



Interaction of anionic surfactant with polymeric nanoparticles of similar charge

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ABSTRACT

The formation of micelle-like nanosize aggregates above a critical aggregation concentration (CAC) by a water-soluble, amphiphilic, and statistical copolymer poly(SAMPS/DA) of sodium *N*-acrylamidomethylpropanesulfonate (SAMPS) and *N*-dodecylacrylamide (DA) was studied. The structural changes that result from the interactions between the polymeric nanoparticles and sodium dodecylsulfate (SDS), an anionic surfactant, were studied with the aid of surface tension, viscosity, steady-state fluorescence, dynamic light scattering, and transmission electron microscopic techniques. In dilute solution with polymer concentration $C_p < CAC$, the copolymer does not interact with SDS at concentrations lower than its CMC value. The polymer only binds to SDS micelles to produce polymer-decorated micelles. In polyelectrolyte solutions with $C_p > CAC$, strong interactions between the polyelectrolyte and SDS were observed even at a very low level of surfactant addition. The interaction is purely hydrophobic in nature. The surfactant monomers bind to the polymer micelles to form smaller spherical aggregates (polymer–SDS complex). When surfactant was added above its saturation concentration, the association complexes are disrupted and only surfactant micelles decorated by polymer chain(s) were observed. The microenvironment of the polymer–SDS complexes was observed to be much less polar than that of neat polymer aggregates and SDS micelles. Also, the internal rigidity of the polymer–SDS complexes was found to be higher than that of the pure polymer or SDS micelles. It was observed that the neat polymer aggregates and polymer-decorated SDS micelles are more stable than the polymer–SDS complexes.

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1. Introduction

Polymer/surfactant mixtures are common in biological systems. Interaction of surfactants with water-soluble polymers has been extensively studied for their widespread applications in industry [1–4]. Because of their characteristic physicochemical properties at different possible combinations the polymer and ionic surfactant mixed systems are interesting. The basic principles of the polymer–surfactant interactions have been discussed by Goddard and Ananthapadmanabhan [4], Kwak [5], and others [6–8]. Various aspects of the polymer–surfactant interactions have been reported by analyzing results of viscosity [9,10] and surface tension [11] studies. Generally, polymer–surfactant interactions involve binding of surfactant on polymer to form polymer/surfactant mixed micelles at concentration much below the critical micellar concentration (CMC) of the surfactant. Some interaction studies reported in the literature focused quantitative measurement of the amount of surfactant associating with polymer molecules [12,13]. Results of these studies show that some surfactants interact strongly to polymer and some do not associate at all. On the other hand, some studies show critical behavior at different concentration of the surfactant in the presence of polymer. The strength

and mechanism of interaction depends on the nature of both surfactant and polymer, and environment. Interaction between neutral polymer and ionic surfactant is usually weak in contrast to strong interaction between a polyelectrolyte and oppositely charged surfactant.

While most of the publications focused on conventional polymer–surfactant interactions, the center of attention of a second class of studies have been the microstructure of the polymer/surfactant complex formed. The morphology of the complex formed between polymer and surfactant molecules has attracted attention in recent literature. After Cabane proposed the necklace 'model' for nonionic polymer and surfactant micelles [14], several other studies on morphology of polymer/surfactant complexes have been reported [15]. To elucidate the structure of polymer–surfactant complex and to estimate the size of the polymer-bound micelles, techniques, such as nuclear magnetic resonance [16], neutron scattering [17], and fluorescence spectroscopy [4,6] have been used. The use of fluorescent probes to study polymer/surfactant systems has been summarized in two excellent reviews [4,18].

Interaction of ionic surfactants with water-soluble amphiphilic polymers, such as hydrophobically modified polymers (HMPs) has attracted significant interest in recent years [4,5,19–21]. Previous studies have shown that HMPs have a tendency to self-assemble and to associate with surfactants, forming hydrophobic cores, which have potential applications in drug delivery [4]. Colby

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et al. have reported the complex behavior of hydrophobically modified poly(alkene oxide) polymers/SDS system, which gives deeper insight into macromolecular architecture [22]. Bastos and coworkers [23] have reported interactions of a series of hydrophobically modified, uncharged dextrin polymers with SDS. Bu et al. have studied the effects of surfactant addition and temperature on the rheological and structural properties of an anionic polyelectrolyte, HM-alginate [24]. It has been observed that usually at a low or moderate level of surfactant addition, the solution viscosity of an aqueous solution of a HMP is increased [20]. The interaction of amphiphilic polymers with surfactants has also been addressed in several theoretical studies [25]. It has been shown that the hydrophobic tails of the polymer and surfactant assemble into mixed micelles that act as cross-link junctions between polymer chains forming a network structure. At low surfactant concentrations, the polymer chains are tightly connected through these hydrophobic junctions, whereas in the presence of excess surfactant many junctions get disrupted.

The present work was undertaken to gain more insight into the nature of polymer–surfactant interactions. We report on the interaction of an anionic surfactant SDS with a statistical copolymer poly(SAMPS/DA) (see Chart 1 for structures), of sodium *N*-acrylamidomethylpropanesulphonate (SAMPS) and *N*-dodecylacrylamide (DA) in aqueous solutions. The aims of this study are: (i) to analyze in detail the process of aggregate formation and the characteristics of the aggregates formed in salt-free aqueous solution of poly(SAMPS/DA), (ii) to explore the possible patterns of aggregation induced by the ionic surfactant, (iii) to examine the strength and mechanism of the copolymer–SDS interactions, and (iv) to investigate the microenvironments and morphology of the polymer–surfactant complexes.

2. Experimental section

2.1. Materials

Dodecylamine, sodium *N*-acrylamidopropanesulfonate (SAMPS), and sodium chloride were obtained from SRL, Mumbai. Acryloyl chloride, CDCl_3 , D_2O , and CD_3OD were procured from Aldrich Chemicals, St. Louis and were used without further purification. 2,2'-Azobis(isobutyronitrile), AIBN (Aldrich), was recrystallized from methanol. SDS (Aldrich) was recrystallized three times from acetone–ethanol (10:1 v/v) mixture and dried under vacuum. The fluorescence probes, pyrene, 1,6-diphenyl-1,3,5-hexatriene (DPH), and 1-anilinonaphthalene (AN) were purchased

from Aldrich and were recrystallized from ethanol or acetone–ethanol mixture at least three times before use. Purity of all the probes was tested by the fluorescence emission and excitation spectra. All the reagents and solvents, especially dimethylformamide (DMF), ethanol, methanol, tetrahydrofuran (THF), acetone, dichloromethane were of good quality commercially available and were dried and distilled fresh before use. Mili-Q (18.2 M Ω) water (pH 6.3) was used for preparation of aqueous solutions.

The copolymer was made by conventional free radical polymerization of SAMPS and DA in 10:1 mol ratio in DMF solvent using AIBN as radical initiator according to a method reported in the literature [26,27]. The comonomer, *N*-dodecylacrylamide (DA), was obtained by the reaction of acryloyl chloride with dodecylamine in chloroform solvent containing 1.2 mol equivalent of triethyl amine. The details of polymer synthesis and molecular characterization are available under “Supporting information”. The chemical structure and purity of the HMP was confirmed by ^1H NMR spectrum measured at 70 °C with a 400 MHz Bruker Biospin AG spectrometer in D_2O solvent: $\delta(\text{ppm}) = 1.96$ (CH_3 , SAMPS), 3.76 (CH_2 , SAMPS), 1.30 (CH_3 , hydrophobic part), 1.71 (CH_2 , hydrophobic part). The degree of hydrophobic modification was determined from the peak ratio of methylene protons in SAMPS and methyl protons of the DA chain. The copolymer chain contains ca. 10 mol.% DA. The average molecular weight (\overline{M}_v) of the HMP as obtained from intrinsic viscosity measurements is 360 kDa (see “Supporting information”). The \overline{M}_v values for structurally similar copolymers prepared by others following the same method have been reported to be in the range of 100–600 kDa [28].

2.2. Methods

2.2.1. Solution preparation

Stock solutions of polymer and surfactants were prepared in Mili-Q water. Solutions for analysis were prepared by using aliquots of these stock solutions and were allowed to equilibrate for at least 24 h at room temperature (~ 303 K). For fluorescence measurements, the stock solutions were made either containing a known concentration of fluorescent probe or made saturated with the probe. Dilutions were made using the same aqueous solution containing the probe molecule. The pH of the final solutions was ~ 6.5 . All measurements started after 24 h of sample preparation.

2.2.2. Surface tension measurements

The surface tension (γ) of the copolymer and surfactant solutions were measured by Du Nüoy ring detachment method with a surface tensiometer (Model 3S, GBX, France) at 303 ± 0.1 K. Ethanol–HCl solution was often used for cleaning the platinum ring and it was burnt in oxidizing flame by use of a Bunsen burner. The instrument was calibrated and checked by measuring the surface tension of distilled water before each experiment. Solutions of polymer and surfactants of different concentrations were made 24 h prior to experiment in Mili-Q water. For each concentration, three measurements for γ were performed and their mean was taken as the value of the equilibrium surface tension.

2.2.3. Viscosity measurements

Viscosities of aqueous polymer solutions were measured by use of a glass Ubbelohde viscometer (ASTM-D-446) with a flow time of 180 s for pure water immersed in water bath maintained at 303 ± 0.1 K. Sample solutions were prepared following the same protocol as described above. Flow-through times of copolymer solutions at various concentrations were determined at least five times for each concentration. Specific viscosities were determined by comparison with flow-through times of water.

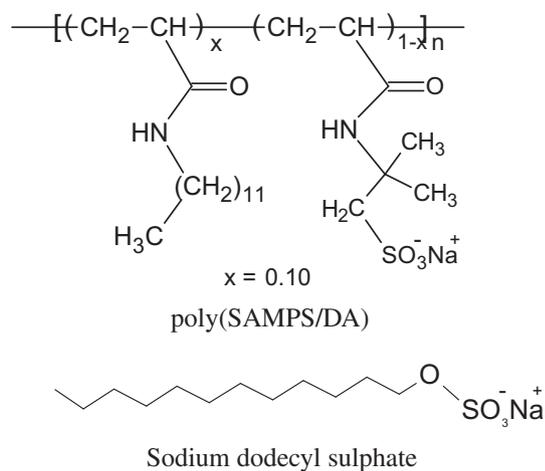


Chart 1. Structures of poly(SAMPS/DA) and sodium dodecyl sulfate (SDS).

2.2.4. Fluorescence measurements

Steady-state fluorescence measurements were performed on a Perkin Elmer LS-55 spectrophotometer equipped with an automated polarization accessory, which uses the L-format instrumental configuration using a quartz cell of 10-mm path-length. The excitation wavelengths were 335 nm (pyrene), 340 nm (AN), and 350 nm (DPH). The excitation slit width (band pass) was set at 2.5 nm for excitation and 2.5–10 nm for the emission. For fluorescence anisotropy measurements, the emission wavelength was set at 450 nm; the instrumental correction factor, $G = I_{HV}/I_{HH}$ was automatically determined by the software controlling the instrument. In all experiments, background spectra, either of the water alone or of the water containing polymer was subtracted from the corresponding sample spectra. The temperature of the samples was controlled using the water jacketed magnetically stirred cell holder in the spectrometer connected to a Thermo Neslab RTE-7 circulating water bath.

2.2.5. Light scattering measurements

The dynamic light scattering (DLS) measurements were carried out using a Zetasizer Nano (Malvern Instrument Lab, Malvern, UK) optical system equipped with a He–Ne laser operated at 4 mW at λ_0 633 nm, and a digital correlator. The scattering intensity was measured at a 173° angle to the incident beam. Polymer surfactant solutions were prepared in Milli-Q water. The solution was filtered through a Millipore Millex syringe filter (0.45 μm) directly into the scattering cell. Prior to the measurements, the scattering cell was rinsed several times with the filtered solution. The DLS measurements started 5–10 min after the sample solutions were placed in the DLS optical system to allow the sample to equilibrate at the bath temperature. For all light scattering measurements, the temperature was 303 ± 0.5 K. The corresponding hydrodynamic diameter (d_H) of the polymer aggregate was obtained using the Stokes–Einstein equation, $D = k_B T / (3\pi\eta d_H)$, where k_B is the Boltzmann constant and η is the solvent viscosity at temperature T .

2.2.6. Transmission electron microscopy

Transmission electron micrographs (TEM) were obtained with a JEOL-JEM 2100 (Japan) electron microscope operating at an accelerating voltage of 200 kV at room temperature. The specimen was prepared by immersing a 400 mesh size carbon-coated copper grid into the copolymer/surfactant solutions (1 g/L) for 1 min followed by blotting the excess liquid and drying in desiccators. The specimens were kept in desiccators overnight for drying before measurement.

3. Results and discussion

3.1. Self-association of poly(SAMPS/DA)

Before the interaction of such a large polymer with surfactants could be understood it is essential to investigate the solution behavior of the copolymer itself in aqueous medium. The conformational behavior of the copolymers poly(SAMPS/DMA) composed of SAMPS and *N*-dodecylmethacrylamide (DMA) having different hydrophobe content have been reported earlier by Morishima and coworkers [29,30]. The copolymers were observed to exhibit a strong tendency for intra-molecular hydrophobic association to form unimer micelles when the DMA content in the polymer is in the range of 10–50 mol.%. It is reported that when the DMA content is either lower or higher than these limits, the polymer bound alkyl chains undergo inter-polymer associations above a critical concentration. Since poly(SAMPS/DA) is structurally similar to poly(SAMPS/DMA), it is expected to exhibit similar association behavior in water. The self-assembly of poly(SAMPS/DA) in aqueous

solution (pH 6.5), was studied using steady-state fluorescence, DLS, and TEM methods.

Steady-state fluorescence spectra of AN probe were measured in the presence of poly(SAMPS/DA) at different concentrations. In dilute solutions, the emission maximum neither showed any shift, $\Delta\lambda (= \lambda_{\text{water}} - \lambda_{\text{sample}})$, of emission maximum nor any intensity rise relative to the spectrum in pure water. However, at higher values of C_p , as shown in Fig. 1, a gradual increase of $\Delta\lambda$ as well as relative intensity (F/F_0), where F and F_0 are the fluorescence intensity in the presence and absence of polymer) was observed with the increase of C_p . As can be seen, both $\Delta\lambda$ and F/F_0 values show a significant increase above a certain polymer concentration, suggesting that an event takes place at this critical concentration, which must be hydrophobic domain formation [31–33] either due to the association of the hydrophobes within the same polymer chain (intra-molecular association) or between polymer chains (inter-molecular association) through hydrophobic interaction of the hydrophobes forming micelle-like aggregates. The feature of the plots shows that the increase of fluorescence properties is sigmoidal and stretches over a large range of concentration (about an order of magnitude). This suggests that unlike low-molecular-weight surfactants, the aggregation process is either non-cooperative in nature.

In order to examine intra-polymer association we have performed fluorescence measurements with AN probe in dilute polymer solution (0.25 g/L) in the presence of different concentrations of NaCl salt. The plot of $\Delta\lambda$ as a function of [NaCl] is shown in the inset of Fig. 1. It is observed that $\Delta\lambda$ does not change significantly with the increase of [NaCl]. This implies that the observed increase of $\Delta\lambda$ or F/F_0 (Fig. 1) with the increase of C_p is a consequence of the inter-molecular association of the hydrophobes at higher polymer concentrations. Thus the C_p corresponding to the onset of the fluorophore property change ($\Delta\lambda$ or F/F_0) is considered here to be the CAC (0.35 g/L) of the copolymer. The CAC value, however, is very low suggesting sufficiently strong hydrophobic associations of the hydrophobes and there is very little water in the core of the aggregates. This is substantiated by the micropolarity of the hydrophobic domains which is much less than that of bulk water as indicated by the higher $\Delta\lambda$ value (see plot in Fig. 1) at $C_p > \text{CAC}$. In fact, the micropolarity of the polymer micelles is similar to that of ionic surfactant micelles. It should be noted that if the domains were formed by intra-polymer hydrophobe association, then the micropolarity of AN probe would not be significantly different from the bulk water. Further, in case of intra-polymer association, the rigidity of the microenvironment of the probe molecule would be less as compared to that

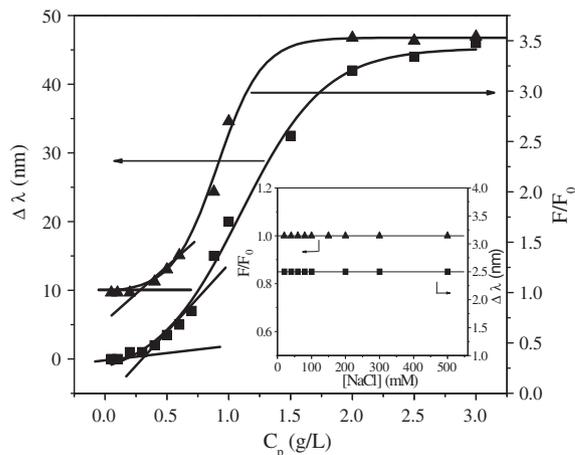


Fig. 1. Plots of shift of emission maximum, $\Delta\lambda (= \lambda_{\text{water}} - \lambda_{\text{sample}})$ and relative fluorescence intensity (F/F_0) of AN versus C_p at 303 K. Inset: plots of shift of emission maximum ($\Delta\lambda$) and relative fluorescence intensity (F/F_0) of AN in 0.25 g/L polymer as a function of [NaCl].

in inter-polymer association. For this, we have measured steady-state fluorescence anisotropy (r) of DPH probe in water in the presence of polymer. DPH is a very hydrophobic probe (it is practically insoluble in water) and is nonfluorescent in water. However, it becomes highly fluorescent when incorporated in hydrophobic environment [34]. Due to the sensitivity of its fluorescence anisotropy to rotational motion, it has been successfully used for measurements of microviscosity of membranes [35,36]. DPH was found to be poorly soluble even in the presence of 0.25 g/L copolymer. However, the solubility increased with the increase of polymer concentration, indicating hydrophobic domain formation through inter-polymer association. The r -value thus measured in solution containing 1.0 g/L polymer is ca. 0.129, which is greater than that of micelles of ionic surfactants, such as SDS ($r \sim 0.06$) [37,38]. This means that the hydrophobes are tightly packed in the aggregate as compared to those of SDS micelles. Such packing of the hydrophobes would be impossible to achieve if the hydrophobic domains were formed through intra-polymer association. Thus it is confirmed that aggregate formation above the CAC occurs as a result of inter-polymer association of the hydrophobe units of the polymer chains. This is also consistent with the decrease of reduced viscosity of the polymer solution as a result of reduction of hydrodynamic volume as discussed under “Supporting information”.

The reduction of hydrodynamic volume with the increase of polymer concentration is further confirmed by direct measurement of the hydrodynamic diameter (d_H) of the aggregates using DLS technique. Two polymer solutions were employed, one having concentration (0.25 g/L) less and the other having concentration (1.0 g/L) greater than the CAC value (0.35 g/L) of the copolymer. The average d_H value obtained with the dilute solution was found to be much larger than that in concentrated solution (ca. 300 nm), confirming aggregate formation through inter-molecular hydrophobic association. In contrast to literature reports [26,30], no particles of hydrodynamic diameters in the range 10–20 nm corresponding to intra-molecular aggregation was observed. This can be attributed to the low hydrophobe content (10 mol.%) of the HMP that eliminates the possibility of intra-molecular aggregation of the copolymer. In fact, fluorescence probe studies as described above did not indicate formation of any aggregate in dilute solution with $C_p < CAC$.

To visualize the shape of the aggregates we have taken TEM images (Fig. 2A) of the 1.0 g/L polymer solution. Clearly, the picture reveals existence of irregular-shaped particles having diameters in the range 80–150 nm. This substantiates the results of viscosity, fluorescence probe, and DLS measurements. Recently, reports from this group have demonstrated spheroidal aggregate formation in aqueous solution of a structurally similar copolymer of sodium *N*-acryloyl-L-valinate and DA [38].

3.2. Interaction with SDS

Since poly(SAMPS/DA) forms aggregates at $C_p > 0.35$ g/L, in this study, we consider the cases when surfactant is added to the solu-

tions in which the HMP is present as stretched polyelectrolyte chains and as micelle-like aggregates. Therefore, the interaction studies were performed using 0.25 g/L and 1.0 g/L poly(SAMPS/DA) solutions.

3.2.1. Surface tension (ST)

The variation of ST with the concentration of SDS surfactant is shown in Fig. 3. In good agreement with the reported values, a CMC of 7.6 mM is observed. As expected, poly(SAMPS/DA) ($C_p = 1.0$ g/L) lowers the ST (γ) of water from 70 to 60 mN/m due to the adsorption of the polymer chains to the air/water interface, showing its amphiphilic character. Addition of SDS to the polymer further reduces γ to ca. 39 mN/m and the plot becomes parallel to the concentration axis indicating a break at ca. 3.8 mM. Interestingly, at [SDS] > 5.0 mM, ST steadily decreases and reaches a minimum (~ 31 mN/m) at 7.9 mM SDS. Further addition of SDS raises ST to a limiting value of ca. 35 mN/m at 17.5 mM SDS. It is important to note that such feature of the ST plot is absent when the polymer concentration is 0.25 g/L that is less than the CAC value. In fact, ST plot is exactly same as that for the pure surfactant with the breakpoint appearing at a slightly lower concentration. That is the presence of polymer with $C_p < CAC$ only lowers the CMC of surfactants suggesting that the polymer acts like an electrolyte. In other words, there is no interaction between surfactant and polymer when the latter exists at concentrations less than the CAC value. This is because the polymer behaves as a stretched polyelectrolyte chain at concentrations below CAC. However, the binding of the polymer with the surfactant micelles (at concentrations greater than its CMC) through the hydrophobic interaction of the hydrophobes in the polymer chain cannot be ruled out. This has been discussed below.

The feature of the ST plot for the 1 g/L polymer is slightly different from other HMP/surfactant systems [22,39]. According to the literature reports the increase of ST between 7.9 and 17.5 mM SDS (region II) is due to the interaction between surfactant molecules and copolymer micelles forming polymer/surfactant complexes. Thus, the surfactant concentration corresponding to the minimum of the ST plot is referred to as critical incorporation concentration (CIC) [39]. In the present system, however, the results of fluorescence probe studies as described below indicate that the binding of SDS to the existing poly(SAMPS/DA) micelles starts at a very low [SDS] (CIC < 1 mM) and the micelles become saturated at about 3.8 mM (critical saturation concentration, CSC) SDS. Indeed, in the case of HMPs it has been reported that the value of CIC is very low or zero [40,41]. On the other hand, Piculell and coworkers have studied interactions of hydrophobically modified hydroxyethylcellulose (HM-HEC) with a range of anionic and cationic surfactants and have shown that the CIC value is a function of the CMC value, surfactant chain length, and nature of the headgroup [42,43].

In the presence of copolymer micelles, the added surfactant molecules can either adsorb onto the air/solution interface or can bind to the polymer micelles or both simultaneously. In this case,

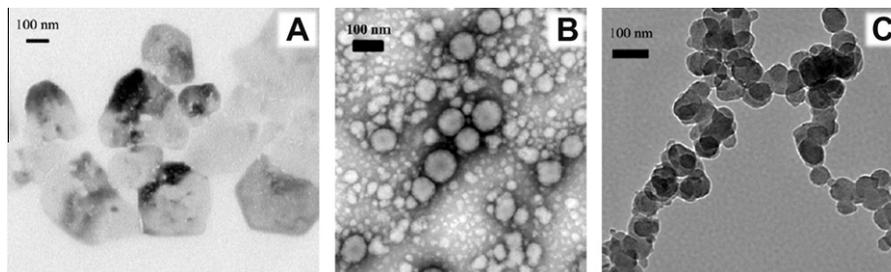


Fig. 2. TEM picture of polymer surfactant complexes: (A) 1.0 g/L aqueous solution of poly(SAMPS/DA) (unstained), (B) 1.0 g/L poly(SAMPS/DA) + 3.5 mM SDS (stained with 1% uranyl acetate), (C) 1.0 g/L poly(SAMPS/DA) + 18 mM SDS (unstained).

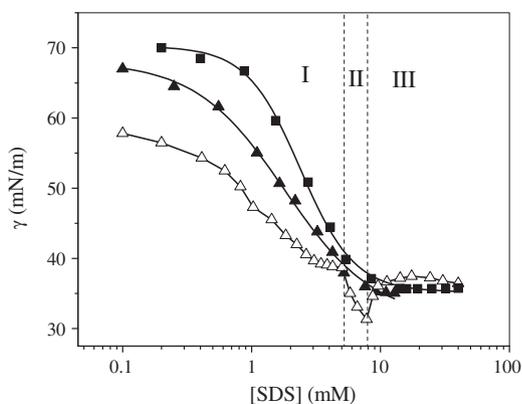


Fig. 3. Plots of surface tension (γ) versus [SDS] in water at 303 K in the presence of copolymer: C_p (g/L) = 0 (■), 0.25 (▲), 1.0 (△), (the plot for 0.75 g/L polymer solution has not been shown for clarity of the figure).

it seems that the adsorption of SDS molecules to the air/water interface and binding of SDS to the polymer micelles occur simultaneously. The ST plot can be divided into three (I–III) concentration regions. In region I, the plot is similar to that for 0.25 g/L polymer and therefore corresponds to formation of SDS micelles above the CMC (ca. 3.8 mM). Below the CMC, the usual decrease of ST is observed because as surfactant is added more surfactant goes to the air/solution interface occupying spaces between the adsorbed polymers. The lower CMC value of SDS is due to the increase of ionic strength of the polymer solution.

It is somewhat unusual to observe a decrease in ST when SDS is added above CSC (region II). This indicates that the air/solution interface is not yet saturated. Possibly, addition of SDS beyond CSC (3.8 mM) leads to disruption of the complex, which directly brings some polymers to the air/solution interface thus causing decrease of ST until a minimum is reached at ca. 7.9 mM SDS. It is clear that micelle formation by SDS surfactant at a concentration greater than CSC triggers the disruption of the polymer/surfactant complex. However, it is interesting to observe that as SDS is added beyond the minimum point the ST starts to rise steadily (region III). The ST continues to increase until a limiting value (35 mN/m) is reached at 17.5 mM SDS and the air/solution interface becomes saturated with SDS surfactant. Indeed, above 17.5 mM SDS, the ST is essentially identical to that of SDS solution without the copolymer, which suggests that SDS has nearly completely displaced copolymer from the interface at this high concentration. This means that the CMC of SDS has been displaced from 7.6 mM in the absence of polymer to 17.5 mM in the presence of polymer suggesting that roughly ca. 9.9 mM of SDS are bound to the polymer. The ST results suggest that the final state comprises poly(-SAMPS/DA) copolymers with no more associations among the hydrophobe units. But in the final state, each hydrophobe unit of the copolymer is immersed in a surfactant micelle such that the polymer looks like a “necklace”. Thus the region III of the ST plot is associated with the necklace type complex formation. Similar behavior has been predicted and also observed with other HMP/surfactant systems [44].

3.2.2. Viscosity studies

It is usually assumed that at a concentration greater than its CIC the binding of surfactant to polymer is cooperative which brings polymer chains together causing an increase of solution viscosity. Nyström and coworkers have studied the interactions of hydrophobically modified alginate (henceforth referred to as HM-alginate) polymer with SDS and observed strong interactions at a very low surfactant concentration [24]. This was manifested by

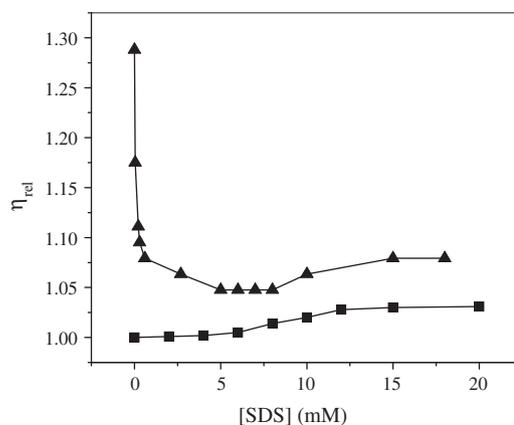


Fig. 4. Variation of relative viscosity with [SDS]; C_p (g/L) = 0 (■), and 1.0 (▲).

the enhancement of viscosity as a result of formation of cross-links between the polymer chains through SDS micelles. However, the associations were observed to be disrupted at high levels of SDS addition. Fig. 4 exhibits plots showing the dependence of the relative viscosity of the solution on [SDS] in the absence as well as in the presence of 1.0 g/L poly(SAMPS/DA). In the absence of polymer the viscosity of the solutions increased slightly above their CMC (~7.6 mM) because of the formation of micelles. In contrast, in the presence of polymer, the plot exhibits a pronounced drop in solution viscosity that reaches minimum at a [SDS] of ca. 4 mM, suggesting a decrease in hydrodynamic volume of the polymer/surfactant mixed micelles in comparison to the pure polymer micelles. Upon increase of SDS concentration above ca. 7.9 mM, the relative viscosity continued to increase, suggesting a gradual restructuring of the polymer. The results are very similar to those obtained from ST studies. It should be noted that the relative viscosity of the 20 mM SDS solution in the presence of polymer is greater than that of pure SDS solution having same concentration. The results are in accord with that expected from an increase in hydrodynamic volume of the polymer–SDS mixed micelles in comparison to the pure SDS micelles (see below). This behavior is thus quite different from that of HM-alginate.

3.2.3. Fluorescence studies using AN and DPH probes

For reasons mentioned above, fluorescence probe studies using AN and DPH as fluorescent probes were performed to investigate aggregate formation in polymer/surfactant mixtures using two different concentrations of poly(SAMPS/DA). The fluorescence titration curves obtained using AN probe has been shown in Fig. 5. In the absence of polymer, upon addition of surfactant, the relative fluorescence intensity (F/F_0) as well as spectral shift ($\Delta\lambda = \lambda_{\text{water}} - \lambda_{\text{sample}}$) increases following a sigmoidal curve. The CMC of SDS, corresponding to the onset from the lower plateau is found to be about 7.5 mM in a rather good agreement with the value obtained in this work from the ST measurement and with those reported in the literature [45]. It is observed that in the presence of 0.25 g/L polymer both F/F_0 and $\Delta\lambda$ remain unchanged until SDS concentration reached ca. 6.0 mM. Above this concentration, however, F/F_0 as well as $\Delta\lambda$ increases sharply reaching maximum at [SDS] ca. 20 mM. The $\Delta\lambda$ and F/F_0 values corresponding to the plateau are exactly equal to the corresponding value of pure surfactant solution suggesting existence of only SDS-rich micelles.

Interestingly, in the presence of 1.0 g/L poly(SAMPS/DA), the feature of the plots are different from that in dilute solution of the polymer. In the plot of F/F_0 versus [SDS], two inflections can be observed. Similar feature can also be observed with the titration curve (Fig. 6) obtained using DPH probe. At low concentrations, the added surfactant monomers are incorporated into the polymer mi-

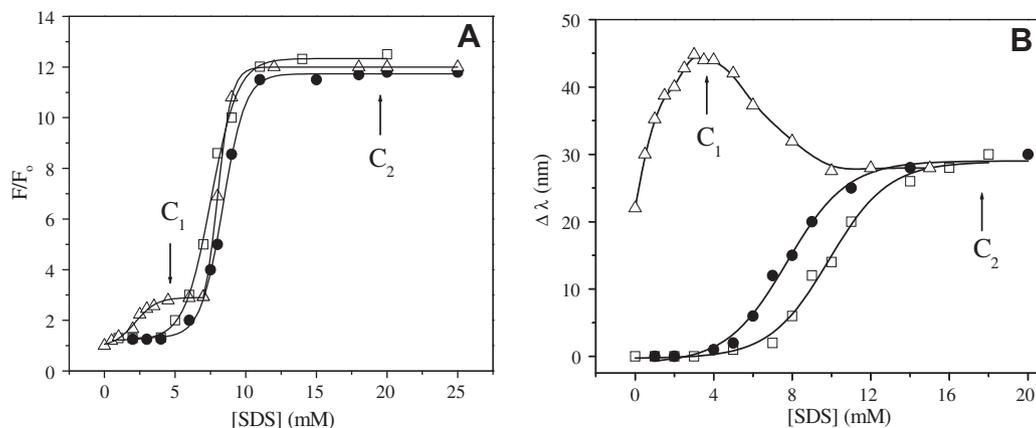


Fig. 5. Plot of (A) relative fluorescence intensity (F/F_0) and (B) shift of emission maximum ($\Delta\lambda = \lambda_{\text{water}} - \lambda_{\text{sample}}$) of AN probe as a function of [SDS] in the presence of 0.0 (□), 0.25 (●), and 1.0 (Δ) g/L poly(SAMPS/DA) in water at 303 K.

celles increasing the hydrophobicity of their microenvironments. This indicates that the critical incorporation concentration (CIC) of SDS is very low (<1.0 mM). The binding continues until the [SDS] reaches a value C_1 (see Figs. 5 and 6) corresponding to the inflection point (ca. 4 mM) above which the polymer/surfactant complexes, which are a loose cross-linking aggregate start to disintegrate and subsequently rehydration of the polymer backbone takes place. This means that polymer/surfactant complexes are formed at [SDS] < 4 mM. Above this concentration the complexes are disrupted to SDS-rich micelles. It appears that the solubilities of AN and DPH probes in SDS-rich micelles are much higher than in surfactant bound polymer micelles. This is indicated by the sharp rise of F/F_0 which plateau at a concentration C_2 (ca. 20 mM).

The corresponding variations of $\Delta\lambda$ with [SDS] in the presence of different concentrations of poly(SAMPS/DA) are presented in Fig. 5B. As observed, $\Delta\lambda$ value initially rises to maximum at C_1 (~4 mM) and then drops down with increase of [SDS], reaching plateau at the same concentration (C_2) as observed with the pure SDS. Similar feature can also be observed with the plot of r versus [SDS] as shown in Fig. 6. In cases of both AN, and DPH, the SDS concentration corresponding to the maximum is exactly the same as the concentration corresponding to the inflection point (C_1) of the respective plot of F/F_0 versus [SDS]. Therefore, they can be ascribed to the same process of surfactant binding to the polymer micelles. Thus, in the concentration range 0 to C_1 , the binding of SDS to the hydrophobic microdomains of pure copolymer micelles gives rise to smaller size SDS-bound polymer micelles, which are less polar and more rigid than the hydrophobic microdomains of

pure polymer micelles. The C_1 value can be considered as the surfactant saturation concentration (CSC). The above study suggests that quite a large fraction of SDS (~4 mM) interacts with the poly(-SAMPS/DA) copolymer. This amount is much larger than the binding of SDS surfactants with neutral polymers, such as hydrophobically modified dextrans [23] and pluronic copolymers [46]. The decay of $\Delta\lambda$ value of AN probe and r -value of DPH probe at SDS concentrations above C_1 confirms disruption of the SDS-bound polymer micelles and consequent formation of SDS-rich necklace-bead-structure. The amount of SDS bound to the polymer is about 12 mM, which is closely equal that obtained from ST measurements.

3.2.4. Microenvironments of the polymer-SDS complexes

As per above discussion two types of polymer/surfactant complexes are formed, one is SDS-bound polymer micelle and the other is polymer-bound SDS micelles henceforth referred to as (polymer-SDS) and (SDS-polymer), respectively. By comparing the variation of $\Delta\lambda$ of the emission spectrum of AN with [SDS] in 1 g/L poly(SAMPS/DA), it was found that $\Delta\lambda$ for polymer-SDS complex was higher than those of pure copolymer aggregates, indicating its more compact and hydrophobic microenvironment. Indeed, the micropolarity parameter [47], I_1/I_3 (see Table 1) is slightly less than that of the pure polymer aggregate. However, in the presence of 20 mM SDS the I_1/I_3 index is lowest and is close to the value of pure SDS micelles. To estimate the microfluidity of the micellar core, we measured the steady-state fluorescence anisotropy (r) of the DPH probe in polymer solution as well as in polymer/surfactant mixtures. DPH is a well known membrane fluidity probe and has been used for studying many lipid bilayer membranes [48,49]. The data in Table 1 show that the fluorescence anisotropy of DPH in the presence of SDS corresponding to CSC value is higher than the polymer aggregates suggesting increase in compactness of aggregates due to tight packing of hydrocarbon chains upon addition of surfactant. However, a large decrease in anisotropy can be observed at higher surfactant concentrations, indicating formation of free SDS micelles. The relatively low micropolarity and microviscosity of the SDS-polymer complex is consistent with its necklace-bead structure.

3.2.5. Hydrodynamic diameter of the polymer-SDS complexes

The polymer-surfactant interaction was also studied by DLS technique. The hydrodynamic diameter ($\langle d_H \rangle$) of the aggregates of pure surfactant and polymer, and polymer-SDS complexes were measured. The size distributions have been depicted in Fig. 7. As observed the value of $\langle d_H \rangle$ of the polymer aggregates in 1.0 g/L

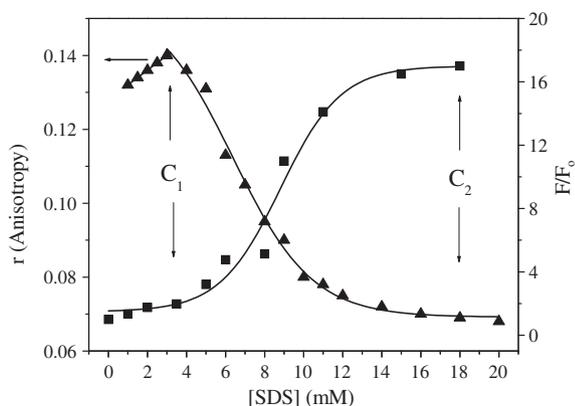


Fig. 6. Variation of relative fluorescence intensity (F/F_0) and anisotropy (r) of DPH probe with [SDS] in the presence of 1.0 g/L poly(SAMPS/DA) at 303 K.

Table 1

The values of anisotropy (r), I_1/I_3 and $\Delta\lambda$ in presence of 1.0 g/L copolymer, poly(SAMPS/DA), and poly(SAMPS/DA)-SDS complex in water at 303 K.

Physical properties	Poly(SAMPS/DA) (1.0 g/L)	Poly(SAMPS/DA) (1.0 g/L) + SDS (mM)		SDS (mM)
		3.5	20	
r (± 0.004)	0.129	0.145	0.08	0.06
I_1/I_3 (± 0.06)	1.65	1.50	1.15	1.22
$\Delta\lambda$ (± 2 nm)	22	44	28	29

polymer solution is ca. 300 nm. Such a large aggregate must form as a result of inter-polymer association of several polymer units and is called multipolymer micelles [27,38,50]. However, upon addition of SDS the size of the polymer micelles is reduced. The decrease in size confirms the shrinking of polymer and formation of more compact structure and is consistent with the decrease of relative viscosity (Fig. 4). In the presence of SDS at a concentration greater than its CMC, the decrease is very large and the bimodal size distribution exactly matches with the one obtained in the presence of 0.25 g/L polymer. However, no aggregates having sizes equal to pure surfactant micelles could be observed. Thus it can be concluded that the large polymer-SDS complexes are disintegrated in the presence of higher concentration of SDS and smaller polymer-decorated surfactant micelles are formed which have d_H values (ca. 6 nm) greater than that of pure SDS micelles (ca. 3 nm). The bimodal distribution clearly indicates existence of SDS-polymer complexes having diameters in two different size ranges.

3.2.6. Structures of the polymer-SDS complexes

Based on the results of ST, viscosity, fluorescence, and DLS studies described above the following mechanism (Scheme 1) for interaction can be proposed. The surfactant molecules through hydrophobic interactions associate first with the polymer aggregates to form the polymer-surfactant complexes, which upon further addition of surfactant (or upon rise of temperature as discussed below) get disrupted and small surfactant micelles that

are decorated with the polymer chains, are formed. Therefore, depending upon surfactant concentration two types of polymer-surfactant complexes are formed. The polymer-decorated micelles are expected to have sizes bigger than pure surfactant micelles. Many authors have proposed necklace-bead-like structure of polymer-surfactant complexes [16,44]. However, only a small rise of relative viscosity and small $\langle d_H \rangle$ value clearly suggest that the necklace-bead structure cannot be stretched one. In other words, the polymer forms multiple loops containing SDS micelles along the chain such that the overall structure becomes spherical. The copolymers with larger chain lengths accommodate more number of SDS micelles forming larger particles while the shorter chain polymers form smaller particles. Recently, Hatton and coworkers, based on light scattering experiments, have proposed similar structures for the mixed micelles of azobenzene-trimethylammonium bromide surfactant in the presence of hydrophobically modified poly(sodium acrylate) complexes [51].

3.2.7. Transmission electron microscopy

To corroborate the results obtained by fluorescence and DLS measurements, here we present TEM images (Fig. 2) of the polymer/surfactant complexes. TEM images were taken of the polymer/surfactant complexes in 1.0 g/L of polymer solution containing two different SDS concentrations, one at 3.5 mM (CSC or C_1) and the other at 18 mM. The regularly shaped spherical morphology can be found with the polymer-SDS complex with a wide range of size distribution (50–250 nm). But in the presence of 18 mM SDS, particles of almost uniform spherical shapes with average diameters around 50 nm can be observed. The size of the aggregates is reasonably in good agreement with the results of direct size measurements by DLS technique. However, particles of micellar dimension (ca. 8 nm) as indicated by the results of DLS measurements could not be observed. This could be due to our inability to attain high resolution of the picture. The TEM results thus support the proposed scheme for the formation of polymer-SDS complexes at different stages of SDS concentrations.

3.2.8. Stability of polymer-SDS complexes

The proposed structures of the polymer aggregates and polymer-SDS complexes are also supported by their relative temperature stabilities. The effect of temperature on the above polymer-SDS complexes was investigated by monitoring the change in microenvironment of the pure polymer (1.0 g/L) and the complexes upon heating above room temperature by use of DPH probe. The steady-state fluorescence anisotropy (r) and intensity (F) of the probe were measured at different temperatures. The plots of variation of r and relative intensity (F/F_0) as a function of temperature are depicted in Fig. 8. It is observed that anisotropy and hence internal viscosity of the polymeric aggregates changes almost linearly upon heating, which means chain melting over a broad temperature range. In other words, the polymer aggregates are very stable. The corresponding change of F/F_0 is also small, indicating release of only a small amount of entrapped DPH molecules from the hydrophobic core. In contrast, for polymer-SDS complex the anisotropy as well as F/F_0 drops down to a lower value corresponding to SDS micelles, suggesting temperature-induced disruption of the polymer-SDS complex. The sharp sigmoid change of r (or F/F_0) with temperature confirms a two-step process. The transition temperature of the polymer-SDS complex is ca. 311 K, suggesting that polymer-SDS complex is less stable than the polymer micelles. Since the transition temperature is around physiological temperature (310 K) the polymer-SDS complexes may have potential applications in temperature-triggered drug release. However, it is interesting to note that the polymer-decorated SDS micelles (SDS-polymer complexes) are more stable than the polymer-SDS complex.

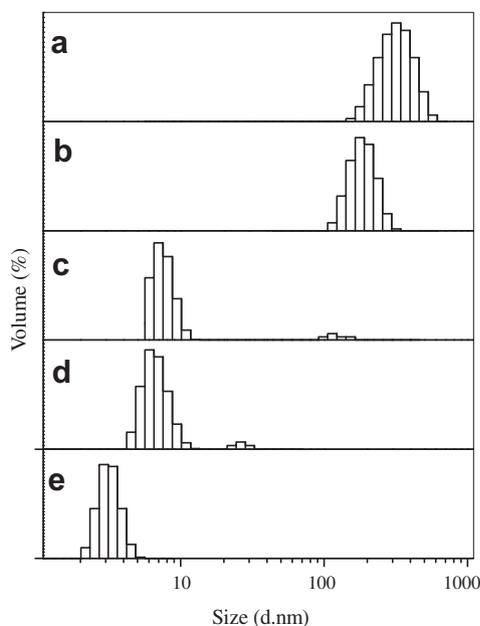
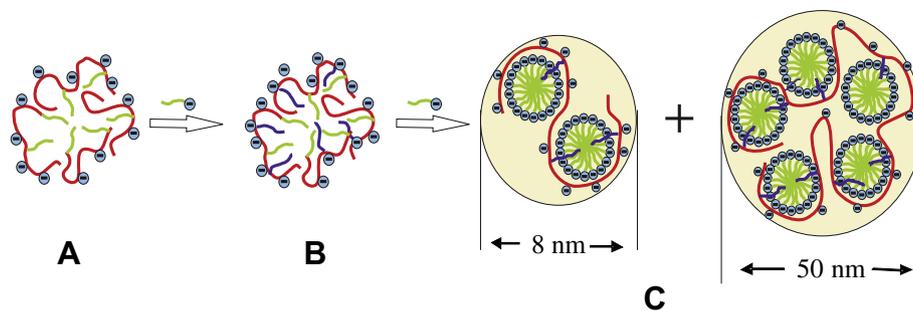


Fig. 7. The size distributions in aqueous [poly(SAMPS/DA)] solution: (a) $C_p = 1.0$ g/L, (b) $C_p = 1.0$ g/L in 4 mM SDS, (c) $C_p = 1.0$ g/L in 18 mM SDS, (d) $C_p = 0.25$ g/L in 18 mM SDS, and (e) 18 mM SDS.



Scheme 1. Schematic representation of SDS binding with poly(SAMPS/DA) polymer micelles: (A) polymer micelles, (B) polymer–SDS complex, and (C) SDS–polymer complex.

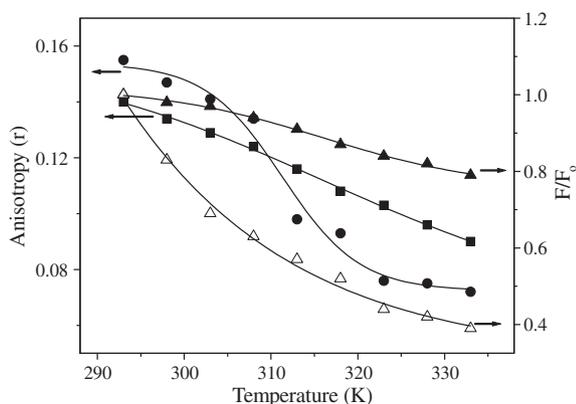


Fig. 8. Variation of relative fluorescence intensity (F/F_0) and fluorescence anisotropy (r) of DPH probe with temperature: (■ and ▲) 1.0 g/L of polymer, (● and △) 3.5 (mM) SDS in 1.0 g/L polymer.

4. Conclusions

In summary, it has been shown that the copolymer, poly(SAMPS/DA), self-assembles in water forming irregular-shaped aggregates through association of the hydrophobic pendant groups. The aggregates have sizes in the nanometer range. The microenvironment of the polymer aggregates is less polar and more viscous than bulk water. Despite negatively charged surface these polymeric aggregates interact strongly with SDS surfactant that has similar charge mainly through hydrophobic association. However, free surfactant and polymer do not interact with each other due to electrostatic repulsion. Surface tension studies show that surfactant binds to poly(SAMPS/DA) in a non-cooperative fashion at CSC. Two types of complexes are formed in the presence of SDS surfactant. At a concentration less than CSC, SDS-bound polymer micelles are produced whereas above CSC, SDS-rich polymer-bound micelles with necklace–bead-structure are formed. The polymer (1 g/L) binds about 3 mM quantity of SDS to produce polymer–SDS complex. On the other hand, the same amount of polymer requires ca. 12 mM SDS to form the necklace–bead structure. The TEM images revealed regular spherical morphology for both types of polymer–surfactant complexes. This suggests a closed necklace–bead structure for the SDS-rich complex. However, in contrast to literature reports, we have not observed any increase of viscosity of polymer solution upon addition of SDS. The microenvironment of the polymer–SDS complex is less hydrophobic and more rigid compared to that of SDS–polymer complex or pure SDS micelles. This means that the latter complex can entrap more hydrophobic drugs than the polymer–SDS complex or the pure polymer micelles. Also the polymer–SDS complex was found to be less stable with respect to temperature change than the polymer-bound SDS micelles (SDS–polymer complexes). In contrast to

polymeric micelles the polymer–SDS complex was found to undergo temperature-induced disruption with the transition temperature at around 310 K. Thus polymer–SDS complexes of poly(SAMPS/DA) may find applications in temperature-triggered drug delivery. Work toward this direction is currently underway.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.06.055.

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