Structure of Polymer/Surfactant Complexes Formed by Poly(2-(dimethylamino)ethyl methacrylate) and Sodium Dodecyl Sulfate

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The small-angle neutron scattering from poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) has been investigated in the presence of the anionic surfactant, sodium dodecyl sulfate (SDS). At pH 9.1, the polymer is a Gaussian coil whose size is determined primarily by nonelectrostatic interactions. The presence of the polymer induces micellization of the surfactant, even at surfactant concentrations below the surfactant's normal critical micelle concentration. The polymer decorates the surfactant micelles and in some respects resembles a polymer adsorbed on a spherical particle.

Introduction

A vast number of studies have been carried out to probe the interactions between polymer and ionic surfactant molecules in aqueous solution.[1] Most of this work has focused on interactions between poly(ethylene oxide) (PEO) and sodium dodecyl sulfate (SDS),[2−5] poly(*N*-vinylpyrrolidone) (PVP) and SDS,[6] PEO and dodecylammonium bromide (C_{12}TAB),[7] and various surfactants with the biopolyampholyte gelatin.[8−10] For strongly interacting systems such as these, the polymer acts as a nucleation site where the surfactants aggregate onto the polymer backbone at concentrations well below the normal critical micelle concentration (cmc) of the surfactant. The concentration above which the surfactant forms a complex with the polymer is known as the critical aggregation concentration (cac) and is virtually independent of polymer concentration and molecular weight. The surfactant molecules aggregate on the polymer chains in the form of bound micelles.[11−13] Each polymer chain links several micelles to form a "pearl necklace" structure.[11] As the surfactant concentration increases further, the polymer chains become saturated with micelles. Conventional (unbound) surfactant micelles begin to form in solution above this surfactant concentration.

The binding of ionic surfactants to oppositely charged polyelectrolytes has also been studied.[1] Complex formation is highly favored via two mechanisms: first, an ion-exchange process; second, at higher surfactant concentration, cooperative binding. As the ratio of surfactant molecules to charged sites on the polyelectrolyte approaches unity, precipitation of the complex occurs due to charge neutralization of the polyelectrolyte and to the hydrophobic nature of the bound surfactants, which adopt a conformation in which their ionic headgroups are effectively removed from the solution. On addition of further surfactant, the insoluble polymer/surfactant complex redissolves. This is due to cooperative binding of surfactant molecules on the polymer chains, whereby hydrophilic micelles or hemimicelles are formed. Beyond this point the overall charge of the complex has the same polarity as that of the surfactant.

In some respects the association between a surfactant and an oppositely charged polyelectrolyte is very similar to that of a surfactant and an oppositely charged surface, where binding of single surfactant molecules is followed, at higher surfactant concentrations, by cooperative binding to form (hemi)micelles. The flexibility of the polyelectrolyte allows more freedom in the structure of the complexed surfactant micelles, although the final structure of these micelles depends on the specific nature of the surfactant and the polyelectrolyte used.

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Poly(2-(dimethylamino)ethyl methacrylate)[14-18] (PDMAEMA) is of interest as it is a weak polybase with a pK_b[18] of 8.0; thus, the polymer charge density depends strongly on the solution pH. This work represents a study of the interaction of the polymer at its natural pH (9.1), where it is only weakly charged, with an anionic surfactant.

Experimental Section

Materials. Poly(2-(dimethylamino)ethyl methacrylate) was prepared via group transfer polymerization according to the procedure described by Baines et al.[14,15] The polymer had a molecular weight (M_n, obtained by ^{1}H NMR) of 8000 g mol^{-1} and a polydispersity (M_w/M_n) of 1.10. This molecular weight corresponds to approximately 50 DMAEMA residues/polymer chain.

Hydrogenated sodium dodecyl sulfate (H-SDS) was obtained from Fluka chemicals (>98% purity). Deuterated sodium dodecyl sulfate (D-SDS) was obtained from Fluorochem (98.2% atom D). Both samples were used as supplied.

Samples were either prepared in MilliQ Millipore water or D_2O (MSD Isotopes Limited).

Small-Angle Neutron Scattering. The small-angle neutron scattering (SANS) from solutions of PDMAEMA in D_2O was measured on the NG3-SANS instrument at the NIST center for neutron research situated in Gaithersburg, MD.

The polymer concentration was held constant at 15,500 ppm and the scattering was measured with added deuterated SDS (D-SDS) at 1500, 3000, and 10 000 ppm. This corresponds to surfactant concentrations below, just above, and well above the surfactant's normal cmc in the absence of polymer. These experiments measure the scattering from the polymer alone as D-SDS is contrast-matched in D_2O. The scattering from the polymer and hydrogenated SDS (H-SDS) at 3000 ppm was also measured and contained contributions from both the polymer and surfactant.

The scattering from the same polymer in acidified D_2O (pH 2) and the scattering from 10 000 ppm H-SDS in D_2O were measured on the LOQ instrument, at the ISIS spallation neutron source, Didcot, U.K.

The scattering intensity ($I(Q)$) from each sample is measured as a function of the scattering vector, Q.

$$Q = 4\pi \sin(\theta/2)/\lambda \tag{1}$$

where λ is the neutron wavelength and θ the scattering angle.

The scattering, which contains information about shapes, sizes, and interactions of the scattering bodies, is given by

$$I(Q) = N_b V_b^2 \Delta\rho^2 P(Q) S(Q) + B_{inc} \tag{2}$$

where N_b is the number concentration of scattering bodies and V_b is the volume of each body. $P(Q)$ and $S(Q)$ are the form factor and structure factor, respectively. B_{inc} is the incoherent background.

$\Delta\rho$ is the difference in the scattering length density (SLD) between the scattering body and the surrounding medium. The SLD can be considered to be a "neutron refractive index" and depends on the chemical composition of the material and its density. It is well-known[19] that hydrogen and deuterium have vastly different scattering lengths, so that substituting deuterium for hydrogen allows systematic variation of the SLD over a wide range. It can be seen from eq 2 that if the SLD of the medium is equal to that of the scattering entity, then it will no longer contribute to the scattering. When the scattering from a body has been removed in this way, then the system is said to be "contrast-matched". By "matching out" individual components we can measure the scattering from each part of the system.

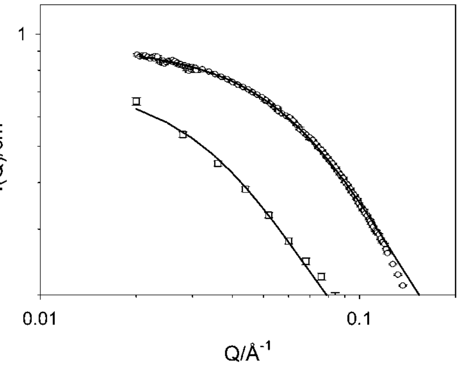

Figure 1. Scattering from PDMAEMA at 15 500 ppm by weight in D_2O. The polymer solutions were prepared from D_2O at pH 9.1 (□) and acidified D_2O at pH 2.0 (○). The solid lines indicate fits to the Debye Gaussian coil model.

The magnitude of a sample's incoherent background increases with the degree of hydrogenation of the system, so it is convenient to work using a medium with a high D_2O content.

The form factor contains information on the shape of the scattering centers. For polymer solutions[19,20] the form factor may be approximated by assuming a Gaussian polymer coil in its Θ state. This was evaluated by Debye[21] as

$$P(Q) = \frac{2[Q^2R_g^{\ 2} - 1 + \exp(-Q^2R_g^{\ 2})]}{(QR_g)^4} \tag{3}$$

where R_g is the radius of gyration.

The structure factor $S(Q)$ contains information about interparticle interactions and is normally only observed for concentrated or charged systems such as surfactant micelles where these interactions are strong. The Hayter−Penfold technique[22,23] has been used to calculate the structure factor for micelles with a given radius, surface charge, and intermicelle separation.

Results and Discussion

Scattering from the Polymer. Figure 1 shows the scattering from polymer solutions, prepared in either D_2O or acidified D_2O (pH 2). When the polymer is dissolved in water, the pH of the solution increased to pH 9.1, due to the basic nature of the polymer chains. At this pH the fraction of charged groups is approximately 0.03% of the total number of monomer residues present in the solution, so the polymer is virtually uncharged. In acidic solution the polymer will become a weak cationic polyelectrolyte due to protonation of its tertiary amine groups. At pH 2, essentially all of the DMAEMA residues are expected to be protonated.[24]

The scattering due to the homopolymer is a low-intensity, slowly decaying curve, both at high and low pH. At low Q, the data fit well to the Debye Gaussian coil model (eq 3) as shown by the solid lines in Figure 1. The radii of gyration for the polymer coil obtained from the fits were 21.3 ± 0.1 Å at pH 9.1 and 38 ± 1 Å at pH 2. Thus, the size of the charged coil in acidic media is nearly twice that measured at high pH; clearly repulsive electrostatic interactions have a considerable effect, leading to an expansion of the polymer coil. Empirical relations

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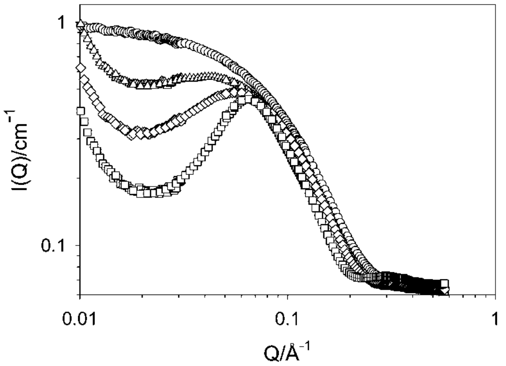

Figure 2. Scattering from a 15 500 ppm by weight PDMAEMA solution with D-SDS in D_2O: (○) pure polymer solution at pH 9.2; (△) polymer with 1500 ppm D-SDS at pH 9.8; (◇) 3000 ppm D-SDS at pH 10.2; (□) 10 000 ppm D-SDS at pH 10.9.

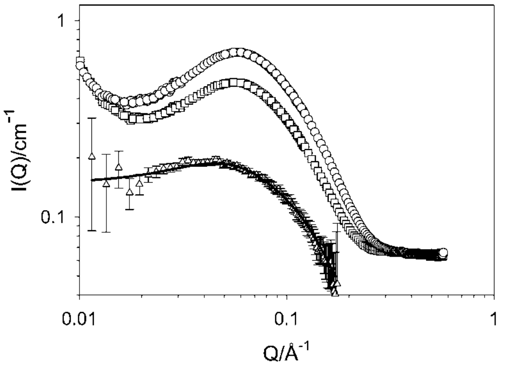

Figure 3. Scattering from 15 500 ppm by weight PDMAEMA and SDS in D_2O: (△) H-SDS 3000 ppm (solid line is a fit to the Hayter−Penfold model giving a radius of 36.6 Å); (□) polymer and 3000 ppm D-SDS; (○) polymer and 3000 ppm H-SDS. pH values are as for Figure 2.

between the radius of gyration and molecular weight exist for many polymers,[25] but unfortunately none are available for PDMAEMA. It was therefore assumed that the neutral PDMAEMA chains would behave as poly(methyl methacrylate) (PMMA), which has an identical backbone. This implies a radius of gyration of 18.6 ± 1.7 Å, which is in good agreement with the value for the uncharged coil obtained from the Debye Gaussian fit. This agreement would suggest that the conformation of PDMAEMA in D_2O at pH 9.1 is determined solely by steric and entropic considerations; the polymer is essentially uncharged, as expected.

Interestingly at the lower pH, there is no evidence of a broad peak in the scattering or an upturn at low *Q*. Such behavior has been observed for many other polyelectrolyte solutions and has been associated with a "correlation hole",[26−29] which is due to intermolecular repulsion. The position of this maximum scales as the polymer concentration, $c_p^{0.5}$, and this might occur outside the present *Q* range.

Scattering from the Polymer in the Presence of Surfactant. Figure 2 shows the scattering from the polymer in D_2O with SDS. Addition of SDS to the polymer causes the shape of the scattering data to change dramatically. Two main features appear: first, the intensity of the scattering at very low *Q* increases; second, a peak appears at around $Q = 0.04-0.06$ Å^{-1}. This effect occurs well below the normal cmc of the surfactant. Under these conditions the deuterated surfactant does not contribute to the scattering, and these features must therefore be due to some change in the conformation of the polymer. Substitution of "contrast-matched" D-SDS with "visible" H-SDS is shown in Figure 3, and there is no significant change in the general form of the scattering. The cmc of hydrogenated SDS in D_2O has been shown to be very similar to the cmc of hydrogenated SDS in H_2O.[28] The scattering data from H-SDS in D_2O and D-SDS in H_2O suggest micelles of similar shape and size.[30,31] From this we may infer that substitution of D-SDS for H-SDS or D_2O for H_2O does not significantly alter the micellar properties of the surfactant. However, for the case of H-SDS the peak occurs with greater intensity as expected. For comparison, we also show the scattering from H-SDS at the same concentration in D_2O. In this situation it is clear that the polymer/surfactant interaction occurs below the cmc, resulting in a greater population of micelles. This behavior is very similar to that found for the interaction of gelatin with SDS.[9] The main difference between the scattering curves is the upturn at low *Q*; this is not seen in the pure SDS sample and is a signature of polyelectrolyte behavior.[26−29]

A similar peak in the scattering of mixed polymer/surfactant solutions was observed from the scattering of the biological polyampholyte gelatin with SDS[9] measured by Cosgrove et al. and also for the neutral polymer poly(ethylene oxide) with D-SDS[31,32] measured by Cabane and co-workers, which was attributed to the polymer becoming structured around SDS micelles. The data reported by Cabane and co-workers also showed an upturn in the scattering at low *Q* values where the intensity was found to have a Q^{-2} dependency. In contrast, the earlier gelatin data of Cosgrove et al. did not show an upturn at low *Q*, although a smaller *Q* range was investigated in this case.

The upturn in the scattering due to polymer/surfactant solutions studied here is linear on a log−log plot, with the intensity of the scattering following a Q^x power law with x falling between −3.6 and −4.4. Ermi and Amis[27,28] conducted SANS experiments on polyelectrolyte solutions in which the scattering was measured to very low *Q* values. They reported that the upturn in intensity followed an $x = -2.2 \pm 0.2$ law. The exponent of −4 suggests a Porod scattering law from a sharp interface, which is consistent with the polymer wrapping itself closely around the (contrast-matched) surfactant micelles. Assuming that the aggregation number of the polymer-adsorbed micelles is the same as that of normal SDS micelles,[31] there will be approximately 3.5 chains for every micelle if all the SDS is complexed, and at these concentrations this is quite reasonable. The PDMAEMA chains have an average degree of polymerization of only 50 so it would be expected that several short chains are associated with each micelle. For these reasons we attribute the peak in the scattering of the PDMAEMA/SDS solutions to the formation of a micellelike polymer/surfactant complex. This process is shown schematically in Figure 4a. When the scattering from the polymer and hydrogenated surfactant is measured in D_2O, all components are visible (Figure 4b). The structure peak in the data arises from intermicelle electrostatic interactions.

Use of the deuterated SDS surfactant (Figure 4c) means that this component does not contribute to the scattering and the data appear similar to that obtained for the

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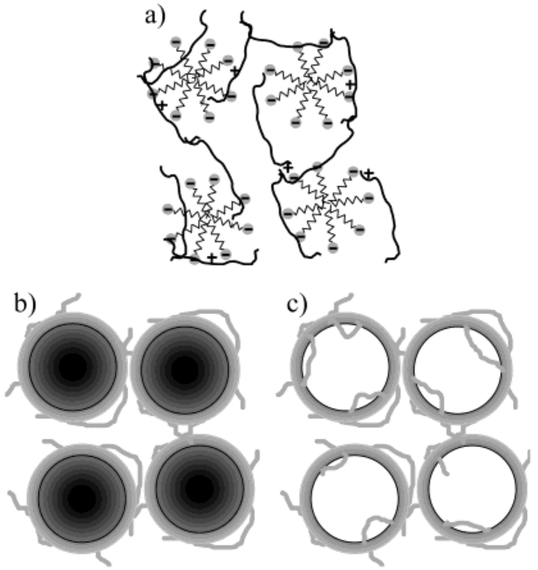

Figure 4. Schematic representation of surfactant micelles structuring the polymer. (a) The polymer induces micellization of the surfactant, and the surfactant micelles "structure" the polymer. (b) Schematic representation of the scattering from the polymer with hydrogenated surfactant in D_2O; the scattering is dominated by the contributions from the surfactant micelles. (c) Schematic representation of the scattering from the polymer with deuterated surfactant in D_2O; the surfactant is "matched out" and therefore does not scatter.

hydrogenated surfactant because the polymer is structured by the surfactant micelles.

Figure 5 shows the peak in the scattering of PDMAEMA chains with SDS in more detail. The peak in the scattering has been fitted to the Hayter–Penfold model for spherical micelles for the higher *Q* data. Typical values for the Debye length and surface charge have been chosen on the basis of our earlier paper on gelatin and SDS and are 20 ± 2 and 21 Å, respectively. However, as in that case, these parameters should not be overinterpreted given that we are fitting a phantom micelle in this case. The scattering here *only* originates from the polymer, which appears as a charged shell. The parameters from these fits show that the polymer-adsorbed micelles are generally similar in shape and size to conventional surfactant micelles; in particular, the micelles formed are approximately the same size as conventional SDS micelles at the lowest surfactant concentration investigated (~50% of the normal cmc of SDS). Specifically the micelle diameters are found to lie between 39 and 40 Å compared to the pure SDS value of 36.6 Å (see Figure 3). A slight contraction in the micellar diameter appears at around the normal cmc, and an expansion is observed at higher surfactant concentrations though these values are only just outside the experimental error of ±0.3 Å.

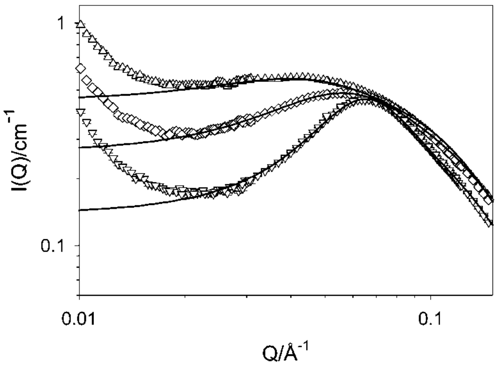

Figure 5. Peak in the polymer scattering arising from the addition of surfactant. The data correspond to polymer with 1500 ppm D-SDS (▽), with 3000 ppm D-SDS (◇), and 10 000 ppm D-SDS (△). The lines on the plot indicate fits to the Hayter–Penfold model.

The volume fractions returned from the fits are inversely proportional to the distance between neighboring micelles; when PDMAEMA is present, the effective volume fractions increases substantially because of the lowering of the cmc and a small increase in the effective complex diameter.

Conclusions

The SANS data show that when DMAEMA homopolymer is dissolved in deionized water, it forms a neutral Gaussian coil whose dimensions are not influenced by electrostatic interactions. When dissolved in acidic media, the coil expands significantly due to the increased cationic charge density on the polymer chains.

Addition of anionic surfactant to the polymer at which pH 9.1 leads to a dramatic change in the measured SANS data. At low *Q* the intensity of the scattering falls off as Q^{-4}, and a peak appears in the scattering at *Q* values of 0.04–0.06 Å^{-1} both for contrast-matched and off-contrast surfactant. The off-contrast data show that micelles form below the normal cmc of the surfactant, with the hydrophobic polymer backbone acting as a nucleating agent. With the micelles rendered invisible (contrast-matched) the peak in the data is attributed to a charged structure resembling that of the micelles. The polymer shape is perturbed significantly as it becomes structured around the surfactant micelles.

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