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Abstract. We examine theoretically the effect of electrostatics on the self-assembly of charged cylindrical micelles which behave as living polymers. The growth of micelles as a function of increasing surfactant and/or electrolyte concentration exhibits three distinct regimes. The most striking feature of the growth law is the existence of a dilute regime, (i), in which the average micelle size varies slowly with concentration. At higher concentrations, regimes (ii) and (iii) are characterized by more rapid growth than for neutral micelles. This may be responsible, in part, for the anomalous scaling of rheological properties, as observed in recent experiments.

Living polymers are chain-like objects which can break and recombine reversibly. Certain solutions of surfactant in water exhibit this behaviour, due to the spontaneous aggregation of extended worm-like micelles [1–6]. At sufficiently high concentrations of surfactant in water, these micelles result from the favourable packing of surfactant molecules into locally cylindrical structures with hydrophobic tails in the interior, and with water exterior. The less favourable packing of the surfactant tails near the end-caps of these cylinders gives rise to a large energy cost, α, for the breaking of micelles. When the micelles are very long, these solutions have many features that are qualitatively similar to those of polymer solutions. Several experiments, for example, have demonstrated polymer-like scaling of dynamical (rheological) properties with surfactant concentration, ϕ. The dynamics of such systems are somewhat more complex, however, because the micelle aggregation number (or, degree of polymerization), $\bar{N}$, is itself a function of concentration, with $\bar{N} \sim \phi^{1/2}$ expected for long semi-flexible cylinders with spherical endcaps [7]. In addition, the process of stress relaxation is enhanced by the presence of breaking and recombination reactions. A recent theory [8], which takes into account both of these effects, predicts a dependence on ϕ of the viscosity, stress relaxation time and the self-diffusion constant that is in reasonable agreement with experiments [9.10] on CTAB/KBr when the concentration of added salt is high. In this paper, we study the effects of electrostatic interactions on the aggregation number of such systems. Our analysis is prompted by recent experiments [9] performed with ionic surfactants at low salt concentrations, which report a stronger concentration dependence of the dynamical properties of the worm-like micelles than is observed at high salt concentrations.

For neutral or highly screened micelles, the large end-cap energy, α, favours the production of fewer end-caps, and hence, large micelles, while the entropy of mixing favours the creation of many more small micelles. This competition gives rise

to a broad distribution of micelle lengths: $c_N \sim \exp[-N/\bar{N}]$, where c_N represents the concentration of micelles with aggregation number, N. Furthermore, the mean aggregation number, $\bar{N}$, exhibits a power law growth with surfactant concentration, ϕ, as well as an exponential dependence on the end-cap energy: $\bar{N} \sim \phi^{1/2} \exp[\alpha/2]$. In addition, a recent theory based on this growth law predicts [8] a power law scaling for the viscosity: $\eta \sim N\phi^3 \sim \phi^{3.5}$. The experimental results at high salt ([KBr] ≥ 0.25 M) are close to this prediction. At lower salt concentrations, however, the observed scaling of both the viscosity and the self-diffusion differ substantially from neutral systems [9]. This anomalous scaling behaviour may be due to a change in the growth law expressing the scaling of micellar length, $\bar{N}$, with concentration, ϕ. In this work, we demonstrate that, as a result of electrostatic effects, there are three distinct regimes for this growth law, depending on concentration: (i) the dilute regime, which is characterized by micellar lengths that are nearly independent of surfactant concentration; (ii) the semi-dilute regime, in which $\bar{N}$ grows much faster than the power law governing the growth of neutral micelles; and (iii) a higher concentration regime, in which the growth follows an effective power law, $\bar{N} \sim \phi^{1/2(1+\Delta)}$, at very low salt concentrations.

The self-assembly of charged micelles is more complex than for neutral systems because the presence of counterions introduces a new length scale, namely the screening length. With added salt in the solution, this is just the usual Debye length, κ^{-1}. In the absence of salt, however, the presence of counterions results in an effective concentration dependent screening length, R_b, which is just the mean separation between micelles. This is because any volume of dimension greater than this length must be approximately neutral. Regime (i) results from a purely energetic minimum in the free energy per surfactant for micelles which are short compared with the screening length [11].

The crossover from regime (i) to (ii) occurs when the micellar length becomes comparable with the screening length of electrostatic interactions. Without added electrolyte, this happens when the volume fraction is approximately equal to ϕ^*, the overlap threshold between the dilute and semi-dilute regimes. Above this concentration, the effect of electrostatics can be understood as an effective reduction, $\Delta E(\phi) \sim -1/\sqrt{\phi}$, in the end-cap energy, α. This is due to the work done by separating charges on the micelle by a distance of order $R_b \sim 1/\sqrt{\phi}$, upon breaking [11]. This results in a strong enhancement of the growth of micelles with increasing concentration: $\bar{N} \sim \phi^{1/2} \exp[\Delta E(\phi)]$.

At still higher concentrations (regime (iii)), the dominant contribution to the effective end-cap energy is due to the increased entropy of mixing of the counterions in the environment of the end-caps. This favours the production of end-caps, and results in an effective reduction of α by a term which varies as $\log \phi$, to leading order. This decreases less rapidly with concentration than the term discussed in the context of regime (ii). Therefore, this effect will dominate at high surfactant concentrations, resulting in an effective power law: $\bar{N} \sim \phi^{1/2+\Delta/2}$, where the enhancement, Δ, of the growth exponent depends on the number of charges on an end-cap [12].

The growth in regimes (i) and (ii) can be derived from the electrostatic self-energy of a charged cylinder in the background of counterions. This calculation is motivated by an exact solution of the Poisson–Boltzmann equation for the counterion distribution surrounding a charged rod of radius a, and bare charge per unit length ν, in the absence of added electrolyte [13]. Cylindrical symmetry and charge neutrality are imposed in a Wigner–Seitz cell of radius R_b. For highly charged cylinders, most of the counterions

are bound within a narrow region near the surface of the cylinders, and the remaining counterion density has only a weak spatial dependence. Furthermore, the net charge density (surface charge plus bound counterions) is nearly independent of cylinder density—provided that the cylinders are long compared with R_b. An approximate variational solution [12] of the Poisson–Boltzmann equation demonstrated that the semi-dilute system of cylinders can be approximated by rods with an effective charge per unit length [14], $\nu^* \simeq 1/l$, where $l = e^2/\epsilon kT$ is the Bjerrum length, and ϵ is the dielectric constant. In this model, the density of unbound counterions is uniform. This model is applied to semi-dilute worm-like micelles, where the effective Wigner–Seitz cell radius is $R_b = a/\sqrt{\phi}$, which corresponds to the mesh size for stiff rods.

The electrostatic self-energy of such a system involves three contributions: the interaction of counterions with each other; the (bare) self-energy of the surface charges; and the interaction of counterions with the surface charge density. With the assumption of a uniform counterion density, the first of these contributions depends only on ϕ, and hence, does not affect the size distribution. Surface charges at positions r and r' along the cylinder repel each other, yielding a contribution to the self-energy which is given by $l/|r - r'|$. For intermediate separations $a \lesssim |r - r'| \ll R_b$, this repulsion is not significantly modified by the presence of counterions. For separations larger than R_b, however, overall charge neutrality results in a highly screened interaction between surface charges. For example, given an individual charge on the surface, the net charge enclosed within a concentric spherical shell of radius greater than R_b is approximately zero. The electrostatic self-energy can be approximated by [11]

$$E_L = l\nu^{*2} \begin{cases} L\log(1/\sqrt{\phi}) - a/\sqrt{\phi} & \text{if } L \geq a/\sqrt{\phi} \\ L\log(L/a) - L & \text{if } L < a/\sqrt{\phi}. \end{cases} \tag{1}$$

Here, the first expression is asymptotically correct for semi-dilute solutions, where the Coulomb energy has been integrated over separations less than $R_b = a/\sqrt{\phi}$, while in the dilute limit the Coulomb interaction is unscreened over the whole length, L, of the cylinder.

In dilute solutions, where the average value of L satisfies $\bar{L} \ll a/\sqrt{\phi}$ (regime (i)), the competition between the end-cap energy, α, and the electrostatic self-energy of (1) results in a well defined minimum of the free energy per surfactant, as a function of aggregation number. This is in contrast to the case of neutral micelles or the case of semi-dilute solutions, for which the length distribution is broad. The minimum of the free energy in the dilute limit for charged micelles results from the divergence of the self-energy *per unit length* in (1). This minimum depends only weakly on ϕ:

$$\bar{L} \simeq \frac{\alpha + \log(\phi/\bar{N})}{l\nu^{*2}}. \tag{2}$$

At higher concentrations such that $\bar{L} \gg a/\sqrt{\phi}$ (the semi-dilute regime, (ii)), the size distribution can be calculated as for the neutral case but with a reduced effective end-cap energy: $\alpha \to \alpha - la\nu^{*2}/\sqrt{\phi}$. Physically, the effective reduction of the end-cap energy is due to repulsion of the surface charges, which favours breaking of micelles. The resulting characteristic aggregation number is

$$\bar{N} \simeq 2\phi^{1/2} \exp\left[\tfrac{1}{2}(\alpha - la\nu^{*2}/\sqrt{\phi})\right]. \tag{3}$$

This does not represent a power law, in contrast to the high salt limit, where the growth law exponent is 1/2. The apparent divergence of the growth rate as $\phi \to 0$

reflects the divergence of the electrostatic energy of long micelles as the screening length increases. This leads to a collapse of the micelles in the dilute limit, so that the case $L < a/\sqrt{\phi}$ in (1) must be considered.

The analytic expressions for the growth in (2) and (3) are derived using one or the other of the limiting forms for the self-energy in (1). Nevertheless, the qualitative behaviour in both the dilute and semi-dilute regimes is borne out by a numerical evaluation [11] of $\bar{N}$, which is necessary for intermediate concentrations, where both overlapping and non-overlapping micelles coexist. The resulting calculation of micellar length is shown in figure 1. The crossover, ϕ^*, between the dilute and semi-dilute regimes occurs for $\bar{L} \simeq a/\sqrt{\phi}$. We can estimate the dependence of ϕ^* on ν^* and α from (2): $\phi^* \simeq (la\nu^{*2}/\alpha)^2$, provided that α is large.
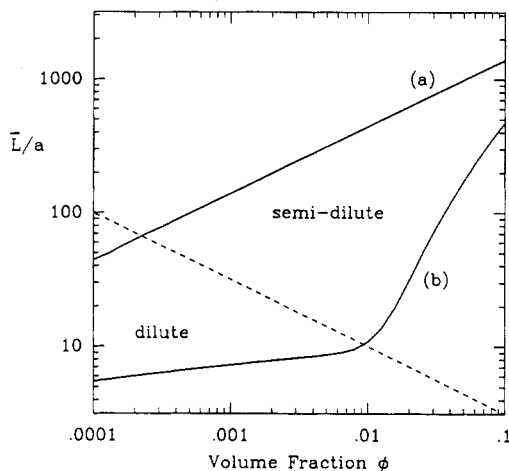

Figure 1. The elongation of micelles with increasing surfactant concentration. Curve (a) is for neutral micelles, while (b) is for $\alpha = 20$, $Na/L = 10$ and $\nu^{*2}la = 1$. The broken line represents the crossover from dilute to semi-dilute solutions. This occurs for stiff rods of length $\bar{L} \simeq a/\sqrt{\phi}$.

In addition to the electrostatic self-energy of the finite-size cylindrical core described above, the growth of micelles is also modified by the increased entropy of the counterions near the end-caps. Physically, this effect arises because the counterions are less tightly bound near the end-caps. Both the fraction of counterions which escape, as well as the effective volume which they occupy depend on ϕ. The resulting contribution to the free energy, valid for semi-dilute solutions, also favours the formation of end-caps to a lesser degree as the concentration is increased. Our estimate of this effect is motivated by the idea that for long micelles, the end-caps are extremely dilute 'species' in a semi-dilute environment of locally cylindrical objects. The difference in the free energy per counterion (and thus per surfactant) for hemispherical end-caps relative to cylinders is found to vary as $\log \phi$, to leading order [12]. In the semi-dilute limit, which in our case corresponds to the combined limits $\phi \to 0$ and $\bar{L} \to \infty$ with $\phi\bar{L}/a \gg 1$, the electrostatic core energy of (1) dominates. On the other hand, at higher concentrations (regime (iii)), the entropic contribution dominates, and the growth may be characterized by an effective power law, $\bar{N} \sim \phi^{1/2(1+\Delta)}$, where Δ is proportional to the effective charge on an end-cap.

So far, our discussion has focused on the case of no added electrolyte. As we have shown, however, the electrostatic self-energy depends only on the screening length (and the effective charge density, ν^*). The self-energy for high salt concentrations, n_s, was calculated by Odijk [15]. Our results can be extended [11] to intermediate and high-salt regimes, in which ϕ is replaced by an effective volume fraction $\tilde{\phi} = \phi + 8\pi l a^2 n_s$. Thus, for example, in a dilution series with a fixed ratio of salt to surfactant [16], we can expect $\bar{L}$ plotted against $\tilde{\phi}$ to appear as in figure 1. In particular, the crossover from screened to unscreened behaviour occurs when the micelle length becomes comparable with the screening length, which corresponds to the *dilute* regime. This is important for experiments, since a direct measure of aggregation number may not be possible for semi-dilute solutions.

We have shown that the growth of charged worm-like micelles is characterized by three regimes: (i) for $\phi < \phi_1$, the micelle size is nearly independent of concentration; (ii) for $\phi_1 < \phi < \phi_2$, the aggregation number $\bar{N} \sim \exp(-A/\sqrt{\phi})$ is a very strong function of concentration; and (iii) for $\phi > \phi_2$, an effective power law growth is evident. The most striking signature of the electrostatic effects is the crossover from a dilute regime, in which the micelle growth is very weak, to a regime of rapid growth. This is in marked contrast to the situation for neutral, or highly screened micelles, in which the growth exhibits simple power law behaviour at all concentrations. For a finite salt concentration, n_s, the growth law can be characterized by an effective concentration, $\tilde{\phi} = \phi + 8\pi l a^2 n_s$, which is directly related to the screening length of the electrostatic interactions. Thus, for example, the crossover between regimes (i) and (ii) occurs for *dilute* solutions, with moderate electrolyte concentrations. In practice, the distinction between regimes (ii) and (iii) may be blurred by the fact that experiments are likely to provide a direct measure of $\bar{L}$ over at most a decade in concentration. Nevertheless, a rapid growth in micelle size has been observed [16], which is in qualitative agreement with regimes (ii) or (iii).

Acknowledgments

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