

Small-Angle Neutron Scattering of Gelatin/Sodium Dodecyl Sulfate Complexes at the Polystyrene/Water Interface

John C. Marshall, Terence Cosgrove,* and Kevin Jack

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

Andrew Howe

Kodak European R&D, Headstone Drive, Harrow, Middlesex HA1 4TY, U.K.

Received April 16, 2002. In Final Form: September 2, 2002

Using isotopic substitution, the small-angle neutron scattering from a gelatin layer preadsorbed upon polystyrene latex has been measured as a function of the added concentration of sodium dodecyl sulfate (SDS). The data have been fitted using a model which includes an exponential volume fraction profile and a term to account for the scattering from spatial concentration fluctuations. Measurements indicate that the gelatin layer thickness increases to a maximum as a function of SDS concentration, while the volume fraction of gelatin adsorbed at the interface simultaneously decreases. Consequently, the adsorbed amount of gelatin peaks at SDS concentrations equivalent to approximately one SDS micelle/gelatin chain. Further addition of SDS sees the adsorbed amount decay below that of the system in the absence of SDS. At the highest SDS concentrations, the gelatin also develops a scattering form similar to that of SDS micelles.

Introduction

Gelatin, the hydrolysis product of the structural protein collagen, has applications in a range of industries. In the photographic industry, gelatin has many functions: binder, viscosifier, gelling agent, and emulsifier and stabilizer of colloidal particles.¹ Additionally, surfactants are often used in conjunction with gelatin to modify rheological, surface tension, and emulsion properties, furnishing systems with the stability and the bulk and interfacial characteristics required in the final product.

The value of small-angle neutron scattering (SANS) and neutron reflectivity in studying polymer–surfactant structures and interactions is reflected in the amount of literature concerning these methods.² For example, the structure of gelatin adsorbed at the air–water interface has been studied by X-ray³ and neutron reflectivity⁴ and on a variety of colloidal surfaces by SANS.^{5–7} Likos et al. have used SANS in conjunction with the Deryagin–Landau–Verwey–Overbeek (DLVO) theory to model colloidal stabilization by an adsorbed gelatin layer.⁸

In addition to investigations by neutron and X-ray techniques, the structure of adsorbed gelatin layers has been studied by a number of other experimental methods. The adsorption of gelatin upon colloidal particles changes the effective particle size and the bulk viscosity, making such systems suited to examination by rheology.^{5,8–11} The thickness of gelatin layers adsorbed upon

silver halide surfaces has been studied via ellipsometry^{12–14} and centrifugation.¹⁵ There is also theoretical work by Dobrynin et al.¹⁶ on the conformation of polyampholyte chains adsorbed at a charged surface. In this work they identified three adsorption regimes determined by the balance of polarized-induced attraction of the chains to the charged surface and chain–chain repulsion. Additionally, the interactions and properties of surfaces coated in gelatin have been investigated using the crossed cylinder surface force apparatus,^{17,18} atomic force microscopy (AFM),^{19–24} and scanning force microscopy.²⁵

There is also extensive literature on gelatin–surfactant interactions, and many experimental techniques have been used including light scattering,^{26,27} laser Raman

- (1) Howe, A. M. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 288.
- (2) Lee, L. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 205.
- (3) Vaynberg, K. A.; Wagner, N. J.; Ahrens, H.; Helm, C. A. *Langmuir* **1999**, *15*, 4685.
- (4) Cooke, D. J.; Dong, C. C.; Thomas, R. K.; Howe, A. M.; Simister, E. A. *Langmuir* **2000**, *16*, 6546.
- (5) Vaynberg, K. A.; Wagner, N. J.; Sharma, R.; Martic, P. *J. Colloid Interface Sci.* **1998**, *205*, 131.
- (6) Cosgrove, T.; Hone, J. H. E.; Howe, A. M.; Heenan, R. K. *Langmuir* **1999**, *14*, 5376.
- (7) Hone, J. H. E. Ph.D. Thesis, University of Bristol, 1999.
- (8) Likos, C. N.; Vaynberg, K. A.; Lowen, H.; Wagner, N. J. *Langmuir* **2000**, *16*, 4100.
- (9) Kao, N.; Bhattacharya, S. N.; Shanks, R.; Coopes, I. H. *J. Rheol.* **1998**, *42*, 493.

- (10) Hone, J. H. E.; Howe, A. M.; Whitesides, T. H. *Colloids Surf., A* **2000**, *161*, 283.
- (11) Howe, A. M.; Clarke, A.; Whitesides, T. H. *Langmuir* **1997**, *13*, 2617.
- (12) Maternaghan, T. J.; Otterwill, R. H. *J. Photogr. Sci.* **1974**, *22*, 2798.
- (13) Bangham, O. B.; Maternaghan, T. J.; Otterwill, R. H. *Photogr. Sci. Eng.* **1979**, *23*, 45.
- (14) Maternaghan, T. J.; Bangham, O. B.; Otterwill, R. H. *J. Photogr. Sci.* **1980**, *28*, 1.
- (15) Coll, H.; Oppenheimer, L. E.; Searles, C. G. *J. Colloid Interface Sci.* **1985**, *104*, 193.
- (16) Dobrynin, A. V.; Obukhov, S. P.; Rubinstein, M. *Macromolecules* **1999**, *32*, 5689.
- (17) Kamiyama, Y. *J. Phys. Chem.* **1990**, *94*, 4611.
- (18) Kawanishi, N.; Christenson, H. K.; Ninham, B. *Macromolecules* **1990**, *23*, 5689.
- (19) Braithwaite, G. J. C.; Luckham, P. F.; Howe, A. M. *J. Colloid Interface Sci.* **1999**, *213*, 525.
- (20) Braithwaite, G. J. C.; Luckham, P. F. *J. Colloid Interface Sci.* **1999**, *218*, 97.
- (21) Haugstad, G.; Gladfelter, W. L.; Keyes, M. P.; Weberg, E. B. *Langmuir* **1993**, *9*, 1594.
- (22) Domke, J.; Rotsch, C.; Hansma, P. K.; Jacobson, K.; Radmacher, M. *ACS Symp. Ser.* **1998**, *694*, 178.
- (23) Domke, J.; Radmacher, M. *Langmuir* **1998**, *14*, 3320.
- (24) Mackie, A. R.; Gunning, A. P.; Ridout, M. J.; Morris, V. J. *Biopolymers* **1998**, *46*, 245.
- (25) Haugstad, G.; Gladfelter, W. L.; Jones, R. R. *Langmuir* **1998**, *14*, 3944.
- (26) Saxena, A.; Antony, T.; Bohidar, H. B. *J. Phys. Chem. B* **1998**, *102*, 5063.
- (27) Maity, S.; Bohidar, H. B. *Phys. Rev. E* **1998**, *58*, 729.

spectroscopy,²⁸ and surface tension measurements.^{29–31} Fluorescence probe studies³¹ have shown that the aggregation number of sodium dodecyl sulfate (SDS) micelles adsorbed on gelatin chains is similar to that of SDS micelles in solutions of low ionic strength. This study also showed that there are two breaks in the surface tension measurements of gelatin/SDS solutions. The first is the critical aggregation concentration (cac) which corresponds to the formation of adsorbed micelles, and the second corresponds to the formation of free SDS micelles in solution. The position of the second break point depended on the gelatin concentration, indicating that free micelles were formed after the saturation of the gelatin chains. In contrast to the polymer-free critical micelle concentration (cmc), ionic strength appeared to have little influence over this break point. A thermodynamic model based on electrostatic interactions was used to describe the interactions between the polymer and anionic surfactant.

SANS studies of the structure of gelatin–surfactant complexes have indicated that a close association of gelatin with the surfactant micelles occurs at low ionic strength. The SANS of the gelatin in these systems displays a scattering pattern that mirrors the micelle scattering, suggesting it wraps around the micelles and adopts their regular structure and repulsive interactions. These interactions are strongly affected by ionic strength and pH, again suggesting the dominance of electrostatic effects.^{32–34} Temperature, however, was not seen to affect the structure of the complexes.³³

Nuclear magnetic resonance (NMR) has been used to study the interactions between gelatin and anionic surfactants in solution. Gelatin diffusion reached a minimum with a surfactant concentration of ~1 micelle/chain. The depth of this minimum was increased with the alkyl chain length and hence the micelle size.³⁵ This was attributed to the formation of transient cross-links by the surfactant micelles and is in agreement with more recent fluorescence probe studies of the system.³⁶ The saturation point of gelatin was determined as 3–4 micelles/chain.³⁷ ¹³C NMR has shown that SDS micelles interact with gelatin through the electrostatic attraction of the cationic residues for anionic SDS headgroups and through the hydrophobic attraction of nonpolar and hydrophobic residues for the alkyl chains of the surfactant.³⁸ This model for the SDS/gelatin interaction is supported by EPR³⁹ and conductometric studies.⁴⁰

Anionic surfactants are able to increase the viscosity of gelatin solutions more effectively than of nonionic polymer

solutions of the same molecular weight and concentration.^{41,42} The structure of surfactant/nonionic polymer complexes has been compared to a bead and necklace model,⁴³ where surfactant micelles are adsorbed upon individual polymer chains. Greener et al.⁴² proposed that the large increase in viscosity observed in gelatin solutions could not be accounted for by the bead and necklace model of micelle adsorption on the polymer chains. Instead, they suggested that, above the critical overlap concentration (C^*), the micelles bind at active sites upon the gelatin chain and form transient cross-links in a dynamic network with more than 1 chain bound to each micelle.

The addition of a surfactant to a gelatin layer adsorbed at an interface generates complex interactions between the gelatin and surfactant and between the surfactant and the interface. These are in addition to the interaction between the gelatin and the interface. Furthermore, each interaction will have some influence over the others. The interactions among gelatin, surfactants, and a hydrophobic solid/water interface have been studied via surface tension, ellipsometry, surface plasmon resonance (SPR), and total internal reflectance fluorescence spectroscopy (TIRF).⁴⁴ Addition of sodium dodecylbenzenesulfonate (SDBS) to a preadsorbed gelatin layer initially resulted in an increase in the amount of gelatin adsorbed and the layer thickness. At higher SDBS concentrations, this was followed by desorption of gelatin and a decrease in layer thickness. The concentration at which desorption commenced decreased with pH, suggesting the desorption was due to complexation between SDBS and gelatin rather than competitive adsorption.

The interaction between surfactants and a gelatin layer adsorbed at an uncharged planar polystyrene–water interface have been investigated by neutron reflectivity.^{45,46} The SDS was adsorbed *within* the existing gelatin layer and did not displace gelatin from the interface. The composition of the gelatin/SDS layer depended upon the order of addition of the two components. It was also found that the layer thickness decreased to less than half of its original value upon addition of 8 mM SDS.

The interaction of gelatin and surfactants at the air/water interface has also been explored by neutron reflectivity.⁴ Complexes of SDS and gelatin are strongly surface active, with gelatin adsorbing at the interface up to the CMC of SDS. At low SDS concentrations (below the cac) the SDS was found at the interface because of the strong gelatin/surfactant interaction. The distribution of surfactant in the layer at the interface was much broader than in the absence of gelatin. Furthermore, the SDS layer thickness indicated that the SDS/gelatin complexes at the interface did not contain micelles.

In our study, SANS has been used to gain insight into the interaction of SDS with a gelatin layer preadsorbed upon negatively charged colloidal polystyrene. Through careful isotopic substitution, SANS experiments enable the selective study of the individual components in this four-component system of polymer, particle, surfactant, and solvent. Furthermore, an improved model is used that

(28) Maity, S.; Jena, S. S.; Pradhan, A.; Bohidar, H. B. *Colloid Polym. Sci.* **1999**, *277*, 666.

(29) Knox, W. J.; Parshall, T. O. *J. Colloid Interface Sci.* **1970**, *33*, 16.

(30) Knox, W. J.; Parshall, T. O. *J. Colloid Interface Sci.* **1971**, *40*, 290.

(31) Whitesides, T. H.; Miller, D. D. *Langmuir* **1994**, *10*, 2899.

(32) Heenan, R. K.; White, S. J.; Cosgrove, T.; Zerbakhsh, A.; Howe, A. M.; Blake, T. D. In *Progress in Colloid Polymer Science*; Ottewill, R. H., Rennie, A. R., Eds.; Springer-Verlag: New York, 1994; Vol. 97.

(33) Cosgrove, T.; White, S. J.; Zerbakhsh, A.; Heenan, R. K.; Howe, A. M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 595.

(34) Cosgrove, T.; White, S. J.; Zerbakhsh, A.; Heenan, R. K.; Howe, A. M. *Langmuir* **1995**, *11*, 744.

(35) Griffiths, P.; Stilbs, P.; Howe, A. M.; Whitesides, T. H. *Langmuir* **1996**, *12*, 5302.

(36) Griffiths, P.; Roe, A. J.; Bales, B. L.; Pitt, A. R.; Howe, A. M. *Langmuir* **2000**, *16*, 8248.

(37) Griffiths, P. C.; Stilbs, P.; Howe, A. M.; Cosgrove, T. *Langmuir* **1996**, *12*, 2884.

(38) Miller, D. D.; Lenhart, W.; Antalek, B. J.; Williams, A. J.; Hewitt, J. M. *Langmuir* **1994**, *10*, 68.

(39) Griffiths, P.; Rowlands, C. C.; Goyffon, P.; Howe, A. M.; Bales, B. L. *J. Chem. Soc., Perkin Trans. 2* **1997**, *12*, 2473.

(40) Sovilj, V. *Colloid Polym. Sci.* **1998**, *276*, 328.

(41) Howe, A. M.; Wilkins, A. G.; Goodwin, J. W. *J. Photogr. Sci.* **1992**, *40*, 234.

(42) Greener, J.; Contestable, B. A.; Bale, M. D. *Macromolecules* **1987**, *20*, 2490.

(43) Cabane, B.; Duplessix, R. *J. Phys. (Paris)* **1987**, *48*, 651.

(44) Muller, D.; Malmsten, M.; Berghensthal, B.; Hessing, J.; Olijve, J.; Mori, F. *Langmuir* **1998**, *14*, 3107.

(45) Turner, S. F.; Rennie, A. R.; Thomas, R. K.; Thirtle, P. N. *Imaging Sci. J.* **1997**, *45*, 270.

(46) Turner, S. F.; Clarke, S. M.; Rennie, A. R.; Thirtle, P. N.; Li, Z. X.; Thomas, R. K.; Langridge, S.; Penfold, J. *Progr. Colloid Polym. Sci.* **1999**, *112*, 206.

accounts for the scattering from local density fluctuations in the adsorbed gelatin layer,⁴⁷ giving a better estimate of the gelatin volume fraction profile.

Experimental Section

Materials. The substrate used in this experiment was an approximately 83% deuterated polystyrene latex prepared by a surfactant free emulsion polymerization as detailed in a recent paper.⁴⁷ The latex was dialyzed against distilled water for 14 water changes and then against MilliQ water for 3 water changes all over a total period of 3 weeks. The latex was concentrated by rotary evaporation and centrifugation and redispersed in D₂O (Goss Scientific Ltd., >99.9 at. % D). The final dispersion had a solids concentration of 9.39% w/w, equivalent to $\phi_p \approx 0.093$, and a surface area content of 6.27 m² mL⁻¹. The H₂O content was determined by high-resolution NMR. The proton peak areas of several H₂O/D₂O mixtures were measured and used as a calibration curve. From this, the H₂O content of the final dispersion was determined to be 5.3% w/w. The solvated hydrodynamic particle size was measured by photon correlation spectroscopy (PCS) (Malvern Autosizer 4700), giving a z-average radius of 444 ± 3 Å. The PCS particle size measurement was performed in 5 mM NaCl to eliminate electric double-layer effects. The ζ potential of the particles was determined to be approximately -37 mV using a Brookhaven Zetaplus electrophoresis instrument. The contrast-match point, and hence scattering length density, of the latex was determined using methods described elsewhere.^{47,48} The contrast-match point of the latex was found to be at a total water content of 13.0% v/v, giving a scattering length density of $5.44 \pm 0.05 \cdot 10^{-6} \text{ Å}^{-2}$.

The gelatin used was lime-processed, deionized, ossein gelatin supplied by Kodak Ltd. (Batch No. AJJ14922) with a mean M_w of 170 000 g mol⁻¹ and an isoelectric point at pH 4.9. Stock gelatin solutions at 110 mg mL⁻¹ in D₂O were prepared by adding the required amount of D₂O to an accurately weighed amount of gelatin. The gelatin was left to soak in a sealed container for at least 1 h for the gelatin granules to swell and absorb the D₂O. The swollen gelatin was then heated in a temperature-controlled water bath to 328 K for 1 h before being allowed to equilibrate at 318 K.

Deuterated sodium dodecyl sulfate (SDS-*d*₂₅) (Aldrich, 98 atom % D) and protonated sodium dodecyl sulfate (SDS-*h*₂₅) (Aldrich 99+%) were obtained commercially. Both of these SDS samples were used as supplied.

Sample Preparation. Two days before the neutron experiment, the gelatin was preadsorbed onto the latex particles as follows. The stock gelatin solution was heated to 318 K for 1 h before use, and then 2.03 mL of a 110.3 mg mL⁻¹ gelatin solution was added to 8.915 mL of the polystyrene latex dispersion. Finally, a small quantity of D₂O (0.077 mL) was added to further dilute the adsorbed layer dispersion to a convenient concentration for use. The final "stock" dispersion of latex with adsorbed gelatin contained latex at a volume fraction of $\phi_p = 0.075$, a total of 4.0 mg of gelatin/m² of latex surface, and a water content of 4.7% v/v. The stock dispersion was stored in an airtight container at room temperature to minimize D₂O/H₂O exchange with the atmosphere.

In these experiments the scattering length density of the solvent and the SDS were matched to that of the bare latex particles. Under these "contrast-match" conditions the scattering from the latex and surfactant are suppressed. This leaves only the scattering from the adsorbed gelatin layer. Once the contrast point for the bare latex had been determined as $(5.44 \pm 0.05) \times 10^{-6} \text{ Å}^{-2}$, two SDS solutions at 64 and 256 mM were prepared by combining SDS-*d*₂₅ and SDS-*h* in proportions such that the scattering length density of the SDS dispersion (in D₂O) was also $5.44 \times 10^{-6} \text{ Å}^{-2}$ (hence forth referred to as cm-SDS).

(47) Hone, J. H. E.; Cosgrove, T.; Spahiannikova, M.; Obey, T.; Marshall, J. C.; Crowley, T. L. *Langmuir* **2002**, *18*, 855.

(48) King, S. M. In *Modern Techniques for Polymer Characterization*; Pethrick, R. A., Dawkins, J. V., Eds.; Wiley: New York, 1999.

(49) Size-exclusion chromatography measurements of molecular weight performed by Dave Kramer at the Gelatin Technology Laboratory, Rochester, New York.

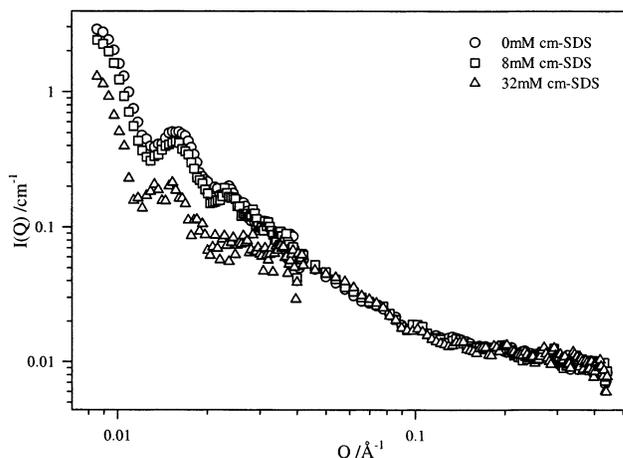


Figure 1. Scattering from gelatin preadsorbed on contrast-matched polystyrene latex (open circles) with added 8 mM cm-SDS (open squares) and 32 mM cm-SDS (open triangles).

Samples were prepared at least 4 h before being measured. The required volumes (0.012–0.2 mL) of SDS stock solution were added to ~0.48 mL of coated latex dispersion, and then ~0.081 mL of H₂O and the required quantities of D₂O (0–0.226 mL) were added. The final samples had a particle volume fraction, ϕ_p , of 0.045, an H₂O content of 13.0% v/v, and cm-SDS concentrations of between 0 and 32 mM. The gelatin concentration in all of the samples was 1.1% w/w. Once the samples had been prepared, they were equilibrated once more at 318 K for at least 2 h before allowing cooling to room temperature. In all cases, the pH of the systems was not controlled; consequently, the pH of the systems varied from 6.8 for adsorbed gelatin only to 7.2 for adsorbed gelatin with 32 mM added SDS.

Measurements. The measurements were performed on the NG-3 instrument at the National Institute of Standards and Technology (NIST), Gaithersburg, MD. All measurements were performed in stainless steel cells with quartz windows, as provided by NIST, with a neutron path length of 2 mm and at 298 ± 0.1 K. The data were corrected for sample transmissions, empty cell scattering, and background noise and put on an absolute intensity scale using previously calibrated standard samples supplied by NIST. The effect of temperature upon the scattering from the samples was not investigated in this experiment. However, previous investigations of the effect of temperature upon the SANS of SDS/gelatin complexes over the Q range investigated here have shown little or no difference both above and below the gel setting temperature;³³ the effects on rheological properties, however, are large.

As it is extremely difficult to prepare samples of this complexity at exactly contrast match, the scattering from the bare particles at the same contrast point is subtracted from all on-contrast samples. The subtraction serves two purposes; first, it removes the incoherent background scattering arising from the H₂O content of the solvent, and second, it removes any residual particle scattering that may remain due to the sample composition deviating slightly from contrast match.

Results and Discussion

General Observations. Figure 1 shows the scattering patterns of gelatin preadsorbed onto polystyrene latex, which is contrast-matched with the solvent, with 0, 8, and 32 mM cm-SDS added. For clarity, all error bars have been omitted.

The most prominent features of the scattering are the oscillations at low Q ($Q < 0.03 \text{ Å}^{-1}$). The presence of these oscillations is good evidence that the observed scattering originates from an adsorbed gelatin layer. The oscillations⁴⁷ are a result of a convolution of the nonscattering "hole" in the adsorbed gelatin layer with the overall shape and thickness of the polymer layer. The prominence and position of these oscillations provide clues to changes in

the layer shape and adsorbed amount. Upon careful examination of Figure 1, it can be seen that the positions of the oscillations gradually move to lower Q upon addition of cm-SDS, which suggests an increase in the overall layer thickness. It is also noticeable that at the highest concentration of cm-SDS the prominence and definition of the oscillations has decreased significantly, which is an indication of the desorption of gelatin from the interface.

Another noticeable feature observed in the SANS of these systems is a broad peak centered at approximately $0.04 < Q < 0.05 \text{ \AA}^{-1}$ (more clearly seen in Figure 4) for systems with cm-SDS concentrations greater than 8 mM. At low ionic strength, solutions of gelatin and cm-SDS in the absence of particles also show a scattering peak in this location.^{33,34} In the simple micellar solutions of SDS at low ionic strength, the peak in the scattering pattern is understood to arise from intermicelle electrostatic repulsion. For solutions of gelatin with cm-SDS at low ionic strength, electrostatic repulsion controls the intermicellar spacing and the peak arises from gelatin chains wrapped around these SDS micelles.

Model Fitting. Various model volume fraction profiles may be used to fit the scattering from polymers adsorbed at interfaces, but theoretical and direct inversion methods for finding volume fraction profiles for adsorbed homopolymer layers indicate that an exponential function is a reasonable approximation.^{6,7} As detailed in a recent paper,⁴⁷ the layer scattering is fitted by including a term to account for the scattering from spatial concentration fluctuations in the polymer layer. The basic model used is based on summing the scattering contributions from the adsorbed layer which follows a Q^{-2} dependence convoluted by the profile shape, the fluctuations which were assumed to have a $Q^{-4/3}$ dependence (Auvray and de Gennes⁵⁰) and a Q -independent incoherent background. Particle polydispersity and a Q resolution function were also incorporated.⁴⁷

During the fitting process, the resolution width and particle polydispersity were held fixed at values determined from fitting the bare particle scattering. However, the particle size was allowed to vary since it is known that polystyrene latex particles, such as those used here, have a rough or "hairy" surface of polystyrene polymer tails and charge groups. These polymer tails have been shown to extend up to 7 nm into the bulk.^{51–57} The tails are not seen in the neutron scattering from the bare latex as they have low mass density, yet it is at this "rough" surface that the gelatin layer adsorbs. By allowing the particle size to vary by small amounts, it is possible to accommodate changes in the "surface roughness" and hence the effective size of particle.

It is known that gelatin rapidly exchanges protons with deuterons in the solvent, and as a result, its scattering length density adjusts according to the D_2O content of the solvent. The scattering length density difference between the gelatin and the solvent was calculated from the maximum and minimum scattering length densities of gelatin (3.2×10^{-6} and $2.1 \times 10^{-6} \text{ \AA}^{-2}$ in D_2O and H_2O ,

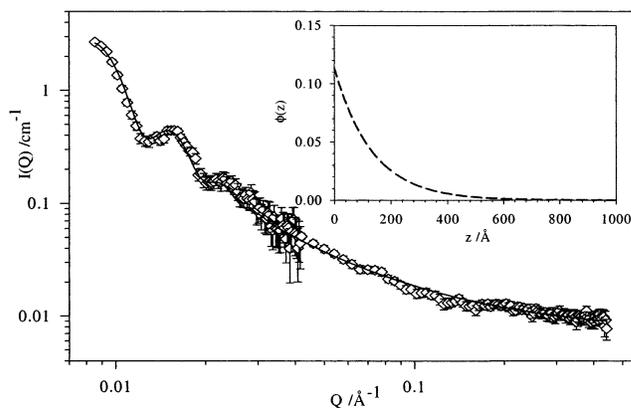


Figure 2. Scattering from gelatin preadsorbed upon contrast-matched polystyrene latex with 4 mM of cm-SDS added (open diamonds) along with a fit to the data (solid line). Inset: Volume fraction profile determined from the fit to the data.

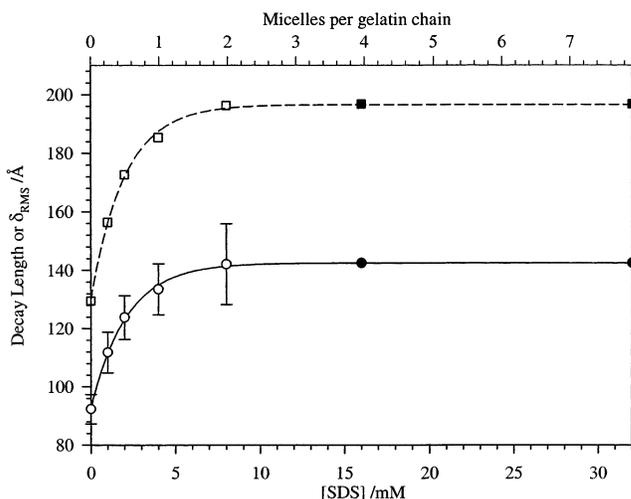


Figure 3. Decay length, z_0 (open circles), and root-mean-square layer thickness, δ_{RMS} (squares), for gelatin preadsorbed on polystyrene latex as a function of cm-SDS concentration. The solid and dashed lines are a guide to the eye. Also plotted are the predicted decay lengths for 16 and 32 mM cm-SDS (closed circles) using the fit to the measured data.

respectively) detailed in the literature^{6,7,34,58} and the D_2O/H_2O ratio of the solvent. This gave a scattering length density difference of $2.38 \times 10^{-6} \text{ \AA}^{-2}$. The polymer mass density used in the fitting process was 1.44 g cm^{-3} as determined by Bohidar and Jena.⁵⁹

Figure 2 shows an example of the scattering from preadsorbed gelatin with added cm-SDS, in this case, where 4 mM cm-SDS has been added. The solid line is the fit to the data. The inset is the volume fraction profile obtained from the fit.

Figure 3 shows a plot of the decay length for the exponential volume fraction profiles plotted against the cm-SDS concentration. Since the root-mean-square layer thickness, δ_{RMS} , is directly related to the decay length, it is also plotted here. The theoretical number of cm-SDS micelles/gelatin chain is plotted on the top abscissa. The number of micelles/chain was calculated using the assumptions that the gelatin has a mean molecular weight of $170\,000 \text{ g mol}^{-1}$ and that the aggregation number for SDS on gelatin was 60 in accordance with Whitesides et al.³¹

(50) Auvray, L.; de Gennes, P. G. *Europhys. Lett.* **1986**, *2*, 647.
 (51) Thun, C.; van de Ven, T. G. M. *Colloids Surf., A* **1998**, *145*, 205.
 (52) van der Put, A. G.; Bijsterbosch, B. H. *J. Colloid Interface Sci.* **1982**, *92*, 499.
 (53) Zukoski, C. F.; Saville, D. A. *J. Colloid Interface Sci.* **1985**, *107*, 322.
 (54) Polverari, M.; van de Ven, T. G. M. *Colloids Surf., A* **1994**, *86*, 209.
 (55) Chow, R. S.; Takamura, K. *J. Colloid Interface Sci.* **1987**, *125*, 226.
 (56) Seebergh, J. E.; Berg, J. C. *Colloids Surf., A* **1995**, *100*, 139.
 (57) Wu, X.; van de Ven, T. G. M. *Langmuir* **1996**, *12*, 3859.

(58) Pezron, I.; Djabourov, M.; Leblond, J. *Polymer* **1991**, *32*, 3201.
 (59) Bohidar, H. B.; Jena, S. S. *J. Chem. Phys.* **1994**, *100*, 6888.

It can be seen from fits to the 0–8 mM data (open symbols) that the decay length appears to rise rapidly between 0 and 4 mM, or up to approximately one micelle/gelatin chain. As further cm-SDS is added, the rate of increase in the decay length falls up to 8 mM. In the case of an adsorbed gelatin layer, adsorption of cm-SDS up to one micelle/chain is likely to increase the layer thickness by binding of gelatin in the bulk into the adsorbed layer through transient cross-links of the cm-SDS micelles.^{35,36,42} Further addition of cm-SDS up to 8 mM coincides with the addition of enough cm-SDS for the formation of approximately three to four micelles/gelatin chain (ignoring the small amount of free unimer that may be in solution). This corresponds to the saturation point cited by Griffiths et al.³⁷ and is in good agreement with other studies that suggest saturation at 1.6 mmol of SDS/g of gelatin⁴⁰ (equivalent to 19 mM cm-SDS in this study). It may be that as cm-SDS is added to the system above 4 mM, the number of micelles/gelatin chain increases along with intermicellar repulsions. Thus, the gelatin chains may expand to reduce these repulsions, making the layer more diffuse. This rise in layer thickness is likely to continue until the gelatin becomes saturated with micelles and the repulsions (both inter- and intracomplex) have reached a plateau. This result is in contrast to those obtained from ellipsometry and neutron reflection of gelatin adsorbed upon an uncharged planar polystyrene surface, which suggest the layer thickness may increase at low anionic surfactant concentrations, but upon saturation, the gelatin layer thickness decreases.^{44,45} It is likely that these differences are due to the negatively charged nature of the polystyrene surface in our study.

The scattering from the systems containing 16 and 32 mM cm-SDS could not be fitted using the same approach as at lower concentrations. In addition to the scattering associated with the adsorbed gelatin layer, the SANS for the systems containing 16 and 32 mM cm-SDS contain a broad peak centered at $0.04 < Q < 0.05 \text{ \AA}^{-1}$ but extending over a much broader Q range. This peak is in the same position as seen for gelatin complexed with cm-SDS micelles, the peak in the scattering mirroring the micelle structure peak.^{33,34} Attempts to fit all the data points in the scattering pattern generated physically unreasonable volume fraction profiles with layer thicknesses in excess of 100 nm. Therefore, the data over the range $0.02 < Q < 0.25 \text{ \AA}^{-1}$ were excluded from the fit, leaving only the oscillations at low Q and the incoherent background at high Q . Since the oscillations at low Q originate from scattering from the adsorbed polymer layer, it is believed that the fitting of this region can still provide useful information on the polymer volume fraction profile, provided the contribution to the intensity from the structure peak is small. It was necessary to constrain the decay lengths, and this was done by using the values suggested by fits to the 0–8 mM data in Figure 3. However, although the decay lengths of the volume fraction profiles are constrained, the initial heights are not. Hence, the adsorbed amounts, surface volume fractions, and bound fractions of gelatin at the interface are determined from a minimization process, albeit from a partially constrained parameter set and a reduced number of data points. The results presented in the following sections that correspond to the higher concentrations of added cm-SDS are shown in a different style (filled symbols) to highlight the different protocol used in their determination.

Plotted in Figure 4 is the scattering from preadsorbed gelatin on contrast matched polystyrene latex with 32 mM of added cm-SDS. Data points included in the fits are plotted as filled symbols; those excluded from the fits are

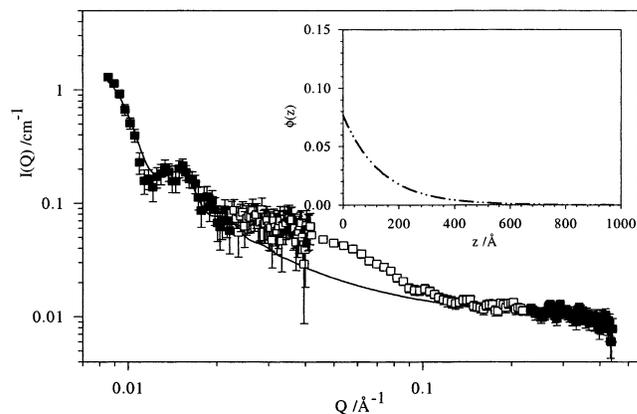


Figure 4. Scattering from gelatin preadsorbed upon contrast-matched polystyrene latex with 32 mM of cm-SDS added (closed squares) along with a fit to the data (solid line). The open symbols represent measured scattering not used in the fitting process. Inset: Volume fraction profile determined from the fit to the data.

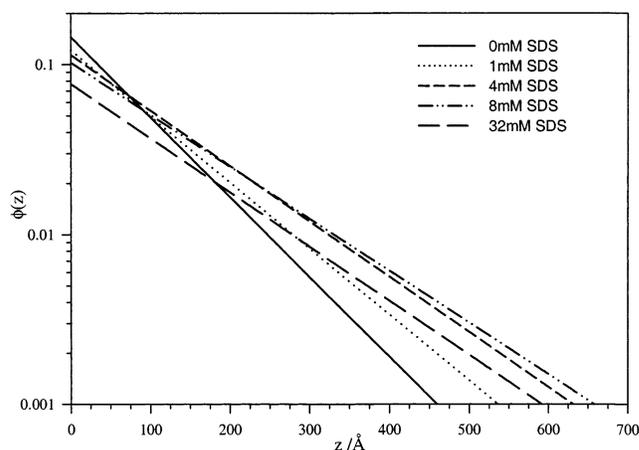


Figure 5. Semilog plot of exponential volume fraction profiles obtained from fits to the scattering from preadsorbed gelatin with added cm-SDS at 0, 1, 4, 8, and 32 mM. Profiles obtained for systems containing 2 and 16 mM SDS have been excluded for clarity.

represented by open symbols. Attempts were made to extract the “micelle” scattering by subtracting the generated fit from the measured data, but unfortunately, the resulting errors in the extracted data made further analysis impossible. The solid line is the best fit to the data. The inset is the volume fraction profile derived from the fit.

Volume Fraction Profile, $\phi(z)$. Figure 5 illustrates what appear to be very complicated changes in the polymer layer upon addition of the anionic surfactant.

This complicated picture can be simplified by isolating each aspect of the volume fraction profiles, i.e. by looking at the information on the layer structure contained within the volume fraction such as the volume fraction of polymer at the interface (ϕ_s), the layer thickness (δ_{RMS}), and the adsorbed amount (Γ).

Volume Fraction at the Interface, ϕ_s . The adsorption of gelatin at the negatively charged, hydrophobic polystyrene surface is likely to occur via a combination of electrostatic and hydrophobic interactions. Since the negative SDS headgroup is thought to begin the aggregation process at the cationic residues of the gelatin,^{26,31,32,34–36,38–40} this will result in the neutralization of the cationic residues and ultimately some rearrangement of the gelatin adsorption close to the surface. The presence

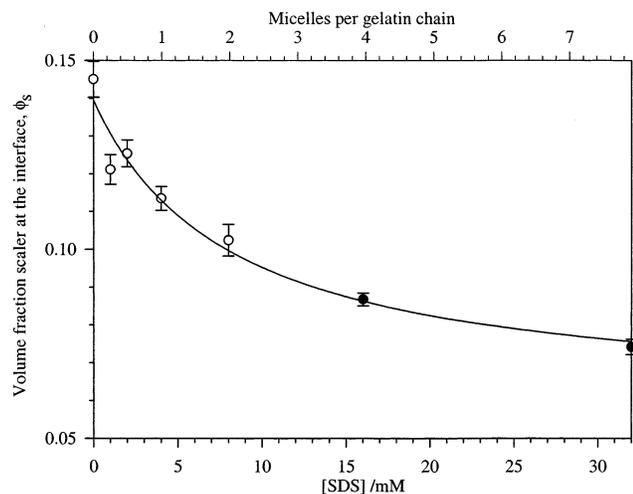


Figure 6. Volume fraction of gelatin preadsorbed at the interface as a function of cm-SDS concentration. Open symbols represent parameters derived from fits to 0–8 mM data. Closed symbols represent parameters derived from the “forced” fit to the data. The solid line is intended as a guide to the eye.

of complexes between single SDS molecules and gelatin has been suggested by surface tension and neutron reflection measurements below the cac (~ 1 mM).^{4,29,31} However it has been shown by equilibrium dialysis measurements that there may be as few as 5 SDS molecules bound to the gelatin below the cac.³¹ Above the cac, the SDS that is already bound favors binding of more SDS via hydrophobic tail interactions and micelles begin to form. The increasing negative charge along the gelatin chains arising from the micelles increases the interchain repulsions as well as the intrachain repulsions. In addition, the increasing negative charge of the gelatin/SDS complex may reduce the affinity of the gelatin for the negatively charged polystyrene surface.

Figure 6 illustrates the change in the volume fraction of the polymer at the interface, ϕ_s , as a function of cm-SDS. As in Figure 3, the top abscissa is scaled for number of micelles/gelatin chain.

There is a clear trend of generally decreasing volume fraction of gelatin at the interface with increasing cm-SDS concentration. Although it is known that SDS can adsorb at the polystyrene/water interface,^{60–64} the work of Turner et al.⁴⁶ concerning gelatin/SDS adsorption at an *uncharged* planar surface shows that SDS does not displace gelatin by competitively adsorbing at the interface. Furthermore, addition of gelatin to a preadsorbed SDS layer was shown to displace surfactant from the interface. Therefore, this decrease in volume fraction at the interface is likely to be a consequence of cm-SDS complexation with the gelatin chains, though this does not preclude SDS adsorption at the latex interface.

Layer Thickness, δ_{RMS} . The root-mean-square thickness (δ_{RMS}) of the gelatin layer as a function of cm-SDS concentration ranges from 130 to 200 Å, as shown in Figure 3. In the absence of cm-SDS, the δ_{RMS} thickness of gelatin obtained from this study (130 Å) is small in comparison to the layer thickness measured by ellipsometry (δ_{ell}) of

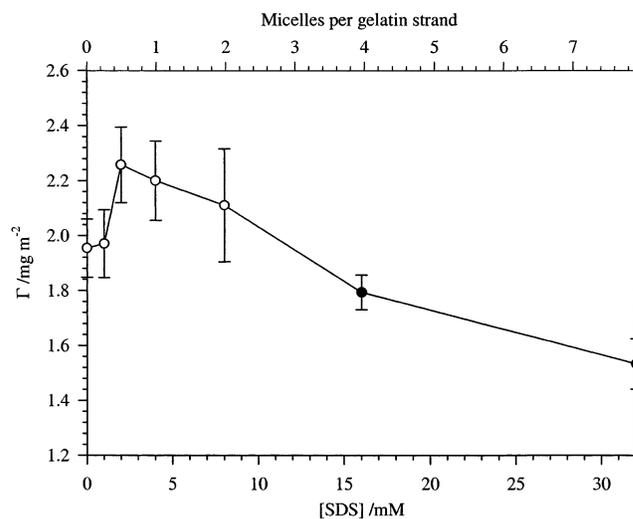


Figure 7. Adsorbed amount of gelatin upon polystyrene latex as a function of cm-SDS concentration. Open symbols represent parameters derived from fits to 0–8 mM data. Closed symbols represent parameters derived from the “forced” fit to the data.

400 Å⁴⁴ and hydrodynamic thickness (δ_h) measurements of up to 390 Å inferred from studies of gelatin rheology on a variety of colloidal surfaces,^{11,65} which are close to values measured by PCS of 200–400 Å^{10,66} on polystyrene latex. The measurements of layer thickness by ellipsometry were carried out on hydrophobic silica surfaces, and therefore, the much larger values reported may be due to the differences in the nature of the surface. Moreover, measurements of δ_h are very sensitive to the tail region of an adsorbed polymer layer, which has a large influence upon the hydrodynamic properties of a system. In contrast, neutrons are relatively insensitive to this region of the adsorbed layer as it represents only a small fraction of the total adsorbed amount. Indeed, gelatin layer thicknesses of only 50 and 54 Å have been reported by neutron reflection and SANS, respectively.^{6,46} The higher value reported here is likely to be a reflection of the improved quality of the data obtained in this study. The increase in thickness corresponds to the chain stretching because of decoration by charged micelles and increased charge repulsion by the surface.

Adsorbed Amount, Γ . The amount of gelatin adsorbed at the interface as a function of cm-SDS concentration is plotted in Figure 7. The change in the adsorbed amount is a combination of the two effects detailed above: the polymer layer thickness; the volume fraction of polymer at the interface. It should be reiterated that since the SDS in this study is contrast matched to the solvent, Γ does not include the amount of SDS adsorbed. As the cm-SDS adsorbs at the cationic sites, some charge neutralization occurs, possibly allowing the adsorption of more gelatin from the bulk into the layer. Furthermore, the “cross-linking” ability of the SDS approaches a maximum at approximately one micelle/gelatin chain.^{35,36,42} These two factors may explain the increase in the adsorbed amount at around 2–4 mM cm-SDS. As more cm-SDS is added to the system, further micelles may condense on the gelatin chains, resulting in an increase in the negative charge and the accompanying inter- and intrachain repulsions. The gelatin chains (and therefore the layer) may expand to reduce these repulsions (Figure 6). As the

(60) Porcel, R.; Jódar, A. B.; Cabrerizo, M. A.; Hidalgo-Álvarez, R.; Martín-Rodríguez, A. *J. Colloid Interface Sci.* **2001**, *239*, 568.

(61) Horváth-Szabó, G.; Høiland, H. *Langmuir* **1998**, *14*, 5539.

(62) Turner, S. F.; Clarke, S. M.; Rennie, A. R.; Thirtle, P. N.; Cooke, D. J.; Li, Z. X.; Thomas, R. K. *Langmuir* **1999**, *15*, 1017.

(63) Tiberg, F.; Brinck, J.; Grant, L. *Curr. Opin. Colloid Interface Sci.* **2000**, *4*, 411.

(64) Hoeft, C. E.; Zollars, R. L. *J. Colloid Interface Sci.* **1996**, *177*, 171.

(65) Ngothai, Y.; Bhattacharya, S. N.; Coopes, I. H. *J. Colloid Interface Sci.* **1997**, *193*, 307.

(66) Dreja, M.; Heine, K.; Junkers, G. *J. Colloid Interface Sci.* **1997**, *191*.

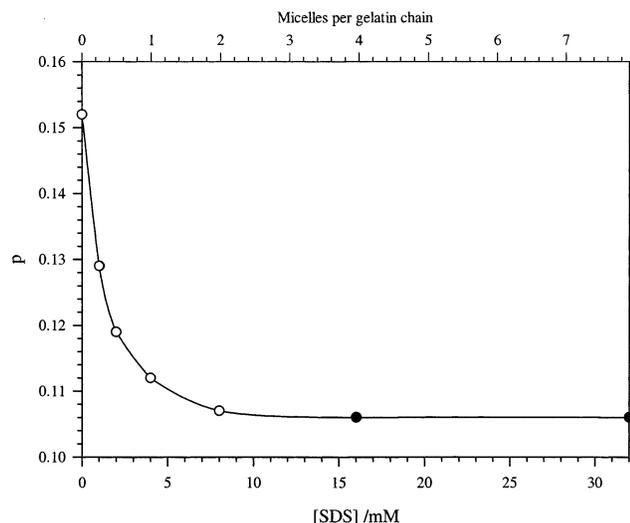


Figure 8. Bound fraction, p , of gelatin adsorbed at the colloidal polystyrene interface as a function of added cm-SDS concentration. The top abscissa denotes the number of cm-SDS micelles available/gelatin chain. The solid line is intended as a guide to the eye only. Closed symbols represent parameters derived from the “forced” fit to the data.

gelatin becomes saturated at around 16 mM cm-SDS,^{37,40} so the repulsions also reach a plateau. The gelatin layer reaches its maximum expansion, and complex-particle repulsions cause the desorption of some of the negatively charged complex from the surface. This is further supported by calculations of the bound fraction, p , according to the following equation:

$$p = \frac{\int_0^a \phi(z) dz}{\int_0^t \phi(z) dz} \quad (1)$$

Here a is the thickness of segments bound directly to the interface (chosen to be 15 Å, the diameter of a gelatin helix), t is the layer span (400 Å), and $\phi(z)$ is the volume fraction profile. The bound fraction as a function of cm-SDS concentration is illustrated in Figure 8, which shows a monotonic decrease corresponding to a relative loss of segments from the surface.

Interestingly, this trend in adsorbed amount has been seen by Muller et al.,⁴⁴ who studied a gelatin layer preadsorbed upon hydrophobic silica (uncharged) in the presence of varying concentrations of sodium dodecylbenzenesulfonate (SDBS) with ellipsometry. As in this study, they found that upon addition of surfactant up to ~2 mM, the adsorbed amount and layer thickness increased, and then, upon further addition of SDBS, the adsorbed amount decreased rapidly. However, in contrast to this study they found that addition of more than 2 mM SDBS resulted in a *reduction* in the layer thickness. It is also noticeable that the adsorbed amounts and layer thicknesses cited by Muller et al. are considerably larger than those presented here. At 2 mM SDS they show a layer thickness of approximately 60 nm and an adsorbed amount of almost 7.5 mg m⁻². Although the systems are not identical, the large difference in layer thickness and adsorbed amount is unexpected. However, the surface used by Muller et al. is of much lower surface charge than the negatively charged polystyrene used in our study, possibly accounting for the differences in behaviors and layer thickness at high surfactant concentrations where surface charge is likely to be of great importance in repelling the micelle decorated gelatin chains. In addition, ellipsometry

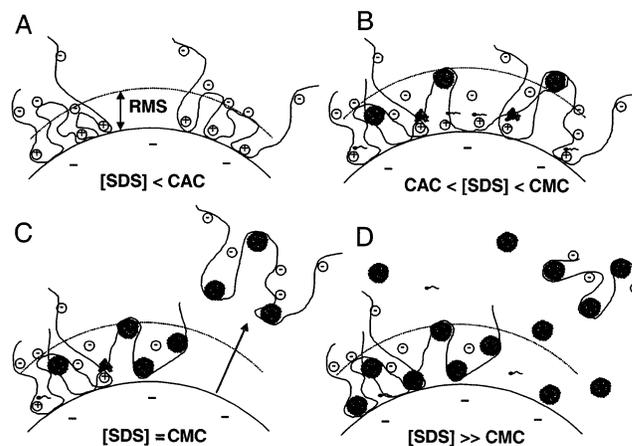


Figure 9. Schematic diagram of the process of complexation of SDS upon a preadsorbed gelatin layer. The outer line is the effective layer thickness.

is unable to distinguish between adsorbed surfactant and adsorbed gelatin, whereas, through careful isotopic substitution, the surfactant can be rendered “invisible” to SANS, as is the case here. This may explain the large difference in magnitude and behavior of the layer thickness and the adsorbed amount at higher SDS concentrations.

Summary

From the volume fraction profiles derived in this study and comparison with the literature, it is possible to speculate on the possible pattern of SDS complexation with an adsorbed gelatin layer; this is illustrated in Figure 9.

Figure 9A shows the adsorbed gelatin layer, binding to the negative hydrophobic surface of the polystyrene particle. Because of the polyampholyte nature of gelatin, the cationic, anionic, and hydrophobic sites are irregularly arranged along the length of the chain, allowing the gelatin to associate with the surface through a combination of electrostatic and hydrophobic interactions.

As cm-SDS is added up to around 4 mM (Figure 9B), the layer thickness is seen to increase along with the adsorbed amount, yet the volume fraction of gelatin adsorbed at the interface decreases. It is estimated that this amount of SDS corresponds to approximately 1 micelle/gelatin chain. Bulk measurements have shown that, at approximately 1 micelle/chain, SDS reaches its maximum ability to act as a temporary cross-link between gelatin chains.^{35,36,42} Our data indicate that further gelatin from the bulk is bound into the layer. Consequently, the layer thickness and the adsorbed amount increase but the increasing negative charge of the gelatin/SDS complex causes further “dissociation” from the interface.

Figure 9C shows the addition of cm-SDS up to 16 mM. The rate of increase in the layer thickness has dropped considerably at this point. The volume fraction of gelatin at the interface is greatly reduced, and the adsorbed amount is now lower than gelatin adsorbed in the absence of cm-SDS. In addition, a broad peak in the scattering from the gelatin is now seen. This amount of cm-SDS roughly corresponds to the saturation of the gelatin with ~4 SDS micelles/chain. The gelatin chains may expand to reduce the intrachain micellar repulsions and as a consequence approach a maximum layer thickness when saturated with cm-SDS. The gelatin now has a large proportion of its chain wrapped around the cm-SDS micelles. Although the gelatin expands to reduce intrachain micellar repulsions, it begins to desorb entirely from the surface of the polystyrene due to inter-complex and

complex-particle repulsions, and thus, the adsorbed amount falls. The micelle-like structure peak is now seen due to the desorption of complex from the interface and an increase in the bulk cm-SDS concentration.

Figure 9D shows that further addition of cm-SDS up to 32 mM guarantees the saturation of the gelatin by micelles both at the interface and in the bulk. The gelatin scattering in the region of $0.02 < Q < 0.25 \text{ \AA}^{-1}$ is more enhanced, and free micelles are now formed in the bulk. We cannot exclude the possibility that SDS could adsorb at the latex-water interface and that such adsorption could contribute to the decrease in ϕ_s shown in Figure 6. Given the position of the "micelle" peak and the fact that the adsorbed layer is relatively "thin" compared to the intermicellar distance required to give such a structure peak, it is most likely that this feature is due to complexation in the bulk.

Conclusions

The effect of contrast-matched SDS upon gelatin preadsorbed at the contrast-matched colloidal polystyrene/water interface has been investigated using SANS. The adsorbed layer thickness as a function of cm-SDS concentration/adsorption was seen to rise to a maximum at approximately the saturation point cited in the literature for bulk gelatin solutions. In addition, the volume fraction

of polymer adsorbed at the interface was seen to diminish simultaneously. The adsorbed amount was seen to rise at low surfactant concentration, peaking at cm-SDS concentrations equivalent to approximately one micelle/gelatin chain; further addition saw the adsorbed amount decay and fall below that of the system containing no surfactant. At the highest surfactant concentrations, the gelatin was seen to develop the scattering form of the contrast-matched SDS micelles providing further evidence of desorption.

The changes in the adsorbed layer conformation and consequently its scattering are explained in terms of simple electrostatic interactions, as used by previous authors for similar systems.

Acknowledgment. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing facilities used in this work. This material is based upon activities supported by the National Science Foundation under Agreement No. DMR-9986442. J.C.M. acknowledges the EPSRC and Kodak Ltd. for funding. K.J. acknowledges support from ICI for the award of an SRF fellowship.

LA0258401