Stretching and Collapse of Neutral Polymer Layers under Association with Ionic Surfactants

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We provide experimental evidence for stretching and collapse of neutral polymer layers, already adsorbed at an oil-in-water interface, due to its interaction with surfactants. Upon stretching, the first interaction length ($2L_0$) follows a power law dependence on surfactant concentration ($\propto C_s^x$, where $x \approx 0.5$ for cationic surfactants) and collapses in the presence of salt, as a relatively weak power law (C_s^{-y}, where $y = 0.17$), in good agreement with brush length decay for polyelectrolyte brushes.

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Associative behavior of polymers has been a topic of intense research for the past few decades, due to its numerous industrial applications such as waterborne paints, cosmetics, pharmaceuticals, etc. [1]. Most of the investigations on associative behavior deal with interactions between polymer and surfactant molecules in solutions [1]. Interaction of surfactant and polymers in the presence of an interface can be much more complicated. Three different scenarios can exist, depending upon the nature of the polymer, the interface, and the surfactant [2]. In the first case, the polymer and the surfactant are noncomplexing but both adsorb at the interface, where there will be competition for surface sites. In the second case, the polymer and the surfactant form a complex but only one adsorbs at the interface. In the third case, both the polymer and the surfactant adsorb at the interface and form a solution complex.

In this Letter, we investigate the third scenario, i.e., the effect of surfactant interaction with a polymer that is already adsorbed at an oil-in-water interface and its influence on colloidal forces. Although there are a number of studies on the associative nature of polymers in bulk solutions [1] and solid interfaces [2,3], there are no reports on the effect of surfactant interaction with a polymer which is already adsorbed at a liquid-liquid interface such as emulsions. Since the interplay of forces acting between the colloidal particles determines the stability of the colloidal system, an understanding of the nature of forces existing between the colloidal particles is challenging from both a fundamental point of view and practical consideration, to tailor colloidal formulations with long-term stability. Here, using the new force measurement approach [4,5], we have been successful in investigating the role of associative polymers on colloidal forces, in the presence of ionic and nonionic surfactants.

The polymer used in these experiments was a statistical copolymer of vinyl alcohol (88%) and vinyl acetate (vac-12%), which is randomly distributed along the polymer chain with an average molecular weight of 40 000 units (40 K). The unperturbed radius of gyration of the free polymer (R_g) was obtained from dynamic light scattering and viscometric measurements. The polymer concentration used in all of our experiments was 0.68 wt %. Surfactants used were cetyltrimethyl ammonium bromide (CTAB), tetradecyltrimethyl ammonium bromide (TTAB), and nonyl phenol ethoxylate (NP10), which was obtained from Sigma, USA. Triply distilled water filtered with a 0.22 μm millipore filter was used. Direct emulsion (i.e., oil in water) of the ferrofluid was used. The ferrofluid oil consists of a collection of ferromagnetic domains of Fe_2O_3, of about 10 nm size, dispersed in the octane. Monodispersed emulsions with droplets with a diameter of about 200 nm were used.

Details of the experimental technique are described in earlier publications [4,5]. We briefly discuss the force measurement procedure. As the ferrofluid droplets are superparamagnetic in nature, an applied field induces a magnetic dipole in each drop, causing them to form chains. Because of the presence of the one-dimensional ordered structure, a Bragg peak can be observed, from which the interdroplet separation (h) can be estimated precisely, using a spectrograph. The sensitivity in the distance measurement, in our experimental setup, was 0.1 nm. The range of force that can be probed using this technique is 10^{-11} to 10^{-13} N. The detection limit of force in the magnetic chaining technique (10^{-13} N) corresponds to the minimum force that is required for formation of chains where the magnetic interaction energies become comparable to thermal energies. To study the effect of polymer adsorption on the force profiles, the emulsion was washed with poly vinyl alcohol (PVA) solution for about 4–5 times and then incubated for about 72 h. For association experiments, the required quantity of surfactants was added to the incubated emulsion and the force measurements have been performed at 23 °C.

The main contributions to the interaction free energy for two colloidal particles, covered with polymers, approaching each other are originating from the loss of configurational entropy of the polymer and the excluded volume interaction. The repulsive force as a function of distance between the ferrofluid droplets, covered with PVA, for various CTAB concentrations is shown in Fig. 1. The force profile in the absence of any surfactant is the reference curve (0 mM). It can be seen that the force

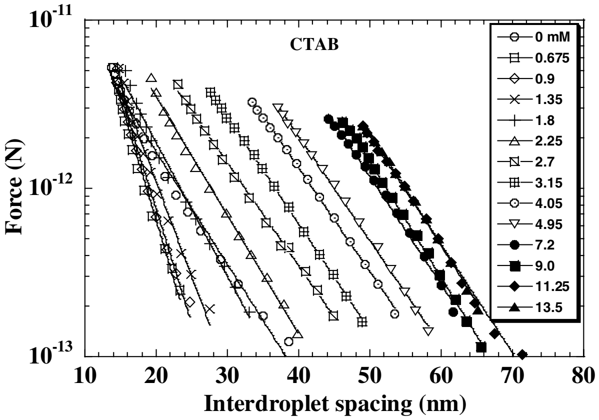

FIG. 1. Forces between the ferrofluid droplets, as a function of distance, for various CTAB concentrations. The best fit obtained using Eq. (1) is shown by the solid line.

profiles are repulsive and exponentially decaying with a characteristic decay length (λ) close to R_g of the free polymer. All the force profiles can be represented by a simple exponential function [4–6]

$$F(h) = k \exp\left(\frac{-h}{\lambda}\right), \tag{1}$$

where h is the interdroplet spacing and λ is the decay length. These observations are consistent with the theoretical predictions obtained using both mean field and scaling approaches [7]. Force measurement studies using a relatively new optical technique [8], on micron sized silica spheres, covered with a neutral polymer, also found a similar exponential decay ($\lambda \approx 0.6R_g$). The λ values obtained from the force profile was about 6 nm, which was in good agreement with the R_g of 6.4 nm obtained from our viscometric measurement.

From the force profiles, we deduce three parameters: λ from the slope, the first interaction length or onset of repulsion ($2L_0$) defined as the distance at which the magnitude of force is 2×10^{-13} N, and the magnitude of force (k). Up to a concentration of 0.9 mM of CTAB, the λ and $2L_0$ decreased slightly, above which the force profile displaced from its equilibrium position without much variation in the λ values. However, the $2L_0$ increases by several nanometers. As the concentration of CTAB increases further, both k and $2L_0$ increase until a CTAB concentration of 11.25 mM. Further increase in the surfactant concentration (up to 35 mM) did not change the force profiles significantly. In the case of TTAB, the force profiles follow the same trend. However, for NP10, force profiles did not show significant variations with increase in surfactant concentration, which was varied from 0.0175 to 3.5 mM [~5 CMC (critical micellar concentration)]. Though the range of force has been increased slightly, the variation was not significant compared to the cationic surfactants.

The $2L_0$ values in the absence of salt are shown in Fig. 2. In the case of CTAB and TTAB, the $2L_0$ values for the lowest concentration of surfactant (below 0.05 mM) correspond to 30 nm, which is about $5R_g$. As the surfactant concentration increases, the $2L_0$ decreases slightly up to a surfactant concentration of 0.7 mM, which we believe is due to the neutralization of the residual anionic surfactant present at the oil-water interface. Here, the Na^+ ions bound to the polymer coil are neutralized by the Br^- ions. Once the charge neutralization is complete, the decay length increases further. This was evident from our earlier investigations with sodium dodecyl sulphate, where we did not notice such a decrease [5]. Further increase in the surfactant concentration leads to a dramatic increase in $2L_0$ until it reaches saturation at around 10 mM for both CTAB and TTAB. The value of $2L_0$ above 10 mM surfactant remains the same, which corresponds to about $10R_g$. In the case of NP10, the change in the $2L_0$ value was not very significant over the surfactant concentration range of 0.0175 to 35 mM ($2L_0$ changes from 31 to 40 nm). At intermediate concentrations (≈ 1 to 10 mM) of CTAB and TTAB, the first interaction length follows a power law dependence $2L_0 \propto C_s^x$, where x for CTAB and TTAB were, respectively, 0.51 and 0.44.

Figure 3 shows the force profiles for different salt (NaCl) concentrations in the case of PVA-CTAB. The polymer and surfactant concentrations remain constant at 0.68 wt% and 35 mM, respectively. Under the above conditions, we probe the effect of salt on already stretched polymer-surfactant brushes. It has been found that the range of repulsion decreases with increasing salt concentration range of 0.5 to 0.005 M for both ionic systems. However, the decay lengths remain comparable to the unperturbed R_g values. The variation of $2L_0$ with

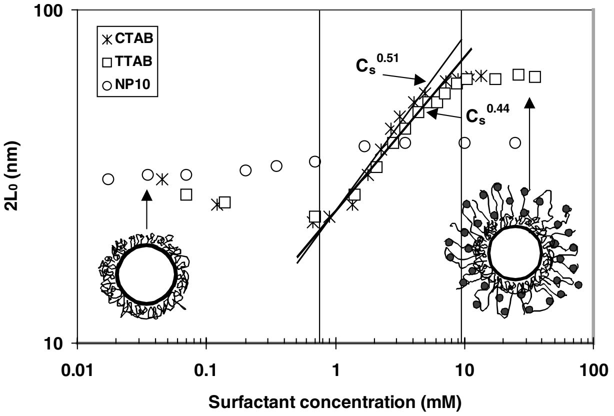

FIG. 2. The first interaction length ($2L_0$) values deduced from the force curves, for different surfactant concentrations. At the intermediate concentrations of CTAB and TTAB, the first interaction length $2L_0$ follows a power law dependence $2L_0 \propto C_s^x$, where the exponent x for CTAB and TTAB were, respectively, 0.51 and 0.44. The structures of polymer-surfactant complex on emulsion droplets at two extremes are depicted in the inset.

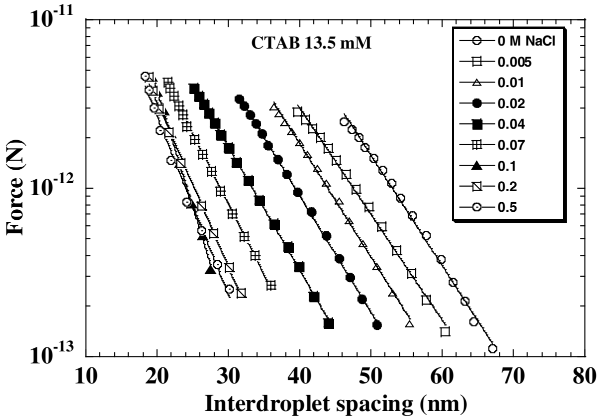

FIG. 3. The force profiles for different salt concentrations for PVA-CTAB. The polymer and surfactant concentration was 0.68 wt% and 13.5 mM, respectively. The concentration of salt for each curves is shown in the inset. The best fit is shown by the solid line.

the addition of salt is shown in Fig. 4. The concentration of CTAB, TTAB, and NP10 in these three cases was 13.5, 35, and 3.5 mM, respectively. The initial values of $2L_0$, without salt, for CTAB and TTAB are about $10R_g$. In the case of NP10, the $2L_0$ value was roughly about $6R_g$. Upon the addition of NaCl, the $2L_0$ value decreases continuously because of the collapse of stretched tails due to screening of bound charges on the polymer coil. For CTAB and TTAB, the $2L_0$ decay follows a power law ($2L_0 \propto C_s^{-y}$ with $y = 0.179$). Here, C_s is the concentration of NaCl. In the case of NP10, the exponent value was very weak (0.06).

At the concentrations of polymer used in our experiments, the oil-water interface is fully covered with adsorbed polymer (i.e., the plateau region in the adsorption curve). Typical measured values of the adsorbed amount of polymers are about 1.5 to 2.2 mg/m^2. Normally, the polymer adsorbed at the oil-water interface adopts some arbitrary conformation with loops, trains, and tails [6–9]. Addition of surfactant leads to changes in the hydrophobic-hydrophilic balance of the polymer coil, which can cause conformational changes in the polymer coil. Theory [7] distinguishes the loops and tails sections of the adsorbed chains and involves three length scales, the adsorbed layer thickness λ, and an adsorption length z^* that separates the regions where the monomer concentration is dominated by loops and by tails. As our experimental decay lengths remain comparable to the unperturbed radius of free polymers throughout the surfactant concentrations, we believe that the ionic surfactants are bound to the sparsely covered "distal regime" which is further stretched by the bound surfactant molecules or micelles. As the concentration increases, more and more surfactant molecules and micelles go into the folded chains (central regime) that stretch more loops further. Therefore, at higher surfactant concentrations, the neutral polymer chains at the interface are likely to adopt a di-bloc polyelectrolyte type of conformations on the emulsion droplet, with one bloc (hydrophobic-vac) anchored at the oil interface and the other block (hydrophilic-PVA) with adsorbed micelles stretched out in the continuous phase. Here, the charges on the chain repel each other and the electrostatic repulsion collectively lead to chain stretching on length scales larger than the electrostatic blob size [10]. The stretching is expected to continue until the coils are saturated with adsorbed surfactant micelles. The conformations of polymer-surfactant complexes at the oil-water interface at the two extremes are depicted in the inset of Figs. 2 and 4.

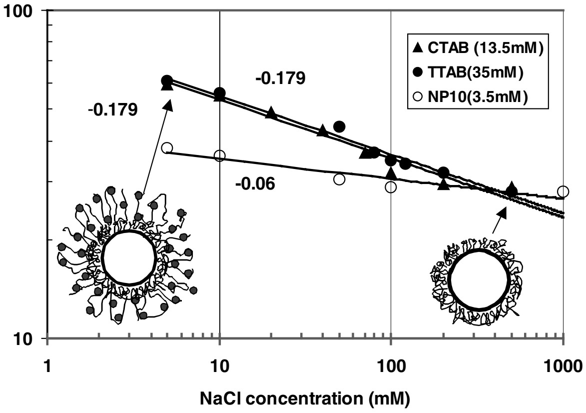

FIG. 4. The first interaction length ($2L_0$) at different concentrations in the presence of salt. For CTAB and TTAB, in the presence of salt, the first interaction length follows a power law scaling $2L_0 \propto C_s^{-y}$ with a critical exponent $y = 0.179$. In the case of NP10, the exponent was very weak (0.06). The structures of polymer-surfactant complex on emulsion droplets at two extremes are depicted in the inset.

We compare our experimental results with the theoretical predictions. According to the approach of Pincus [11], for a planar surface to which a polyelectrolyte is end-grafted, the brush height L in the absence of electrolyte is $L \approx f^{0.5}Na$. The ideally flexible polymers, each containing N monomeric units and having a fixed fraction f of monomers, possess an ionic group where a is the monomer dimension. Therefore, the chains are highly stretched for finite charging and the brush thickness is independent of the grafting density. The neutral polymer coils with bound ionic micelles should mimic the above situation. Surprisingly, at intermediate concentrations of CTAB and TTAB, the first interaction length $2L_0$ follows a power law dependence $2L_0 \propto C_s^x$, where x is about 0.5. This shows that the chain stretching due to surfactant interaction with adsorbed polymer layers resembles brush length expansion in the case of polyelectrolytes.

The electrolyte plays a crucial role in determining the brush structure only when its concentration is sufficiently large and the corresponding Debye length κ^{-1} is comparable to the neutralization length ξ. As the salt concentration increases ($\kappa^{-1}\xi \geq 1$), the Debye screening length reduces the counterion osmotic pressure, which stretches the polymer coil. In the above case, the brush is expected to collapse with increasing salt concentration but only as a relatively weak power law [11] $L \approx Na(2ad^2C_s)^{-1/3}$. Although theories predict a variation in the exponent values between 0.33 to 0.6 (e.g., Pincus 0.33 [11]; Fixman 0.5 [12]; Zhulina 0.33 [13]; Argiller and Tirrel 0.66 [14]; von Goeler and Muthukumar 0.33 [15]), the experimental observations reveals that the exponent value is lower than predicted. For example, the scaling exponent was found to be 0.17 and 0.08, respectively, for polyelectrolyte brushes densely coated on polystyrene lattices and a sparsely covered diamond surface [16]. The experimental value of the exponent for a flat surface reported by Tirrell was 0.21 [17]. For fixed chain density, the energy penalty for excluded volume interactions is stiffer for a surface of lower curvature.

Recently, the bob model of Daoud-Cotton [18] is slightly modified [16], ignoring the local chain stiffening (same as in the Pincus approach [11]) but modified the excluded volume for interacting polyelectrolyte segments in line with the Odijk approach [19]. According to this model [16], for a flat surface ($R \rightarrow \infty$), $L_\infty \sim C_s^{-1/6}$and the limit ($R \rightarrow 0$), $L_0 \sim C_s^{-1/10}$, where R is the radius of the particle. Strikingly, our experimental results reveal that the collapse of the brush follows a similar power law dependence, with an exponent of 0.179, in good agreement with that exponent observed in the case of polystyrene lattices (0.17) covered with a polyelectrolyte. The diameter of the polystyrene particle used in the experiment is 137 nm, which is comparable to the size of ferrofluid droplets (188 nm) used in our force experiments. Therefore, the observed power law scaling reinforces the fact that the neutral polymers are converted into partial polyelectrolytes when they associate with ionic surfactants. In the case of NP10, though association between the polymer and the surfactant molecules takes place, due to the absence of electrostatic repulsion, the chain stretching and collapse is less prominent compared to charged micelles.

Another interesting observation is that the force profiles were remarkably reproducible in the presence of polymer-surfactant complexes. In the presence of polymer alone, the force profiles often show slight hysteresis with time, due to changes in polymer conformation. However, no such hysteresis has been observed under associating conditions, over a period of eight months. As the associating polymer has the ability to increase the onset of repulsion considerably (by hundreds of nanometers), it imparts better stability to the colloidal formulations, which will have many promising industrial applications.

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