end{cases} \quad (\text{II.11})$$

B. Results. The argument $x = v/(w^2 \varphi_{\text{cmc}})$ in eq II.11 determines the strength of effective interaction between the polymer and the small molecules. Two limiting cases arise: (i) strong effective interaction ($x \ll 1$), where $\varphi_{\text{cac}} \ll \varphi_{\text{cmc}}$; (ii) weak interaction ($x \gg 1$), where $\varphi_{\text{cac}} \lesssim \varphi_{\text{cmc}}$. The two limiting behaviors, together with a third one corresponding to polysoaps (section IV), are presented in the diagram of Figure 2. Note that the distinction between strong and weak interaction involves not only the bare interaction between the species, as compared to the interaction among small molecules, but also intrachain features. In our opinion, this observation was not given proper attention by previous studies.

1. Strong Interaction. In the case of strong effective interaction between the two species, $w^2 \gg v/\varphi_{\text{cmc}}$ (upper part of the diagram in Figure 2), the attraction among small molecules has no effect on the cac, and according to eq II.11, it becomes independent of the cmc

$$\varphi_{\text{cac}} \sim v/w^2 \ll \varphi_{\text{cmc}} \quad (\text{II.12})$$

In practice, this case corresponds to systems containing oppositely charged species, e.g., a polyacid and a cationic surfactant.⁵ Because of the strong electrostatic interactions, the cac in such systems is usually found to be 2–3 orders of magnitude lower than the cmc. In order for the requirement of polymer flexibility to be fulfilled, the

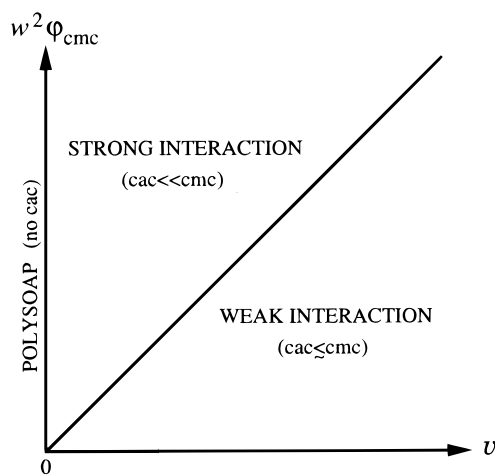


Figure 2. Summary of self-assembly regimes: (i) a strong-interaction regime ($w^2 \varphi_{\text{cmc}} > v$) where $\varphi_{\text{cac}} \ll \varphi_{\text{cmc}}$, corresponding experimentally to systems containing oppositely charged species; (ii) a weak-interaction regime ($w^2 \varphi_{\text{cmc}} < v$) where $\varphi_{\text{cac}} \lesssim \varphi_{\text{cmc}}$, corresponding to systems where at least one of the species is neutral; (iii) a polysoap regime ($v = 0$) where association is gradual (no cac), corresponding to polymers which form intrachain aggregates by themselves.

system must contain additional salt which would screen the electrostatic interactions on length scales comparable to those of the induced attractive correlations.

Both v and w are expected to be dominated in such systems by electrostatics and, therefore, mainly depend on the polymer ionization degree, I , and salt concentration, c_{salt} . A polyelectrolyte solution is a complicated system by itself, exhibiting diverse behavior as a function of I and c_{salt} .³³ However, two observations can generally be made: (i) the monomer–monomer parameter, v , should have a stronger dependence on I than the monomer–small solute one, w (the simplest dependence would be $v \sim I^2$ and $w \sim I$); (ii) both v and w should have a similar (increasing) dependence on the Debye screening length, $\lambda_D \sim c_{\text{salt}}^{-1/2}$, i.e., a similar decreasing dependence on c_{salt} . Consequently, $\varphi_{\text{cac}} \sim v/w^2$ should increase with c_{salt} and, somewhat more surprisingly, be only weakly dependent on I . A model which is focused on the bare interaction between the species would necessarily yield a *strongly decreasing* dependence of φ_{cac} on I . The weak dependence on I is a characteristic result of our approach, which takes into account intrachain features. It stems from a competition between two effects that compensate each other: a mutual affinity effect (increasing I strengthens the attraction between the oppositely charged species), and an intrachain effect (larger I implies stronger intrachain repulsion).³⁴

Apart from these rather general conclusions, we may try to reach more quantitative predictions.³⁵ The excluded-volume parameter for a flexible (weak) polyelectrolyte should roughly scale like $v \sim I^2 \lambda_D^2 \sim I^2 c_{\text{salt}}^{-1}$.³⁶ (This result can be simply interpreted as an electrostatic energy I^2/λ_D integrated over a volume λ_D^3 .) Similarly, we write for the monomer–small solute parameter $w \sim I c_{\text{salt}}^{-1}$. The resulting cac should scale, therefore, as

$$\varphi_{\text{cac}} \sim I^s (c_{\text{salt}})^t \quad s = 0, \quad t = 1 \quad (\text{II.13})$$

A more detailed calculation, however, yields a different scaling and is discussed in section III (eq III.6).

Table 1. Dependence of c_{ac} on Polyelectrolyte Ionization Degree in the Strong-Interaction Regime³⁷

polymer	surfactant	salt	c_{salt} (mM)	I (M)	φ_{cac} (mM)	ref
PMAMVE	DTAB	KBr	5	0.5	0.16	38
				1	0.16	
PMAEVE	DTAB	KBr	5	0.5	0.09	38
				1	0.1	
PMAMVE	DTAC	NaCl	20	0	6	39
				1	5	
chitosan	SDS	NaBr	20	0.76	0.028	40
				0.84	0.028	
				0.99	0.028	
PMASt	C ₁₂ PyCl	NaCl	25	0.5	0.025	41
				1	0.025	
PMAIn	C ₁₂ PyCl	NaCl	25	0.5	0.012	41
				1	0.016	
PMAEVE	C ₁₂ PyCl	NaCl	25	0.5	0.15	41
				1	0.22	
PMAE	C ₁₂ PyCl	NaCl	25	0.5	0.13	41
				1	0.27	
PAA	TTAB	NaBr	10	0.14	0.0068	42
				0.26	0.0092	
				0.5	0.025	
				1	0.029	
PAA	DTAB	NaCl	30	pH = 5.3 ^a	0.4	43
				pH = 6.4	0.7	
				pH = 8.1	0.9	
				pH = 10.8	0.95	
PVS	DTAB	KCl	10	0.18	0.18	44
				0.34	0.11	
				0.50	0.12	
				0.68	0.06	
				0.74	0.05	
1	0.05					

^a pH values were reported; I depends monotonically on pH.

Table 1 summarizes various experimental results for the dependence of φ_{cac} on I in the presence of salt. The first six experimental systems presented in the table exhibit vanishing dependence on I , the next four, an increasing dependence, and the last one, a weak decrease. The fact that most experiments found a vanishing or slightly *increasing* dependence of φ_{cac} on I clearly indicates the important role of intrachain features in the self-assembly. If intrachain features are disregarded, one would expect, upon increasing I , a stronger attraction between the oppositely charged species and, hence, a sharp *decrease* in the cac , i.e., an opposite trend to the one observed in Table 1.

As mentioned above, the solution must contain enough salt for our description to hold. Electrostatic interactions should be screened on length scales comparable to the correlation length in the surfactant solution, i.e., the Debye screening length, λ_D , should be smaller than a few nanometers. For monovalent salt, it means that the salt concentration should exceed about 10 mM. This might explain the inconsistent trends observed in systems containing only about this amount of salt (Table 1).

Figure 3 shows experimental results for the dependence of φ_{cac} on φ_{salt} , taken from 11 different experiments with different mixtures of polymers, surfactants and monovalent salts. All systems exhibit an increasing dependence on c_{salt} , in qualitative agreement with our finding. Previous works focused on small differences in the slopes of $\log(\varphi_{cac})$ vs $\log(c_{salt})$ for different systems, attributing them to different ionization degrees of the charged aggregates.^{21,46} While such effects are probably

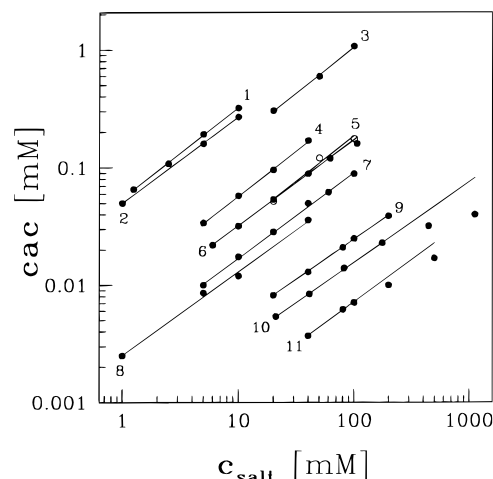


Figure 3. Dependence of cac on monovalent salt concentration in various polyelectrolyte–oppositely charged surfactant systems.³⁷ From top to bottom: (1) NaPA, DTAB, NaBr (ref 45); (2) PMAMVE, DTAB, KBr (ref 38); (3) PVS, C₁₀PyBr, NaBr (ref 16); (4) NaDxS, C₁₁PyBr, NaCl (ref 46); (5) PAS, SDeS, NaCl (ref 15); (6) NaDxS, DTAB, NaCl (ref 47); (7) NaDxS, C₁₂PyCl, NaCl (ref 46); (8) PMABVE, DTAB, KBr (ref 38); (9) NaDxS, C₁₃PyBr, NaCl (ref 46); (10) PSS, DTAB, NaCl (ref 47); (11) NaDxS, C₁₄PyBr, NaCl (ref 46). Fitted slopes lie in the range 0.68–0.77.

present, we would rather like to draw the attention to the striking *uniformity* of the slopes—all of the graphs in Figure 3, representing 11 different polymer–surfactant systems, have fitted slopes in the narrow range of 0.68–0.77, namely $\varphi_{cac} \sim (c_{salt})^t$ with $t \approx 0.68–0.77$.⁴⁸ This uniformity was not pointed out before. It might indicate that specific molecular details are not essential to determining the onset of self-assembly, as suggested here. Quantitatively, the observed power law disagrees with the exponent $t = 1$ in eq II.13. We return to this point in section III.

It is important to note again that our results hold for flexible polymers only. A different behavior as a function of c_{salt} is observed for stiff polymers such as DNA or proteins.⁴⁹ Similarly, the cac in salt-free solutions of strongly charged polyelectrolytes, which cannot be regarded as flexible chains, depends sensitively on I .⁵⁰

2. Weak Interaction. In the other limiting case of eq II.11, $w^2 \ll v/\varphi_{cmc}$ (lower part of the diagram in Figure 2), the effective interaction between the polymer and small molecules is weak and the cac and cmc become comparable (yet still $\varphi_{cac} < \varphi_{cmc}$)

$$\varphi_{cac} = A\varphi_{cmc} \quad (\text{II.14})$$

where $A = F[v/(w^2\varphi_{cmc})] \lesssim 1$ can be considered essentially as a prefactor which is not very sensitive to changes in v , w , or φ_{cmc} [since $F(x)$ is close to saturation; cf. eq II.11]. Experimentally, this weak-interaction limit applies to systems where at least one of the species is uncharged, e.g., neutral polymers interacting with ionic surfactants⁶ or polyelectrolytes interacting with non-ionic surfactants.^{8,9} The cac is expected to depend in this case on molecular details. However, *most of this complicated dependence is incorporated in φ_{cmc} itself*. In other words, changing various parameters (e.g., ionic strength) may lead to considerable changes in both the cmc and cac ; yet, according to eq II.14, their ratio is expected to remain roughly constant. We note again that the model is not presumed to properly account for the cmc itself. It is expected, however, to correctly capture

Table 2. Relation between φ_{cac} and φ_{cmc} in the Weak-Interaction Regime

polymer	surfactant	salt/counterion	φ_{cac} (mM)	φ_{cmc} (mM)	$\varphi_{cac}/\varphi_{cmc}$	ref
PEO	DS ⁻	NaDS	4.2	8.2	0.51	51
		LiDS	3.9	7.7	0.51	
		NaDS, 0.1 M NaCl	0.8	1.4	0.57	
PEO	SDS	no salt	NR ^a	8.2	0.65	22
		0.075M NaCl			0.67	
		0.15M NaCl			0.69	
		0.2M NaCl		0.94	0.76	
		0.4M NaCl		0.59	0.78	
PVP	SDS	0.01M NaCl	2.2	5.5	0.40	54
		0.1M NaCl	0.84	1.9	0.44	
PAA	C ₁₀ E ₈	—	0.7	1	0.7	9
		C ₁₂ E ₈	0.063	0.08	0.79	
		C ₁₄ E ₈	0.007	0.009	0.78	

^a Only the ratio $\varphi_{cac}/\varphi_{cmc}$ was reported. φ_{cmc} values were taken from refs 52 and 53.

the relation between the φ_{cac} and φ_{cmc} , due to the particular behavior of the polymer at the φ_{cac} .

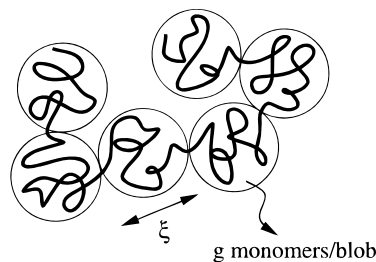
The simple prediction given in eq II.14 is verified in various experiments, as summarized in Table 2. In each of the four experimental systems presented in Table 2, the ratio $\varphi_{cac}/\varphi_{cmc}$ remains roughly constant, sometimes over a wide range of φ_{cmc} values.⁵⁵

III. Scaling Approach

A. The Model. The treatment given in section II for the onset of self-assembly is not accurate enough and should be regarded as a first step in a more rigorous calculation. Its description of the φ_{cac} resembles a “shifted” Θ collapse—a sharp transition of polymer conformation occurring when the second virial coefficient changes sign. In practice, however, flexible polymers do not exhibit a sharp coil-to-globule collapse at the φ_{cac} . Their association with small surfactant molecules exhibits a steep, albeit continuous, increase at the φ_{cac} , the finite slope being associated with the “binding cooperativity”.⁵⁶

The difference between a Θ point and the φ_{cac} lies in the different ranges of competing interactions. In a regular Θ point the competing interactions (between monomers and between monomers and solvent molecules) have a similar short range. This leads to a sharp conformational collapse which is stabilized by three-body interactions (third virial coefficient term). By contrast, in the system discussed here the strong, short-range repulsion between monomers is overcome by weaker, yet longer-range attractive correlations. These attractive correlations are induced by the small associating molecules interacting with the polymer, as has been found in section II. As a result of the competition between interactions of different ranges, the polymer undergoes a more moderate *partial collapse* into subunits (“blobs”), such that the interaction between monomers within each blob is dominated by the short-range repulsion, whereas the interaction between blobs is dominated by the attractive correlations.

This behavior resembles the one previously discussed by de Gennes and Brochard for a polymer in a binary mixture close to the critical demixing point.²⁹ An important difference, however, is that the correlation length in the system of ref 29 may become arbitrarily large. The solution discussed here, by contrast, is not close to a critical point but approaches a point of phase

**Figure 4.** Schematic sketch of a partially collapsed chain.

separation or micellization. Thus, the correlations may become strong but their range remains finite.

Partial collapse is essentially a “smoothed” Θ transition—the rescaled “chain of blobs” is at a Θ point, while on length scales smaller than the blob size the chain is almost unperturbed. Throughout the regime of partial collapse, as small solute molecules are added, the subdivision of the chain into blobs is adapted so as to keep the rescaled chain at a Θ point. Association, thus, progresses *continuously*, as the blobs become smaller and more numerous, and the local monomer concentration gradually increases. In the following analysis, the added solute molecules (e.g., surfactants) do not appear explicitly. They are accounted for via the effective interaction which they induce in the polymer. This interaction has a typical amplitude, e^2 , and a typical range, ξ , both of which implicitly depend on the solute concentration φ . Since, for very long chains, ξ is the only length scale in the problem, it must also be the typical size of a blob.²⁹

Let us consider, therefore, a chain of blobs of size ξ , each containing g statistical (Kuhn) segments, as sketched in Figure 4.⁵⁷ If each blob contains a large number of segments, its size ξ is related to the number g by a power law

$$\xi \sim g^\nu a^z v^{(1-z)/3} \quad (\text{III.1})$$

where a is the length of a Kuhn segment. In the case of excluded-volume repulsion in three dimensions, the Flory argument yields $\nu = 3/5$ and $z = 2/5$.⁵⁸ Further properties of the “chain of blobs” can be studied using scaling arguments, as presented in detail in Appendix B. This calculation leads to the following relations between g , ξ and the phenomenological parameters introduced in section II:

$$g \sim \left(\frac{v}{v_{ps}}\right)^{1/\alpha} \left(\frac{a^3}{v}\right)^{z/\alpha}$$

$$\xi \sim \left(\frac{v}{v_{ps}}\right)^{\nu/\alpha} \left(\frac{a^3}{v}\right)^{\nu z/\alpha} a^z v^{(1-z)/3}$$

$$\alpha \equiv 2 - 3\nu \quad (\text{III.2})$$

where $v_{ps}(\varphi)$ is the effective reduction in the second virial coefficient due to the added solute (surfactant), defined in eq II.8.

B. Results. Several interesting observations arise from eq III.2. In order for the results to be consistent, g and ξ must increase with decreasing $v_{ps}(\varphi)$ so that the entire chain should reduce to a single blob for small enough φ . Hence, the self-consistency condition is

$$\alpha > 0 \Leftrightarrow \nu < 2/3 \quad (\text{III.3})$$

This self-consistency condition gives a precise definition for the requirement of polymer flexibility—on the scale of the correlation length in the solution the chain statistics should satisfy $\nu < 2/3$. (In particular, the chain should not be stretched, having $\nu = 1$.) For example, in polyelectrolyte solutions this condition sets a lower bound for salt concentration, below which the chain would be too stretched on the length scale of ξ , and the partial-collapse picture described here would become invalid.

Repeating the calculation for chains embedded in d dimensions, the same result as eq III.2 is obtained, with $\alpha = 2 - d\nu$. This self-consistency condition, $\alpha > 0$, is similar to well-known results for the critical behavior of disordered systems. For both equilibrated (annealed) and frozen (quenched) disorder—Fisher renormalization⁵⁹ and the Harris criterion,⁶⁰ respectively—the critical behavior is affected by impurities if $\nu < 2/d$, i.e., $\alpha > 0$. Thus, in a similar way, small solute molecules affect the conformational transition of a polymer if $\nu < 2/d$.⁶¹

We stress again that the solution discussed here is not close to a critical point and, hence, the correlations induced in the polymer may be strong but their range remains finite. As a result, the blobs cannot be arbitrarily large, i.e., g and ξ are bounded by certain maximum values, g^* and ξ^* . Since ξ^* characterizes the range of correlations in the solution of small molecules (surfactants), it can be estimated by the typical size of aggregates (micelles) formed at the cmc, i.e., typically a few nanometers. The value of g^* , in turn, is given by the number of monomers in a blob whose size is equal to ξ^* .

The onset of association in the mixed system (the cac) is expected when blobs can form, i.e., when the value of g required for partial collapse (eq III.2) becomes smaller than the threshold g^* . Setting the right-hand side of eq III.2 for g equal to g^* , and substituting eq II.8 for v_{ps} and the function $F(x)$ defined in section II, we find the following expression for the cac:

$$\varphi_{\text{cac}} = \varphi_{\text{cmc}} F \left[(g^*)^{-\alpha} \left(\frac{a^3}{v} \right)^z \frac{v}{w^2 \varphi_{\text{cmc}}} \right]$$

$$F(x) \sim \begin{cases} x & x \ll 1 \\ 1 & x \gg 1 \end{cases} \quad (\text{III.4})$$

Comparison to eq II.11 shows that the less refined analysis of section II corresponds, in fact, to complete collapse ($g = 1$), rather than the actual partial collapse ($g = g^*$).

The similarity to the Harris criterion persists. Suppose that we could somehow control the correlations in the solution, i.e., tune g^* , while keeping the concentration of small molecules φ fixed (this might be achieved, for example, by changing the temperature). In such a scenario, instead of φ_{cac} , there would be a certain value of g^* corresponding to the onset of self-assembly. For $\varphi/\varphi_{\text{cmc}} \ll 1$ we find from eq III.4 that this value of g^* satisfies $g^* \sim \varphi^{-1/\alpha}$. It implies that in the absence of “impurities” ($\varphi = 0$) only complete collapse of an infinite chain can take place ($g^* \rightarrow \infty$), whereas for finite φ a smoother, partial collapse into finite blobs is possible. This is analogous to Harris’ result for the broadening of a critical point by impurities,⁶⁰ where, instead of a sharp transition at a critical temperature $T = T_c$, there is a smooth crossover along a range of temperatures ΔT .

Harris’ result for this broadening is $\Delta T/T_c \sim \varphi^{1/\alpha}$, where $\varphi \ll 1$ is, in this case, the concentration of impurities. Recall that the number of monomers serves as a conjugate variable to $\Delta T/T_c$ in the analogy between polymers and critical phenomena,⁵⁸ i.e., $g^* \rightarrow \infty$ corresponds to $\Delta T/T_c \rightarrow 0$. The smoothing of the Θ collapse of an infinite chain into partial collapse of finite blobs, due to small solute molecules, is thus analogous to the smoothing of critical points by impurities.⁶²

Another result of the partial-collapse picture is that at the cac, since the “chain of blobs” is at a Θ point, it should obey Gaussian statistics. Hence, the radius of gyration of the polymer should scale with the polymerization degree, N , as $N^{1/2}$. This prediction is still to be confirmed experimentally. Contraction of the polymer at the cac was observed in several systems.^{63–65} Additional support is found in light-scattering and potentiometric experiments reporting a surprisingly weak interaction between charged aggregates of ionic surfactant and neutral polymer.^{66,67}

In the strong-interaction regime [small argument of $F(x)$ in eq III.4], the partial-collapse analysis leads to an expression for the cac which is different from the one given in section II (compare to eq II.12)

$$\varphi_{\text{cac}} \sim (g^*)^{-\alpha} \left(\frac{a^3}{v} \right)^z \frac{v}{w^2} \quad (\text{III.5})$$

In polyelectrolyte systems relevant to this regime, the Kuhn length a should be taken as the electrostatic persistence length.^{33,35} For flexible, weak polyelectrolytes it depends on the polymer ionization degree, I , and salt concentration, c_{salt} , as $a \sim \ell_D \sim I c_{\text{salt}}^{-1/2}$.⁶⁸ As in section II, we take the simple, weak-polyelectrolyte expressions for v and w :³⁶ $v \sim I^2 c_{\text{salt}}^{-1}$ and $w \sim I c_{\text{salt}}^{-1}$. The last factor to account for in eq III.5 is the threshold number of monomers, g^* , whose dependence on I and c_{salt} is unknown. We consider two simplified cases: (i) constant threshold for the number of monomers in a blob, g^* ; (ii) constant threshold for the spatial size of a blob, $\xi^* \sim (g^*)^\nu a^z v^{(1-z)/3}$. In reality, neither of these cases is expected to be strictly correct. The resulting dependence of the cac on I and c_{salt} for the two simplified cases is

$$\varphi_{\text{cac}} \sim I^s (c_{\text{salt}})^t$$

$$s = \begin{cases} z = 2/5, & \text{constant } g^* \\ z + (\alpha/3\nu)(2+z) = 2/3, & \text{constant } \xi^* \end{cases}$$

$$t = \begin{cases} 1 - z/2 = 4/5, & \text{constant } g^* \\ 1 - z/2 - (\alpha/6\nu)(2+z) = 2/3, & \text{constant } \xi^* \end{cases} \quad (\text{III.6})$$

where we have used again the Flory values $\nu = 3/5$ and $z = 2/5$.⁵⁸

Comparison to eq II.13 shows that the partial-collapse analysis has led to quantitatively different results. Instead of a vanishing dependence on I , we find a weakly increasing one. Both vanishing and weakly increasing dependencies were observed experimentally (Table 1). As discussed in section II, these findings qualitatively support our approach, emphasizing the significance of intrachain interactions. To quantitatively

determine the correct dependence on I , more experiments are needed, in particular at higher ionic strength.

Equations II.13 and III.6 differ also in the quantitative dependence on c_{salt} . The dependence in eq III.6 agrees with the experimentally observed power laws (Figure 3), having exponents of $t \approx 0.68 - 0.77$.

IV. Comments on Amphiphilic Polymers and Polysoaps

Our basic conjecture, regarding instability of polymer conformation at the onset of self-assembly, can be qualitatively supported by considering a special class of polymers—associating polymers that form intrachain aggregates in the absence of any additional associating solute. Good examples for this case are amphiphilic side-chain polymers, which consist of a hydrophilic backbone (usually a polyacid) and many hydrophobic side chains.^{38,39,69} Within a certain range of hydrophobicity, those polymers exhibit intrachain aggregation while still remaining water-soluble, in which case they are called *polysoaps*. By synthesizing polymers with various side-chain lengths and controlling their ionization degree, a crossover between regular polyelectrolyte behavior and intrachain association (polysoap) can be observed.⁶⁹

According to our description, a polysoap is already partially collapsed. No further instability is supposed to occur upon addition of small solute molecules and, hence, no sharp onset of self-assembly is expected. Association of small molecules to such a chain should progress gradually as a function of concentration, by means of partitioning of molecules between the aqueous solution and the already-collapsed polymeric aggregates.

The association of ionic surfactants with such hydrophobically modified polyelectrolytes, poly(maleic acid-co-alkylvinyl ether), was thoroughly studied.^{38,39,69} When the polymer is in the regular polyelectrolyte regime (e.g., having short side chains of 1–4 hydrocarbon groups), a sharp, cooperative binding is observed. On the other hand, when the polymer behaves as a polysoap (having longer side chains and exhibiting intrachain aggregation), surfactant association is found to be gradual with no apparent cac .³⁸ We regard this experimental observation as a strong support for our conjecture, associating the cac with partial collapse.

Furthermore, let us consider amphiphilic polymers which still behave like polyelectrolytes but lie very close to the polysoap regime. This can be achieved, for example, by tuning their ionization degree. The effective second virial coefficient of such polymers should be small, leading, according to eq III.5 (or II.12), to low cac . The physical reason is that close to the polysoap regime the stability of the polymer is only marginal; i.e., v is close to zero even in the absence of additional solute (surfactant). Hence, a small amount of solute is sufficient to cause self-assembly. In this region of $v \geq 0$, therefore, intrachain features, rather than the affinity between the two species, determine the onset of self-assembly. As a result, the cac can be significantly reduced without a significant change in the bare interaction. Moreover, it can be reduced even if the bare affinity becomes *weaker* (e.g., by reducing I). There are two available experimental works demonstrating this surprising effect,^{38,70} as shown in Figure 5. Both experiments involved amphiphilic polyelectrolytes whose charge density was varied. Although reducing charge density must *weaken* the interaction with the oppositely charged

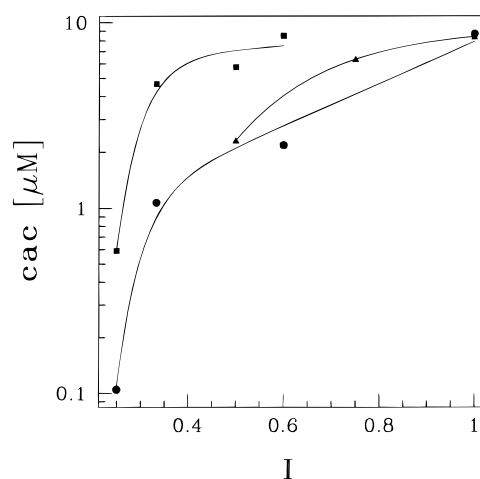


Figure 5. Dependence of cac on polymer charge close to the polysoap regime. Triangles: PMABVE, DTAB, 5 mM KBr (ref 38). For $I < 0.5$ this polymer becomes a polysoap. Circles: $(\text{CH}_2)_x(\text{CH}_2)_y^-$ ionine bromide, SDS, no salt; squares – with 20 mM NaBr (ref 70). A distance of three hydrocarbon groups between charged groups along the backbone has been defined as $I = 1$. The lines are merely guides to the eye.

surfactant, the cac was shown to *decrease*, the effect becoming sharp close to the polysoap limit.

The polymers discussed above have many hydrophobic groups along their backbone. Also worth mentioning are experiments involving polyelectrolytes with a very small number of hydrophobic groups.⁷¹ In this case too, the cac was found to significantly decrease upon increasing the degree of hydrophobic modification, implying a sensitive dependence on intrachain features.

V. Conclusions

Focusing on the onset of self-assembly (the cac), we have presented a unified description of the interaction between a flexible polymer and small associating molecules in dilute solution. Utilizing a conjecture of partial collapse of the polymer at the onset of self-assembly, we have obtained simple predictions which seem to be well supported by experiments on diverse polymer–surfactant systems.

Apart from the bare interaction between the two species, we argue that intrachain interactions have an important role as well. In certain cases, such as systems involving amphiphilic polymers, intrachain features may even become the dominant factor determining the cac . The interplay between various interactions in the system (monomer–solute, monomer–monomer and solute–solute) leads to three self-assembly scenarios, which are summarized in the diagram of Figure 2. By modifying intrachain features of the polymer, one can obtain a crossover between the various self-assembly regimes without necessarily changing the bare interaction between the two associating species. An interesting experiment would be to take a weakly interacting system (e.g., a polyacid like PAA and a nonionic surfactant like C_nE_m) and by modifying the polymer (e.g., changing hydrophobicity) gradually shift it to the strong-interaction regime and finally to the polysoap regime; the cac is predicted to decrease from a value close to the cmc to much lower values and finally to disappear.

Despite the vast experimental literature available on polymer–surfactant systems, additional experiments are still required in order to verify the theory presented in this work. In particular, measurement of polymer

statistics at the cac (i.e., dependence of size on polymerization degree) may provide a clear verification of the partial-collapse conjecture.

We have presented a scaling function relating the cac and cmc and demonstrated its universal features. The scaling function was explicitly calculated in a mean-field approximation and at the next level beyond mean field. It is worth noting, however, that we expect the scaling law of eqs II.11 and III.4 to be of more general validity than any specific model discussed here. It should be interesting, therefore, to gain more information on the scaling law, e.g., by computer simulations, and check the analytic results. We have pointed at interesting similarities between the effect of small associating molecules on polymer conformation and general results concerning the effect of impurities on critical phenomena.

One future extension of this work would be to apply the partial collapse approach to more concentrated solutions, where the onset of self-assembly involves many-chain effects and leads to interesting phase behavior and gelation.^{10,31} Another direction may be to consider more complicated polymers such as polypeptides, where surfactant binding was shown to promote the formation of secondary structures.⁷² In addition, the partial-collapse approach is valid only for flexible polymers, as demonstrated in section III. The interaction of stiff polymers with small associating molecules is governed by different physics, requiring a separate treatment.⁷³

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Appendix A: The Scaling Function beyond Mean Field Theory

We present in detail a statistical-mechanical model leading to explicit expressions for the scaling function, $F(x)$, introduced in section II. A systematic expansion is derived, which yields the simple mean-field result, eq II.9, as a leading order, yet allowing us to proceed beyond the mean-field approximation.

Consider P polymer chains of N monomers each, which are immersed in a dilute solution containing S small molecules (e.g., surfactants). We use the grand-canonical ensemble, where S is not fixed but controlled by a chemical potential, μ . The coordinates of the monomers are denoted by $\{\mathbf{x}_n^p\}_{p=1\dots P, n=1\dots N}$ and those of the small solute molecules are $\{\mathbf{y}_s\}_{s=1\dots S}$. Let the potentials of solute–solute, monomer–monomer, and monomer–solute interactions be, respectively, $U(\mathbf{r} - \mathbf{r}')$, $V(\mathbf{r} - \mathbf{r}')$, and $W(\mathbf{r} - \mathbf{r}')$. The partition function of the system is where all energy and interaction parameters

$$Z = \frac{1}{P!} \sum_{S=0}^{\infty} \frac{1}{S!} e^{\mu S} \int \prod_{p=1}^P \prod_{n=1}^N d\mathbf{x}_n^p \prod_{s=1}^S d\mathbf{y}_s \exp(-\mathcal{H}_{\text{id}} - \mathcal{H}_{\text{int}})$$

$$\mathcal{H}_{\text{int}} = \frac{1}{2} \sum_{p \neq p'} \sum_{n \neq n'} V(\mathbf{x}_n^p - \mathbf{x}_{n'}^{p'}) + \frac{1}{2} \sum_{s \neq s'} U(\mathbf{y}_s - \mathbf{y}_{s'}) + \sum_p \sum_n \sum_s W(\mathbf{x}_n^p - \mathbf{y}_s) \quad (\text{A.1})$$

are given in units of $k_B T$, the thermal energy, and $\mathcal{H}_{\text{id}}\{\mathbf{x}_n^p\}$ is the Hamiltonian of P ideal (Gaussian) chains.⁷⁴ Our aim is to trace out the degrees of freedom of the small molecules ($\{\mathbf{y}_s\}$) and find the resulting effective interaction between monomers.

We introduce continuous densities for the two species

$$c(\mathbf{r}) \equiv \sum_{p,n} \delta(\mathbf{r} - \mathbf{x}_n^p), \quad \varphi(\mathbf{r}) \equiv \sum_s \delta(\mathbf{r} - \mathbf{y}_s)$$

and their conjugate fields, $\gamma(\mathbf{r})$ and $\psi(\mathbf{r})$, respectively, such that

$$\delta[c(\mathbf{r}) - \sum_{p,n} \delta(\mathbf{r} - \mathbf{x}_n^p)] = \int \mathcal{D}\gamma \exp\{-i\gamma[c(\mathbf{r}) - \sum_{p,n} \delta(\mathbf{r} - \mathbf{x}_n^p)]\}$$

$$\delta[\varphi(\mathbf{r}) - \sum_s \delta(\mathbf{r} - \mathbf{y}_s)] = \int \mathcal{D}\psi \exp\{-i\psi[\varphi(\mathbf{r}) - \sum_s \delta(\mathbf{r} - \mathbf{y}_s)]\} \quad (\text{A.2})$$

The partition function is then rewritten as

$$Z = \int \mathcal{D}c \mathcal{D}\varphi \mathcal{D}\gamma \mathcal{D}\psi \exp(-\mathcal{H}_{\text{cont}}) \times \zeta_p \times \zeta_s$$

$$\mathcal{H}_{\text{cont}} = \int d\mathbf{r} d\mathbf{r}' \left[\frac{1}{2} c(\mathbf{r}) V(\mathbf{r} - \mathbf{r}') c(\mathbf{r}') + \frac{1}{2} \varphi(\mathbf{r}) U(\mathbf{r} - \mathbf{r}') \varphi(\mathbf{r}') + c(\mathbf{r}) W(\mathbf{r} - \mathbf{r}') \varphi(\mathbf{r}') \right]$$

$$- i \int d\mathbf{r} [\gamma(\mathbf{r}) c(\mathbf{r}) + \psi(\mathbf{r}) \varphi(\mathbf{r})]$$

$$\zeta_p = \frac{1}{P!} \int \prod_{p,n} d\mathbf{x}_n^p \exp[-\mathcal{H}_{\text{id}} - i \sum_{p,n} \gamma(\mathbf{x}_n^p)]$$

$$\zeta_s = \sum_{S=0}^{\infty} \frac{1}{S!} e^{\mu S} \int \prod_{s=1}^S d\mathbf{y}_s \exp[-i \sum_{s=1}^S \psi(\mathbf{y}_s)] = \exp[\varphi_b \int d\mathbf{r} e^{-i\psi(\mathbf{r})}] \quad (\text{A.3})$$

In the last equation we have exploited the independence of the integral term on s and the expansion of the exponential function in power series, where $\varphi_b \equiv e^\mu$ is the average solute concentration in the bulk reservoir. (We assume an ideal solution of small solute molecules in the bulk reservoir, i.e., a vanishing ψ and $\mu = \log \varphi_b$.)

It is convenient to transform to Fourier space, $\tilde{f}_k \equiv \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r})$, whereupon $\mathcal{H}_{\text{cont}}$ becomes

$$\mathcal{H}_{\text{cont}} = \int d\mathbf{k} \left[\frac{1}{2} \bar{V}_k |\tilde{c}_k|^2 + \frac{1}{2} \bar{U}_k |\tilde{\varphi}_k|^2 + (\bar{W}_k \tilde{c}_k + i\tilde{\psi}_k) \tilde{\varphi}_k + i\tilde{\gamma}_k \tilde{c}_k \right]$$

Tracing over the solute concentration profile, $\tilde{\varphi}_k$, is straightforward, giving (up to a constant factor)

$$Z = \int \mathcal{D}\tilde{c}_k \mathcal{D}\tilde{\gamma}_k \mathcal{D}\tilde{\psi}_k \times \exp\left\{ \int \mathbf{d}\mathbf{k} \left[\frac{1}{2} \tilde{U}^{-1}_k (\tilde{W}_k \tilde{c}_k + i\tilde{\psi}_k)^2 - \frac{1}{2} \tilde{V}_k |\tilde{c}_k|^2 - i\tilde{\gamma}_k \tilde{c}_k \right] \right\} \times \zeta_p \times \zeta_s \quad (\text{A.4})$$

In the usual case, where the potentials of interaction, $U(\mathbf{r}, \mathbf{r}')$, $V(\mathbf{r}, \mathbf{r}')$, and $W(\mathbf{r}, \mathbf{r}')$, depend only on $(\mathbf{r} - \mathbf{r}')$, they are diagonal in k -space and can be simply inverted, e.g., $\tilde{U}^{-1}_k = 1/\tilde{U}_k$.

To trace out also the solute field, ψ , we proceed by an expansion of ζ_s in small ψ . Physically, ψ accounts for interactions between the small solute molecules. The small parameter of the expansion, therefore, is the strength of solute–solute correlations in the solution. The following calculation is expected to give good results in the regime of strong polymer–solute interaction [$F(x \ll 1)$] and less accurate results in the limit of weak polymer–solute interaction [$F(x \gg 1)$], where solute–solute correlations become important.

Gaussian Approximation. In the Gaussian approximation ζ_s is expanded to second order in ψ

$$\zeta_s \approx \text{const} \times \exp\left[-\varphi_b \int \mathbf{d}\mathbf{r} \left(i\psi + \frac{1}{2}\psi^2\right)\right] = \text{const} \times \exp\left[-\varphi_b \left(\frac{1}{2} \int \mathbf{d}\mathbf{k} |\tilde{\psi}_k|^2 + i\tilde{\psi}_0\right)\right] \quad (\text{A.5})$$

where $\tilde{\psi}_0 \equiv \tilde{\psi}_{k=0} = \int \mathbf{d}\mathbf{r} \psi(\mathbf{r})$. Substituting this expression in eq A.4 we get

$$Z \approx Z_2 = \int \mathcal{D}\tilde{c}_k \mathcal{D}\tilde{\gamma}_k \mathcal{D}\tilde{\psi}_k \exp(-\mathcal{H}_2) \times \zeta_p \quad \mathcal{H}_2 = \int \mathbf{d}\mathbf{k} \left[\frac{1}{2} (\tilde{U}^{-1}_k + \varphi_b) |\tilde{\psi}_k|^2 - i\tilde{W}_k \tilde{U}^{-1}_k \tilde{c}_k \tilde{\psi}_k + \frac{1}{2} (\tilde{V}_k - \tilde{W}_k^2 \tilde{U}^{-1}_k) |\tilde{c}_k|^2 + i\tilde{\gamma}_k \tilde{c}_k \right] - i\varphi_b \tilde{\psi}_0 \quad (\text{A.6})$$

For $c = 0$, instability with respect to small perturbations in ψ will occur if there exists \mathbf{k} such that the coefficient of $|\tilde{\psi}_k|^2$ vanishes, i.e., $1/\tilde{U}_k + \varphi_b = 0$. The cmc is therefore identified as

$$\varphi_{\text{cmc}} = \min_{\mathbf{k}} (-1/\tilde{U}_k) \quad (\text{A.7})$$

Tracing $\tilde{\psi}_k$ out of eq A.6 gives (again, up to a constant factor)

$$Z_2 = \int \mathcal{D}\tilde{c}_k \mathcal{D}\tilde{\gamma}_k \exp\left\{ \int \mathbf{d}\mathbf{k} \left[-\frac{1}{2} \left(\tilde{V}_k - \frac{\varphi_b \tilde{W}_k^2}{1 + \varphi_b \tilde{U}_k} \right) |\tilde{c}_k|^2 - \frac{\varphi_b (\tilde{W}_k \tilde{c}_k + \varphi_b \tilde{U}_k/2)}{1 + \varphi_b \tilde{U}_k} \delta(\mathbf{k}) - i\tilde{\gamma}_k \tilde{c}_k \right] \right\} \times \zeta_p \quad (\text{A.8})$$

Thus, as we found in section II, the small solute induces an effective reduction in the potential between monomers, which becomes more significant as the cmc is approached

$$\tilde{V}_{k,\text{eff}} = \tilde{V}_k - \frac{\varphi_b \tilde{W}_k^2}{1 + \varphi_b \tilde{U}_k} \quad (\text{A.9})$$

The second term in eq A.9 can be identified as the Fourier transform of the induced potential between

monomers, as is phenomenologically introduced in Appendix B, $\tilde{\Phi}_k = -\varphi_b \tilde{W}_k^2 / (1 + \varphi_b \tilde{U}_k)$.

As in the previous sections, the cac is assumed to correspond to the vanishing of the effective interaction

$$\varphi_{\text{cac}} = \min_{\mathbf{k}} \frac{-1/\tilde{U}_k}{1 - \tilde{W}_k^2 / (\tilde{V}_k \tilde{U}_k)} \quad (\text{A.10})$$

If we neglect the finite range of the various interactions and substitute the corresponding simplified potentials (taking the monomer–monomer interaction as repulsive and the monomer–solute and solute–solute ones as attractive, i.e., $u, v, w > 0$)

$$V(\mathbf{r} - \mathbf{r}') = v\delta(\mathbf{r} - \mathbf{r}'), \quad U(\mathbf{r} - \mathbf{r}') = -u\delta(\mathbf{r} - \mathbf{r}'), \\ W(\mathbf{r} - \mathbf{r}') = -w\delta(\mathbf{r} - \mathbf{r}')$$

our mean-field result eq II.9 is recovered

$$\varphi_{\text{cac}} = \varphi_{\text{cmc}} F[V/(w^2 \varphi_{\text{cmc}})] \\ F(x) = 1/(1 + 1/x) \quad (\text{A.11})$$

Beyond Gaussian Approximation. We now calculate the first correction to the Gaussian approximation (i.e., mean field) considering terms of third order in ψ

$$Z \approx Z_3 = \int \mathcal{D}c \mathcal{D}\gamma \mathcal{D}\psi \exp(-\mathcal{H}_2 - \mathcal{H}_3) \times \zeta_p \\ \mathcal{H}_3 = -\frac{i}{6} \varphi_b \int \mathbf{d}\mathbf{r} \psi^3 \quad (\text{A.12})$$

To the same order of approximation we can write

$$\int \mathbf{d}\mathbf{r} \psi^3 \approx \int \mathbf{d}\mathbf{r} \langle \psi^3 \rangle = \int \mathbf{d}\mathbf{k} \mathbf{d}\mathbf{k}' \langle \tilde{\psi}_k \tilde{\psi}_{k-k'} \tilde{\psi}_{k'} \rangle \quad (\text{A.13})$$

where $\langle \dots \rangle$ denotes a thermal average using the Gaussian approximation (\mathcal{H}_2). By means of our results for Z_2 , eqs A.6 and A.8, we find

$$g_1(\mathbf{k}) \equiv \langle \tilde{\psi}_k \rangle = i \frac{\tilde{W}_k \tilde{c}_k + \varphi_b \tilde{U}_k \delta(\mathbf{k})}{1 + \varphi_b \tilde{U}_k} \\ g_2(\mathbf{k}, \mathbf{k}') \equiv \langle \tilde{\psi}_k \tilde{\psi}_{k'} \rangle = g_1(\mathbf{k}) g_1(\mathbf{k}') + \frac{\tilde{U}_k \delta(\mathbf{k} - \mathbf{k}')}{1 + \varphi_b \tilde{U}_k} \\ g_3(\mathbf{k}, \mathbf{k}', \mathbf{k}'') \equiv \langle \tilde{\psi}_k \tilde{\psi}_{k'} \tilde{\psi}_{k''} \rangle = 3g_2(\mathbf{k}, \mathbf{k}') g_1(\mathbf{k}'') - 2g_1(\mathbf{k}) g_1(\mathbf{k}') g_1(\mathbf{k}'') \\ = g_1(\mathbf{k}) g_1(\mathbf{k}') g_1(\mathbf{k}'') + \frac{3\tilde{U}_k \delta(\mathbf{k} - \mathbf{k}')}{1 + \varphi_b \tilde{U}_k} g_1(\mathbf{k}'') \quad (\text{A.14})$$

The expression for g_3 should now be integrated according to eq A.13. However, focusing on the effective pairwise potential between monomers, we look for terms which are quadratic in c . There is only one such term, coming from the integration of $g_1(\mathbf{k}) g_1(\mathbf{k} - \mathbf{k}') g_1(\mathbf{k}')$. This gives

$$\mathcal{H}_3 = -\frac{\varphi_b^2 \tilde{U}_0}{2(1 + \varphi_b \tilde{U}_0)} \int \mathbf{d}\mathbf{k} \frac{\tilde{W}_k^2}{(1 + \varphi_b \tilde{U}_k)^2} |\tilde{c}_k|^2 + \text{nonquadratic terms} \quad (\text{A.15})$$

The effective potential, therefore, is

$$\tilde{V}_{k,\text{eff}} = \tilde{V}_k - \frac{\varphi_b \tilde{W}_k^2}{1 + \varphi_b \tilde{U}_k} \left[1 + \frac{\varphi_b \tilde{U}_0}{(1 + \varphi_b \tilde{U}_0)(1 + \varphi_b \tilde{U}_k)} \right] \quad (\text{A.16})$$

where the second term can be identified, again, as the induced potential, $\tilde{\Phi}_k$. Substituting the simpler potentials, $\tilde{V}_k = v$, $\tilde{U}_k = -u$, $\tilde{W}_k = -w$, we find the corrected scaling function (given in an implicit form)

$$\begin{aligned} \varphi_{\text{cac}} &= \varphi_{\text{cmc}} F[v/(w^2 \varphi_{\text{cmc}})] \\ F^{-1}(y) &= \frac{y(1-y+y^2)}{(1-y)^3} \\ F(x) &\simeq \begin{cases} x - 2x^2 & x \ll 1 \\ 1 - 1/x^{1/3} & x \gg 1 \end{cases} \quad (\text{A.17}) \end{aligned}$$

Appendix B: Scaling Analysis of Partial Collapse

On the basis of a scaling analysis we obtain a more detailed description of the polymer at partial collapse, leading to more accurate predictions regarding the cac. (The reasoning presented in this Appendix is similar to that of ref 29.) As shown in section II, the interaction with the small molecules induces attractive correlations between monomers in the chain. In the following analysis, therefore, the small molecules (e.g., surfactants) do not appear explicitly, but are represented by an effective attractive potential exerted between monomers

$$\Phi(r) = -e^2 \chi(r/\xi)$$

Following the notation of ref 29, e^2 is a coupling constant, ξ a correlation length, and $\chi(r/\xi)$ a dimensionless function which decays fast to zero for $r > \xi$. The two microscopic parameters, e^2 and ξ , are to be related to our phenomenological interaction parameter, w . Assuming weak correlations, $\Phi < 1$ (in units of $k_B T$), we readily obtain for the effective excluded-volume parameter of the chain

$$v_{\text{eff}} = v + \int \mathbf{dr} \Phi(r) = v - k_1 e^2 \xi^3$$

where k_1 is a dimensionless constant. Comparing to eq II.8, we can identify

$$e^2 \sim \frac{V_{\text{ps}}}{\xi^3} \quad (\text{B.1})$$

In accordance with the model presented in section III, we consider a chain of blobs of size ξ , each containing g statistical segments (see Figure 4). The potential of interaction between two blobs consists of a hard-core part for $r < \xi$, and an attractive part for $r > \xi$ coming from the integrated interaction of g^2 pairs of monomers

$$\Phi_{\text{blob}}(r) \sim \begin{cases} \infty & r < \xi \\ g^2 \Phi(r) & r > \xi \end{cases}$$

The resulting excluded-volume parameter for the blobs is

$$v_{\text{blob}} = \int \mathbf{dr} [1 - e^{-\Phi_{\text{blob}}(r)}] \simeq k_2 \xi^3 - k_3 \xi^3 e^{k_4 g^2 e^2} \quad (\text{B.2})$$

where k_2 , k_3 , and k_4 are dimensionless constants. (Note

that although $\Phi < 1$, $\Phi_{\text{blob}} \sim g^2 \Phi$ may be large.) The condition for partial collapse is $v_{\text{blob}} = 0$, i.e.

$$g^2 e^2 = \log(k_2/k_3)/k_4 = \text{const} \quad (\text{B.3})$$

Two relations for e^2 , g , and ξ have been obtained (eqs B.1 and B.3). A third relation comes from the statistics of the polymer, i.e., the power law relating the blob size and number of segments in the blob

$$\xi \sim g' a^z v^{(1-z)/3} \quad (\text{B.4})$$

where a is the length of a Kuhn segment. From the three relations—B.1, B.3, and B.4—we get

$$\begin{aligned} g &\sim \left(\frac{v}{v_{\text{ps}}}\right)^{1/\alpha} \left(\frac{a^3}{v}\right)^{z/\alpha} \\ \xi &\sim \left(\frac{v}{v_{\text{ps}}}\right)^{\nu/\alpha} \left(\frac{a^3}{v}\right)^{\nu z/\alpha} a^z v^{(1-z)/3} \\ \alpha &\equiv 2 - 3\nu \quad (\text{B.5}) \end{aligned}$$

References and Notes

- (1) *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC: Boca Raton, FL, 1993.
- (2) *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Marcel Dekker: New York, 1998.
- (3) Goddard, E. D. In ref 1, Chapter 10. Goddard, E. D.; Ananthapadmanabhan, K. P. In ref 2, Chapter 2.
- (4) Diamant, H.; Andelman, D. *Europhys. Lett.* **1999**, *48*, 170.
- (5) Goddard, E. D. In ref 1, Chapter 4II.
- (6) Goddard, E. D. In ref 1, Chapter 4I.
- (7) Saito, S.; Anghel, D. F. In ref 2, Chapter 9.
- (8) Vasilescu, M.; Anghel, D. F.; Almgren, M.; Hansson, P.; Saito, S. *Langmuir* **1997**, *13*, 6951.
- (9) Anghel, D. F.; Saito, S.; Băran, A.; Iovescu, A. *Langmuir* **1998**, *14*, 5342.
- (10) Lindman, B.; Thalberg, K. In ref 1, Chapter 5.
- (11) Feitosa, E.; Brown, W.; Hansson, P. *Macromolecules* **1996**, *29*, 2169. Feitosa, E.; Brown, W.; Vasilescu, M.; Swanson-Vethamuthu, M. *Macromolecules* **1996**, *29*, 6837. Feitosa, E.; Brown, W.; Swanson-Vethamuthu, M. *Langmuir* **1996**, *12*, 5985.
- (12) Israelachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1991; Chapter 17.
- (13) Linse, P.; Piculell, L.; Hansson, P. In ref 2, Chapter 5.
- (14) Smith, M. L.; Muller, N. *J. Colloid Interface Sci.* **1975**, *52*, 507. Nagarajan, R. *Colloid Surf.* **1985**, *13*, 1; *J. Chem. Phys.* **1989**, *90*, 1980. Hall, D. G. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 885. Ruckenstein, E.; Huber, G.; Hoffmann, H. *Langmuir* **1987**, *3*, 382.
- (15) Shirahama, K.; Yuasa, H.; Sugimoto, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 375.
- (16) Shirahama, K.; Tashiro, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 377.
- (17) Zimm, B. H.; Bragg, J. K. *J. Chem. Phys.* **1959**, *31*, 526.
- (18) Satake, I.; Yang, J. T. *Biopolym.* **1976**, *15*, 2263.
- (19) Delville, A. *Chem. Phys. Lett.* **1985**, *118*, 617. Škerjanc, J.; Kogej, K.; Vesnaver, G. *J. Phys. Chem.* **1988**, *92*, 6382.
- (20) Kuhn, P. S.; Levin, Y.; Barbosa, M. C. *Chem. Phys. Lett.* **1998**, *298*, 51.
- (21) Konop, A. J.; Colby, R. H. *Langmuir* **1999**, *15*, 58.
- (22) Cabane, B.; Duplessix, R. *J. Phys. (Paris)* **1982**, *43*, 1529.
- (23) Abuin, E. B.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6274.
- (24) Winnik, F. M.; Winnik, M. A.; Tazuke, S. *J. Phys. Chem.* **1987**, *91*, 594. Winnik, F. M.; Ringsdorf, H.; Venzmer, J. *Langmuir* **1991**, *7*, 912.
- (25) Gao, Z.; Wasylishen, R. E.; Kwak, J. C. T. *J. Phys. Chem.* **1991**, *95*, 462.
- (26) We have recently demonstrated how the introduction of polymeric degrees of freedom into such a one-dimensional lattice model leads to an effective "cooperativity" among bound surfactants. See Diamant, H.; Andelman, D. Unpublished work; cond-mat/9804086.

- (27) Wallin, T.; Linse, P. *Langmuir* **1998**, *14*, 2940. Sear, R. P. *J. Phys. Condens. Mater.* **1998**, *10*, 1677.
- (28) Nikas, Y. J.; Blankschtein, D. *Langmuir* **1994**, *10*, 3512.
- (29) de Gennes, P.-G. *J. Phys. (Paris)* **1976**, *37*, L-59. Brochard, F.; de Gennes, P. G. *Ferroelectrics* **1980**, *30*, 33.
- (30) de Gennes, P.-G. *J. Phys. Chem.* **1990**, *94*, 8407. Andelman, D.; Joanny, J.-F. *J. Phys. II Fr.* **1993**, *3*, 121. Châtelier, X.; Andelman, D. *J. Phys. Chem.* **1996**, *100*, 9444.
- (31) Piculell, L.; Lindman, B.; Karlström, G. In ref 2, Chapter 3.
- (32) This is always the case for annealed impurities, i.e., additional degrees of freedom which are allowed to equilibrate.
- (33) Barrat, J.-L.; Joanny, J.-F. *Adv. Chem. Phys.* **1996**, *94*, 1.
- (34) Note that this analysis applies only in the case where ν has a purely electrostatic origin. Results are different when additional interactions, e.g., hydrophobic ones, become significant, as is demonstrated in section IV.
- (35) In view of the complexity of polyelectrolyte solutions,³³ the following, more quantitative, attempts should be considered with caution. Being aware of the limitations of such calculations, we restrict ourselves to the simplest case of very weak polyelectrolytes.
- (36) Fixman, M.; Skolnick, J. *Macromolecules* **1978**, *11*, 863.
- (37) Many workers have chosen to present experimental results by means of $c_{1/2}$ (sometimes referred to as $1/Ku$), the surfactant concentration at which the binding reaches half of its saturation value, rather than the cac. The effect of parameters such as c_{salt} and I_{on} on $c_{1/2}$ is a combination of two different effects: one on the cac value and another on the binding cooperativity (isotherm slope). As a result, this presentation tends to obscure the universal nature of the phenomenon. In Table 1 and Figure 3 we present only cac values, i.e., the concentrations corresponding to the onset of association. Although less sharply defined, these are the values relevant to our analysis.
- (38) Benrraou, M.; Zana, R.; Varoqui, R.; Pefferkorn, E. *J. Phys. Chem.* **1992**, *96*, 1468.
- (39) Anthony, O.; Zana, R. *Langmuir* **1996**, *12*, 1967.
- (40) Wei, Y. C.; Hudson, S. M. *Macromolecules* **1993**, *26*, 4151.
- (41) Shimizu, T.; Seki, M.; Kwak, J. C. T. *Colloid Surf.* **1986**, *20*, 289.
- (42) Kiefer, J. J.; Somasundaran, P.; Ananthapadmanabhan, K. P. *Langmuir* **1993**, *9*, 1187.
- (43) Chandar, P.; Somasundaran, P.; Turro, N. J. *Macromolecules* **1988**, *21*, 950.
- (44) Satake, I.; Takahashi, T.; Hayakawa, K.; Maeda, T.; Aoyagi, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 926.
- (45) Hansson, P.; Almgren, M. *J. Phys. Chem.* **1995**, *99*, 16684.
- (46) Malovikova, A.; Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1984**, *88*, 1930.
- (47) Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1982**, *86*, 3866.
- (48) This value seems to be much lower in the case of multivalent salt. See: Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1983**, *87*, 506.
- (49) Ananthapadmanabhan, K. P. In ref 1, Chapter 8.
- (50) Hayakawa, K.; Kwak, J. C. T. In *Cationic Surfactants*; Rubingh, D. N., Holland, P. M., Eds.; Marcel Dekker: New York, 1991.
- (51) Wang, G.; Olofsson, G. *J. Phys. Chem. B* **1998**, *102*, 9276.
- (52) Corti, M.; Degiorgio, V. *J. Phys. Chem.* **1981**, *85*, 711.
- (53) Kamenka, N.; Zana, R. *J. Colloid Interface Sci.* **1997**, *188*, 130.
- (54) Murata, M.; Arai, H. *J. Colloid Interface Sci.* **1973**, *44*, 475.
- (55) Moreover, according to eq II.11 there should be a weak decreasing dependence of $\varphi_{\text{cac}}/\varphi_{\text{cmc}}$ on φ_{cmc} , which seems to agree with the data of Table 2.
- (56) Interestingly, the cac was found to be accompanied by a coil-to-globule collapse in certain DNA-surfactant systems: Mel'nikov, S. M.; Sergeev, V. G.; Yoshikawa, K. *J. Am. Chem. Soc.* **1995**, *117*, 2401, 9951.
- (57) Note that the following analysis treats a single chain and is applicable, therefore, only in the dilute polymer limit.
- (58) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
- (59) Fisher, M. E. *Phys. Rev.* **1968**, *176*, 257.
- (60) Harris, A. B. *J. Phys. C* **1974**, *7*, 1671.
- (61) Note that for a self-avoiding walk with a Flory exponent, $\nu = 3/(d + 2)$, the self-consistency condition is satisfied for $d < 4$. This is in accord with the fact that short-range interactions (in our case the interaction induced by the small molecules) become irrelevant to polymer statistics for $d \geq 4$.
- (62) As the small molecules interacting with the polymer are allowed to equilibrate (i.e., they are represented by annealed degrees of freedom), the Fisher renormalization⁵⁹ seems a priori to be the more relevant analogy. Note, however, that the scaling analysis given above has not included any explicit annealing. Minimization with respect to φ has already been performed in the calculation of ν_{ps} in Section II (eq II.8). Once this dependence has been specified, the partial collapse analysis regards the correlations (i.e., ν_{ps}) as an effective quenched perturbation—hence the similarity to Harris' analysis. In fact, the calculation of Appendix B is analogous to a general derivation of the Harris criterion; see: Ma, S.-K. *Modern Theory of Critical Phenomena*; Benjamin-Cummings: Boston, MA, 1976; Chapter X. Our self-consistency condition thereby parallels the requirement that the disorder be a relevant variable in the renormalization-group sense. Indeed, Fisher's change of exponents, $\nu \rightarrow \nu/(d\nu - 1)$, does not give relevant results in the current case (e.g., for a two-dimensional polymer with excluded volume, this transformation gives a change of ν from $3/4$ to the unphysical value of $3/2$).
- (63) Holmberg, C.; Nilsson, S.; Singh, S. K.; Sundelöf, L.-O. *J. Phys. Chem.* **1992**, *96*, 871. Nilsson, S. *Macromolecules* **1995**, *28*, 7837.
- (64) Cabane, B.; Duplessix, R. *Colloid Surf.* **1985**, *13*, 19.
- (65) Jennings, D. E.; Kuznetsov, Y. A.; Timoshenko, E. G.; Dawson, K. A. *J. Chem. Phys.* **1998**, *108*, 1702.
- (66) Norwood, D. P.; Minatti, E.; Reed, W. F. *Macromolecules* **1998**, *31*, 2957. Minatti, E.; Norwood, D. P.; Reed, W. F. *Macromolecules* **1998**, *31*, 2966.
- (67) Gilanyi, T.; Wolfram, E. *Colloid Surf.* **1981**, *3*, 181.
- (68) Ullner, M.; Jönsson, B.; Peterson, C.; Sommelius, O.; Söderberg, B. *J. Chem. Phys.* **1997**, *107*, 1279. Ha, B. Y.; Thirumalai, D. *Macromolecules* **1995**, *28*, 577. Reed, W. F.; Ghosh, S.; Medjahdi, G.; Francois, J. *Macromolecules* **1991**, *24*, 6189.
- (69) Binana-Limbelé, W.; Zana, R. *Macromolecules* **1987**, *20*, 1331. Binana-Limbelé, W.; Zana, R. *Macromolecules* **1990**, *23*, 2731. Cochin, D.; Candau, F.; Zana, R. *Macromolecules* **1993**, *26*, 5755, 5765. Cochin, D.; Candau, F.; Zana, R.; Talmon, Y. *Macromolecules* **1992**, *25*, 4220. Zana, R.; Kaplun, A.; Talmon, Y. *Langmuir* **1993**, *9*, 1948. Kamenka, N.; Kaplun, A.; Talmon, Y.; Zana, R. *Langmuir* **1994**, *10*, 2960. Anthony, O.; Zana, R. *Macromolecules* **1994**, *27*, 3885. Anthony, O.; Zana, R. *Langmuir* **1996**, *12*, 3590.
- (70) Chen, L.; Yu, S.; Kagami, Y.; Gong, J.; Osada, Y. *Macromolecules* **1998**, *31*, 787.
- (71) Magny, B.; Iliopoulos, I.; Zana, R.; Audebert, R. *Langmuir* **1994**, *10*, 3180.
- (72) Satake, I.; Gondo, T.; Kimizuka, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 361.
- (73) Diamant, H.; Andelman, D. *Phys. Rev. E* **2000**, *61*, 6740.
- (74) See, e.g., Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, England, 1986; Chapter 2.