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Effect of polymer-surfactant association on colloidal force

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We investigate the forces between emulsion droplets in the presence of neutral polymer-surfactant complexes. The polymer used in our experiment was statistical copolymer of polyvinyl alcohol. The anionic surfactant used is sodiumdodecyl sulphate, the cationic surfactants are cetyltrimethylammonium bromide and tetradecyltrimethylammonium bromide, and the nonionic surfactant is nonylphenol ethoxylate (NP10). It has been found that the force profiles in the presence of surfactant-polymer complexes follow an exponential scaling with a characteristic decay length, close to the radius of gyration of the polymer alone. A continuous increase in the onset of repulsion is observed in the case of all three ionic surfactants, whereas no such variation was noticed in the case of nonionic surfactant, NP10. The experimental observations suggest that in the presence of charged surfactant molecules or micelles, the neutral polymer chain at the interface is converted into partial polyelectrolytes, where the charges on the chain repel each other and the electrostatic repulsion collectively leads to chain stretching. These results suggest that the associative polymers can be potential candidates for making the emulsions stable for a sufficiently long period.

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I. INTRODUCTION

Polymer-surfactant interactions have been a topic of intense research for the last 3 decades [1–27]. Understanding of the associative behavior of such polymer-surfactant complexes is not only of fundamental interest, but also finds many industrial applications. The ability of polymer-surfactant complexes to alter the rheological properties of aqueous solutions led to many formulations in the area of medicine, food, detergent, enhanced oil recovery, cosmetics, etc. There are numerous studies to obtain insights into the polymer-surfactant or polyelectrolyte surfactant complexes, using various techniques such as small angle neutron scattering (SANS), x-ray reflectivity, light scattering, electron spin resonance, surface tension, viscometry, nuclear magnetic resonance (NMR) spectroscopy, dye solubilization, conductimetry, etc. [13–21]. Some of the most recent studies on surfactant associations include surfactant assisted entanglement of interfacial polymer chains using dynamic light scattering [23], investigations on the binding isotherm of star polymers with surfactants by NMR and small angle neutron scattering [24], foaming behavior of anionic surfactants in the presence and absence of nonionic polymer [25], interaction between poly(acrylic acid) and an ethoxylated nonionic surfactant [26], and interaction of microblocky twin tailed acrylamido terpolymers with different kinds of surfactants [27]. It should be realized that this topic of polymer-surfactant association is so vast and we have tried to list only some of the recent papers concerning polymer-surfactant association. Most of the above investigations were aimed to understand the nature of interactions from fundamental point of view, which could be finally transformed into technological applications. In this paper, we try to obtain some insights into the polymer-surfactant association process from the colloidal force measurements.

Force measurement techniques have been widely used to gain insights into the colloidal stability. The net force acting between the colloidal particles determines the stability of the colloidal system. The most important forces that determine the stability of the colloidal dispersions are van der Waals attractive forces, electrostatic forces and steric forces due to the adsorbed polymers. Although, stabilization of the colloidal dispersions with macromolecules has been explored in various technological applications for many years, the interactions between polymer bearing surfaces have been studied directly only after the introduction of the surface force measurement apparatus [28]. Steric stabilization of the colloidal dispersions has triggered a lot of interest in recent years due to its several advantages over its electrostatic counterpart and more importantly due to its numerous industrial applications [29,30]. It is well known that electrostatically stabilized colloids often coagulate when the ionic strength of the medium is increased sufficiently, due to the reduction in the spatial extension of the electrical double layers [31]. One major advantage of using macromolecules as stabilizers is that the double layers are less sensitive to electrolyte concentration. The forces between surfactant and polymer covered interfaces have been investigated thoroughly using various force measurement techniques, as a result, this topic is rich and understood to a great extent [32–35]. Compared to the understanding of forces in the presence of surfactants or polymers, the understanding of polymer-surfactant complexes is still in infancy. In recent years there have been some attempts to explore the forces in the presence of associative polymers and polyelectrolytes [36–41]. The effect of an anionic surfactant addition to the forces between surfaces precoated with a high charge density cationic polyelectrolyte

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was investigated by Claesson [36]. Similarly the associative behavior of ionic surfactants and polylectrolytes has been studied [37]. Atomic force microscopy is employed to investigate the interaction forces between a mica surface and a colloidal glass sphere in the presence of a high molecular weight cationic polyelectrolyte and an anionic surfactant [38]. Most of the force measurements have been carried out by using the surface force apparatus SFA. Numerous other approaches have also been invented for measuring surface forces directly and indirectly. Recently a new technique [42–45], called magnetic field induced chaining technique (MCT) has been introduced to probe the forces between tiny colloidal particles. In the case of SFA, the force is measured between semimacroscopic surfaces (mica) whereas in MCT, the forces between individual colloidal droplets are measured. Using this technique, one can measure the colloidal forces in a wide variety of materials encountered in emulsions and dispersions.

In this paper we report the results of the force measurement between emulsion droplets for understanding the associative behavior of polymer-surfactant complexes and its influence on the long-term stability of the emulsions. We investigate the forces between individual emulsion droplets (oil in water) in the presence of polyvinyl alcohol (PVA) and under varying surfactant concentrations. We compare the force measurement data in the presence of polymer-surfactant mixture with those obtained in the presence of polymer and the surfactant independently.

II. MATERIALS

Emulsion used in our studies was Ferro fluid (oil in water). Ferro fluid oil consists of a collection of ferromagnetic domains of Fe_2O_3 dispersed in the octane. The typical size of the Fe_2O_3 particles is about 10 nm. The inner surfactant used to stabilize the oxide particles against van der Waals attraction was oleic acid. The technique used to make the stock emulsion is the classical inversion method [46]. After mixing, we obtain a polydispersed emulsion with a droplet size ranging from 0.1 to 1 μm. Monodispersed emulsions with narrow size distributions were obtained using fractionation technique [47]. The size distribution of the final emulsion has been measured by using a Malvern Instruments master sizer. Emulsion droplets with a diameter of about 200 nm have been used in our studies. The polydispersity of the emulsions used in our experiments was about 7%.

The polymer used in these experiments was a statistical copolymer of vinyl alcohol (CH_2CHOH 88%) and vinyl acetate [CH_2CH ($OCOCH_3$) 12%], which is randomly distributed along the polymer chain, of three average molecular weights of 40 000, 115 000, and 155 000 (here after referred as PVA 40, 115, and 155 K respectively), obtained from Aldrich, U.S. and used as such. Here the vinyl alcohol is hydrophilic and the vinyl acetate is hydrophobic in nature. These polymers are water soluble at room temperature and the theta temperature of PVA-vac in water is around 97 °C. By varying the content of acetate, the hydrophobicity of the polymer can be altered. The radius of gyration R_g of these polymers obtained from the hydrodynamic radii measurement corresponds to about 8, 12, and 16 nm, respectively. The experiments were carried out at a concentration well below the overlap concentration (C^*) for the two polymers. The polymer concentration was 0.68 wt % for 40 K and 0.5 wt % for 115 K. PVA is a neutral polymer and hence the electrostatic effect need not be considered in the interpretation.

Anionic surfactant used in our experiments was sodium-dodecyl sulphate (SDS) ($C_{12}H_{25}\text{-}SO_4$ Na). The purity of SDS was 99.9% and was obtained from Sigma (U.S.). The purity of the cationic surfactants cetyltrimethylammonium bromide (CTAB), Tetradecyltrimethylammonium bromide (TTAB) and the nonionic surfactant nonylphenol ethoxylate (NP10) were also 99%. The critical micellar concentration (CMC) of SDS, CTAB, TTAB, and NP10 are 8.0, 0.9, 3.5, and 0.7 mM, respectively. Triply distilled water was used in the preparation of surfactant and polymer solutions. Addition of hydrochloric acid or NaOH controlled the pH of the solutions, wherever it was required.

III. EXPERIMENT

We briefly describe the principle of the force measurement approach, for details one may refer to earlier publications [42–45]. As the ferrofluid droplets are superparamagnetic in nature, an applied field induces a magnetic dipole in each drop, causing them to form chains. Without external field, these droplets have no permanent magnetic moments because of the random orientation of the magnetic grains within the droplets, due to thermal motion. An external magnetic field orients these magnetic grains slightly toward the field direction, which results in a dipole moment in each droplet. The magnitude of the magnetic dipole moment increases with the strength of the applied field until saturation is reached. At low concentration, one-droplet-thick chains are well separated and oriented along the field direction. Due to the presence of the one-dimensional ordered structure, Bragg peak can be observed, from which the interdroplet separation is estimated precisely. The condition for forming a linear chain is that the repulsive force between the droplets must exactly balance the attractive force between the droplets induced by the applied magnetic field. The spacing between droplets is directly measured from the determination of the spectral distribution of the scattered light at a constant angle. For perfectly aligned particles with a separation "d," the first order Bragg condition leads to $2d=\lambda_o/n$. Where n is the refractive index of the suspending medium ($n=1.33$ for water) and λ_o is the wavelength of the light Bragg scattered at an angle of 180 deg. The peak position moves toward smaller wavelength as the field is increased. Because the droplets are monodispersed and negligibly deformable owing to their large capillary pressure, the corresponding interfacial separation is $h=d-2a$. The magnitude of the induced dipole is controlled by the strength of the applied field. The block diagram of the force measurement apparatus is shown in Fig. 1. It comprises a solenoid-type electromagnet and variable current source, to subject the magnetic emulsions to variable magnetic field. By varying the mag-

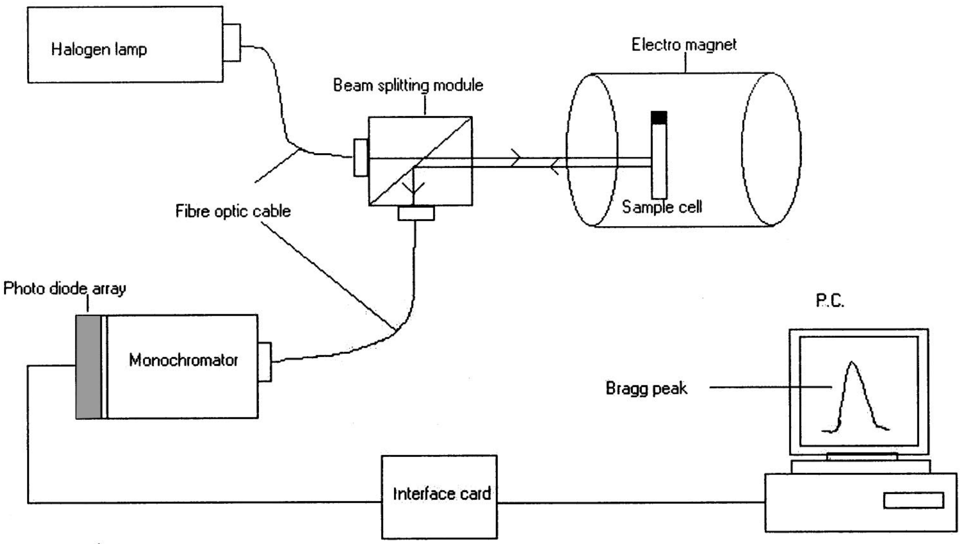

FIG. 1. Block diagram of the force measurement experimental setup.

netic field strength, the distance between the colloidal particles can be controlled. A white light source illuminates the colloidal particle. Optical fibers direct and steer the incoming and out going light beam and a polarizing beam splitter turns the reflected light 90 deg with respect to the incoming beam. A monochromator with holographic grating diffracts the light beam. A photodiode array with an interface card and a computer is used for detection of Bragg peak position, width, and intensity.

The force measurement procedure is briefly discussed below. To form a stable chain of droplets, the repulsive force between the droplets must exactly balance the attractive force between the dipoles induced by the applied magnetic field. The dominant force in a field induced droplet chain is the dipole-dipole attraction. The van der Waals contribution also becomes significant at short distances. The attractive dipole force within an infinitely long chain is [48]

$$F_{\text{chain}} = -\sum_{n=1}^{\infty} n \frac{6m^2}{(nd)^4} = -\frac{1.202}{2\pi\mu_0}\frac{3m^2}{d^4}. \qquad (1)$$

Here, m is the induced magnetic moment of each drop, which can be determined self consistently from the intrinsic susceptibility of the ferrofluid, spherical shape of the drop, and the presence of neighboring drops,

$$m = \mu_0 4\pi a^3 \chi_s H_T/3. \qquad (2)$$

Here, μ_0 is the magnetic permeability of free space and H_T is the total magnetic field acting on each drop. H_T is the sum of external applied field (H_{ext}) and the field from the induced magnetic moments (H_1) in all the neighboring drops in the chains. For a droplet within an infinitely long chain of particles with equal spacing d, the total dipole field from all other particles is

$$H_1 = 2\sum_{n=1}^{\infty} \frac{2m}{(nd)^3} = 1.202\frac{4m}{4\pi\mu_0 d^3}. \qquad (3)$$

Therefore, for an infinite dipole, H_T becomes

$$H_T = H_{\text{ext}} + H_1. \qquad (4)$$

Using Eqs. (1)–(4), the repulsive force between the droplet interfaces is calculated. The multipole term has been neglected in these calculations, since its contribution is less than $10^{-3}F_m$ [48].

In order to study the effect of polymer adsorption on the force profiles, we first take an emulsion washed at very low concentrations of SDS (around $\frac{1}{40}$ of the CMC). Then the emulsion is washed with the polymer (PVA) solutions of desired concentration. After 4/5 washes, at the desired concentrations, we keep the emulsion for at least 48 h to reach the equilibrium adsorption values. Normally we do not see much variation on the force profiles after 48 h of incubation. The pH of the solutions was fixed at 5 (which is close to natural value induced by the polymer). The emulsions remain perfectly stable after the wash in the concentration range reported here. However, with concentrations much above C^* (e.g., $4C^*$), we have noticed destabilization. Force measurements in such cases are not possible. After the polymer washing procedure, the polydispersity of the emulsion is slightly narrowed down. Though we have not measured the polydispersity value after the wash, the Bragg peak full width at half maximum (FWHM) has been found to be narrower than the one before washing, indicating that the emulsion polydispersity is reduced.

IV. RESULTS

The initial emulsion is stabilized with SDS (anionic surfactant) and the droplet surface is negatively charged. The force measurement in the presence of SDS shows a clean electrostatic repulsive force profile due to the charges at the interface of the droplets and the force profiles very well follow one of the electrostatic repulsive force equations depending [32,42] on the κa values. When the droplet double layer is very thin, ($\kappa a < 5$) the force profile follows the equation

$$F_r(d) = 4\pi\varepsilon\psi_0^2 a^2\left[\frac{\kappa}{d} + \frac{1}{d^2}\right]\exp[-\kappa(d-2a)], \qquad (5)$$

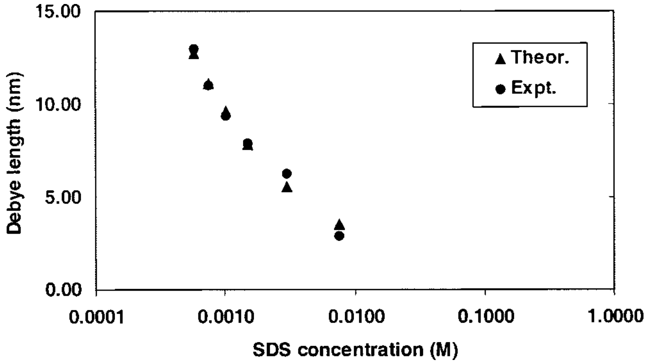

FIG. 2. The Debye length values obtained from the experimental slope of the force profile at different surfactant concentrations and the corresponding theoretically obtained values.

where ε is the dielectric permittivity of the suspending medium, ψ_0 is the electrical surface potential, and κ is the inverse Debye length essentially depending on the electrolyte concentration (C_s) and can be represented as [32]

$$\kappa^{-1}=\left(\frac{1}{4\pi}\right)[2L_B^2C_s]^{-0.5}, \tag{6}$$

where L_B is the Bjerrum length. When the concentration is above the CMC value (C_{CMC}), the Debye length is empirically deducible from the amount of free ions only and does not include the presence of charged micelles [49],

$$\kappa^{-1}=\left(\frac{1}{4\pi}\right)L_B^2[2C_{\mathrm{CMC}}+(C_s-C_{\mathrm{CMC}})Q]^{-0.5}. \tag{7}$$

For systems with thin double layer ($\kappa a<5$), the expression for the interaction force can be obtained by Derjaguin approximation, where the surface potential is assumed to be constant and independent of the inter particle spacing h,

$$F_r(d)=2\pi\varepsilon\psi_0^2a\kappa\frac{\exp[-\kappa(d-2a)]}{[1+\exp(-\kappa(d-2a)]}. \tag{8}$$

The intensity of the electrostatic forces is governed by the surface potential while the Debye length dictates the range of repulsion. We have already shown that the experimental slopes for different surfactant concentrations were in good agreement with the theoretical slopes. The unknown parameter in the theoretical equation is the surface potential, which was evaluated from the best fit. Figure 2 shows the Debye length values obtained from the experimental slope of the force profile at different surfactant concentrations and the corresponding values derived from Eqs. (6) and (7). Both the values were in reasonable good agreement with each other. The measured surface potential values were in very good agreement with those values obtained independently from the electrophoresis mobility. If we need to get rid of the excess charges at the oil interface, a small quantity of the SDS based ferrofluid emulsion is washed with a nonionic surfactant (NP10) a few times. It is very easy to check whether the droplet interface is charge free, from the force measurement experiment. When the droplets are charge free, we can see a clean hard sphere profile at very short interdroplet separation. Our experience shows that 3/4 washes under controlled pH would be sufficient enough to get a clean hard sphere profile.

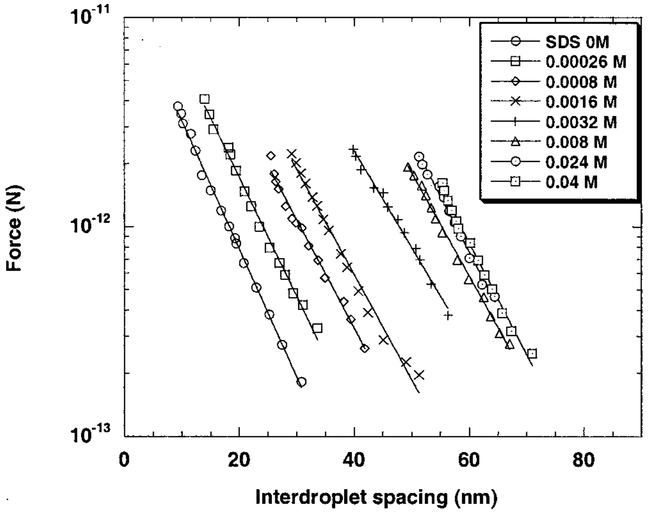

FIG. 3. The variation of force profiles in the presence of PVA of molecular weight 40 K at a concentration of 0.5 wt % for various sodiumdodecyl sulphate concentrations.

Earlier it has been demonstrated that the force profiles in the presence of adsorbed polymers and weak polyelectrolytes decay exponentially with a decay length proportional to the radius of gyration [43]. It has also been found that the decay length is insensitive to the bulk polymer concentration and the nature of the liquid-liquid interface. For both molecular weights of the polymers, we have performed the force measurement studies before adding surfactants into the system. The force profiles were clearly exponential with characteristic lengths close to the radius of gyration. Recent investigations using optical tweezers [50] (which allow potential measurements between two colloidal particles) on micron-sized silica spheres adsorbed with polymers also found a similar exponential decay length proportional to the radius of gyration, in agreement with both mean field and scaling theory [51,52].

Figure 3 shows the variation of force profiles in the presence of PVA of 40 K at a concentration of 0.5 wt % for various sodiumdodecyl sulphate concentrations. The surfactant concentrations were varied from about $\frac{1}{50}$ of CMC to two times CMC. The force profile without any SDS is also shown in the Fig. 3 (open circles), which can be considered as the reference curve. The force profiles can be represented by a simple exponential function similar to the one observed in the case of pure polymers [43,50]

$$F(h)=k\exp\left(\frac{-h}{\lambda}\right), \tag{9}$$

where h is the interdroplet spacing and λ is the decay length. The characteristic decay length without surfactant in this case was 7.6 nm, which is close to the hydrodynamic radius of gyration of the PVA. In the presence of very small amount of surfactant ($0.26\,\mathrm{m}M$) the magnitude of force profile

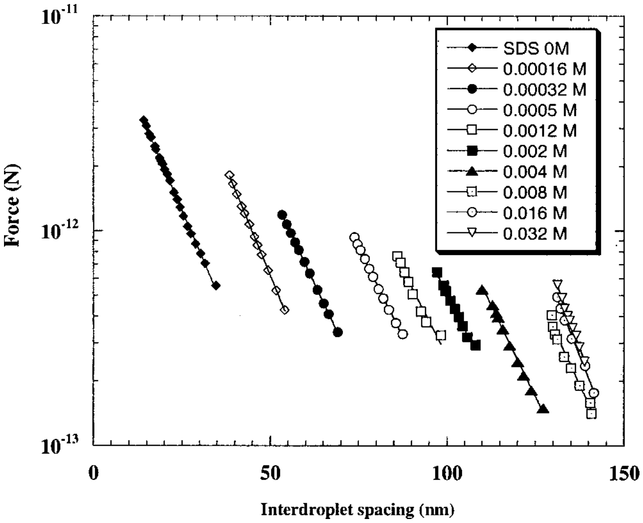

FIG. 4. Variation of force profiles in the presence of PVA of molecular weight 115 K at a concentration of 0.5 wt % for various sodiumdodecyl sulphate concentrations.

changed drastically, without much variation in the decay length. Here the decay length increases slightly from 7.6 to 8.4 nm. However, the first interaction distance (which we define as the distance at which the force value is 2.0×10^{-13} N, which is close to our detection limit of 10^{-13} N) increases from 36 to 44 nm. As the concentration of SDS increases further, both the magnitude and the first interaction distance increase. The increase in the magnitude of force continues up to the CMC of SDS. On further increase in the surfactants concentration, the force profiles are not altered considerably.

Let us consider the case where the droplets are covered with polymer alone. At the concentrations used in our experiments, the oil-water interface is fully covered with adsorbed polymer (i.e., the plateau region in the adsorption curve). This has been confirmed earlier from force measurement studies and from surface tension experiments [45]. Typical values of the adsorbed amount of polymers above the plateau concentration are about 1.5–2.2 mg/m^2. In the case of PVA 40 K, the first repulsion is observed at a distance of about 36 nm, which is $\approx 4R_g$.

Figure 4 shows the force profile for PVA of molecular weight 115 K. The observed results were similar to that of 40 K. The value of decay length in the absence of surfactant was 11.2 against the unperturbed coil diameter of 12 nm. The values of Debye lengths for various surfactant concentrations due to electrostatic contributions (without polymer) and the experimentally observed decay length in the presence of associative polymers of two molecular weights are shown in Fig. 5. In the case of associative polymers, the characteristic decay length increases up to roughly the critical micellar concentration and decreases further. For both molecular weights, the variations were almost identical. The experimental decay lengths in the presence of polymer surfactant complexes show that the characteristic decay length remains the same as the free polymer coil radius of gyration.

The experimental results on the force profiles provide ample reasons to believe that the association or binding of surfactant molecules takes place at low surfactant concentrations. There are two possibilities, when surfactant is added to the emulsion droplets covered with polymer. First case is that the surfactant molecules can preferentially adsorb at the oil-water interface, displacing the adsorbed polymer. If this happens, the magnitude of the force profile should decrease and the force profile would be shifted to the opposite direction than the observed direction. Ultimately when the polymer coils are entirely replaced by the surfactant micelles, the force profile should follow the classical electrostatic repulsive profile with a decay length equal to the Debye length up to the depletion of free polymer coils. Clearly the experimental decay length at a large surfactant concentration of four times CMC is much larger (about 10 nm) compared to the expected Debye length of 2.8 nm. Therefore, we can clearly rule out this possibility of electrostatic repulsion. The second possibility is that the surfactant molecules and micelles can remain in the continuous phase, without being associated or bound to the polymer chains. If this happens we do not expect much changes in either the magnitude or the strength of the force profiles, except a slightly compressed polymer coil due to free micelles in the bulk solution. Obviously this is not the case as seen in our force profiles. Therefore, by considering the above facts, it is clear that the surfactant molecules interact with the micelles at low concentrations of SDS, leading to significant changes in the magnitude of the force profiles.

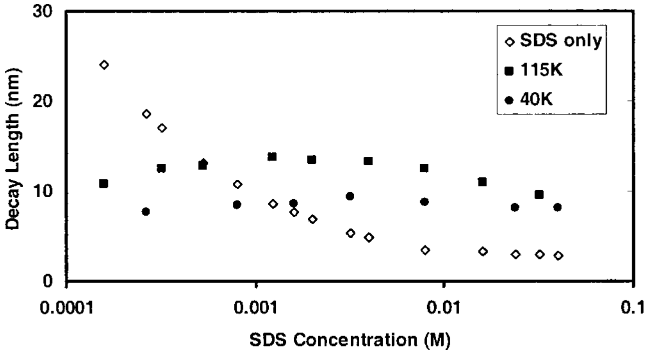

FIG. 5. The expected values of Debye lengths for various surfactant concentrations due to electrostatic contributions and the experimentally observed decay length in the presence of associative polymers of molecular weight 40 and 115 K.

Figure 6 shows the variation of the first interaction length as a function of SDS concentration for both PVA. Here the first interaction distance $(2L_0)$ increases rapidly with increasing surfactant concentrations up to the CMC value and then it almost saturates. The experimental observations suggests that in the presence of charged surfactant molecules or micelles, the neutral polymer chain at the interface is converted into partial polyelectrolytes, where the charges on the chain repel each other and the electrostatic repulsion collectively leads to chain stretching. Probably this would explain the large shift in the onset of repulsion observed in our experiments, in the presence of polymer surfactant complex. The longest decay length observed in the case of PVA 115 and 40 K was around the CMC value. Independent experiments, from viscometry, on the radius of gyration of the

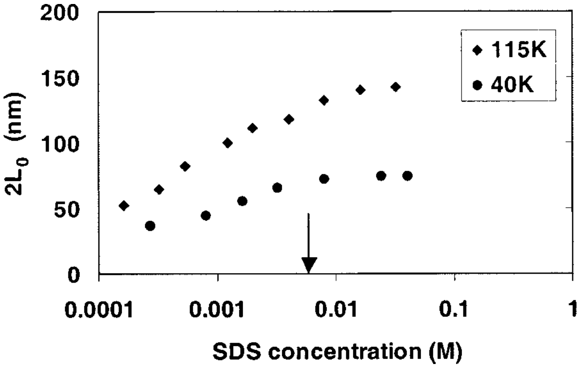

FIG. 6. The first interaction length $2L_0$ (onset of repulsion) as a function of SDS concentration for PVA molecular weight 40 and 115 K.

polymers also confirm the same trend in the R_g variations with the maxima around the same surfactant concentration.

The experimental force profiles show that the surfactant polymer binding process is a continuous process in the SDS concentration range of 0.1–10 mM. This shows that even at low surfactant concentrations, the surfactant molecules bind the polymer, without much change in viscosity or conductivity values. We have not observed large variations in the solution viscosities in our experimental values of the polymer and surfactant concentrations. In the case of PVA 40 K at 0.5 wt %, the viscosity (η/η_0) increased from 1 to 2 in the surfactant concentration range of 0.8–10 mM. Even the turbidity changes were not significant. This is mainly because the polymer concentrations used in our experiments are much lower. Up to four times of CMC of surfactants, we have not observed any gelation or macroscopic phase separations in our emulsions and the emulsions remain stable.

Finally, in order to check the universality of the associative behavior of PVA, we have performed the force measurements in the presence of two cationic surfactants, CTAB and TTAB, and a nonionic surfactant, NP10. The polymer used in this case was PVA 155 K and the concentration was 0.5%. In the case of cationic surfactant TTAB and CTAB, we have observed similar behaviors in the force profiles where as no association is observed in the case of NP10. The variation in the first interaction length ($2L_0$) for the cationic, anionic, and nonionic surfactants is shown in Fig. 7. The CMC values are indicated in brackets in the figure inset. We can see that the first interaction length remains the same in the case of NP10 up to a surfactant concentration of 2.5 mM, which corresponds to about four times CMC. This shows that the association does not takes place in this case or the association is very weak. In the case of CTAB and TTAB, the range of interaction starts rising at surfactant concentrations very close to the CMC values. In the case of SDS, CTAB, and TTAB the onset of association begins at surfactant concentrations of 0.118, 1.35, and 1.4 mM, respectively. So, the difference in these three cases is that the surfactant concentrations at which the association begins are different for the cationic and anionic surfactants. In the case of SDS, the association begins even at very low concentrations well below

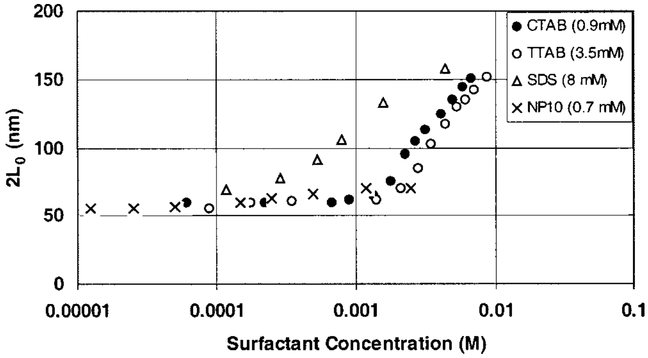

FIG. 7. The variation in the first interaction length ($2L_0$) for CTAB, TTAB, SDS, and NP10. The polymer used in this case was PVA 155 K and the concentration was 0.5 wt %.

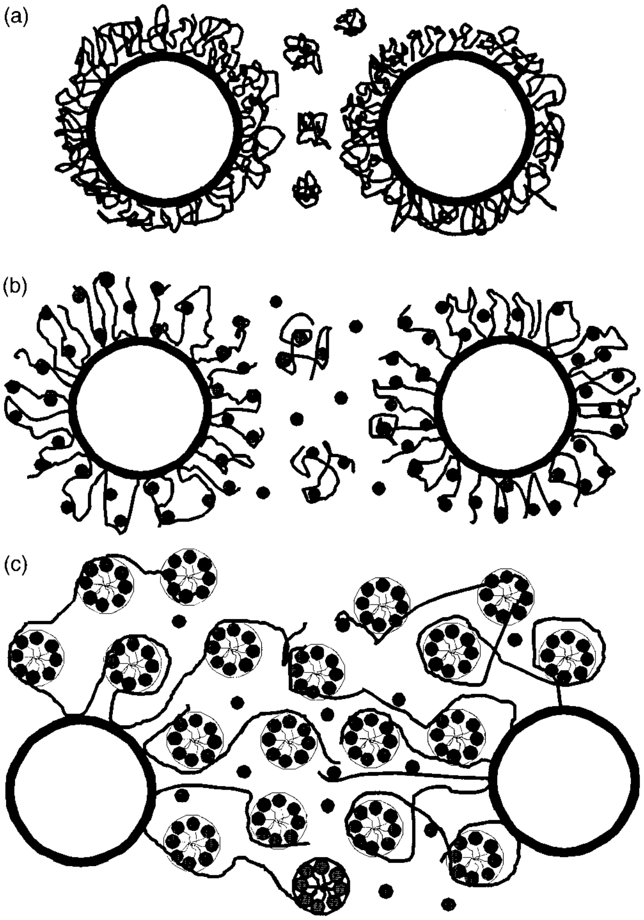

FIG. 8. Schematic illustration of the polymer-surfactant association at the droplet interface. (a) Without any surfactant, the conformation of polymer at the droplet interface. Here, the adsorbed polymer adopts some arbitrary conformation with loops, trains and tails. (b) Conformation of polymer-surfactant molecules, well below the CMC value, where the added surfactant tends to associate with the polymer chains leading to a "stretched-tail-like" conformation. No micelles are present at this stage. (c) Conformation of polymer-surfactant complexes above the so-called CAC. Under this condition, the neutral polymer chain at the interface behaves like a partial polyelectrolyte complex where the charges on the chain repel each other and the electrostatic repulsion collectively leads to chain stretching on length scales larger than the electrostatic blob size.

the CMC value ($\frac{1}{60}$ of CMC). However, in the case of cationic surfactant the association begins at concentrations close to CMC. At the moment, we do not have an explanation for this behavior. The interesting aspect we have noticed is that the emulsions stabilized with the cationic or anionic surfactant-polymer complexes are highly stable compared to the electrostatically or sterically stabilized emulsions [53].

The experimental results show that the ionic surfactant molecules interact with the polymer coils, which leads to a conversion of neutral polymer chains to a partial polyelectrolytelike complexes with a stretched conformation [54]. The drastic increase in the first interaction distance with increasing surfactant concentrations suggests that the polymer chain adopts a ‘‘stretched-tail-like’’ conformation due to bound surfactant molecules. As the concentration increases, more and more surfactant molecules and micelles (above critical aggregation concentration called CAC) go into the folded chains (loops), which stretch the loops further. Earlier investigations [14,18] on the associative behavior of SDS on polyethylene oxide is that the polymer adsorbed on the surface of SDS micelles. These micelles are slightly smaller than free micelles and are uniformly spaced on each polymer coil. The equilibrium spacing between the micelles on the polymer coil is governed by the balance of adsorption energy of the polymer segments and the electrostatic repulsion between the micelles. This picture seems to be true only in the case of ionic surfactants, whereas no electrostatic repulsion between the micelles is expected in the case of nonionic surfactants. This could be the reason why we have not observed any stretching of the polymer coils in the presence of nonionic surfactant. It has been found that within the aggregates, there is strong repulsion between the polymer monomers, but as a whole, it retains the unperturbed radius of gyration of the polymer without micelles. What we have observed on the decay length from the force profile is consistent with SANS experimental results (i.e., the radius of gyration remains more or less the same). We have also found that our experimental decay lengths were consistent with the unperturbed radius of gyration values obtained from viscometric measurement.

The possible picture evolving from the association of polymer and the surfactant is sketched in Fig. 8. Figure 8(a) shows the polymer covered ferrofluid droplets in the absence of surfactants. Here, the polymer is adsorbed at the oil-water interface with some arbitrary conformation of loops, trains, and tails. Figure 8(b) shows that the individual unimers (small open circles) of the surfactants associate with polymer coil at concentrations below CMC. Figure 8(c) shows the conformation above CMC where micelles (filled circles) coexist with individual surfactant molecules, which associates with polymer coils, and the electrostatic repulsion between the charged micelles or surfactant molecules leads to stretching of polymer coil. In fact, the stretching process can continue up to the critical association concentration, which seems to be dependent on the surfactant molecules and the nature of the oil-water interface. Once the concentration exceeds the CAC, the free micelles and polymer-micelles complexes can coexist. A saturation in the onset of repulsion is expected when the polymer coil is fully stretched.

V. CONCLUSIONS

We have studied the forces between emulsion droplets in the presence of a neutral polymer—polyvinyl alcohol with ionic and nonionic surfactants. The force profiles in the presence of associative polymer follow an exponential scaling with a characteristic decay length, close to the radius of gyration of the polymer alone. This decay length was weakly dependent on the surfactant concentration. The onset of the repulsive force dramatically increases with increase in the surfactant concentration, suggesting that the adsorbed polymer coils adopt a stretched conformation due to association of surfactant molecules. The variation in the onset of repulsion indicates that the surfactant-polymer binding is a continuous process. These results suggest that the associative polymers can be potential candidates for making the emulsions stable for a sufficiently long period.

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