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Investigation of a 31% Charged Cationic Polyelectrolyte Interacting with Sodium Dodecyl Sulfate in Bulk Solution and as a Preadsorbed Layer on Mica. Low Ionic Strength

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Received April 21, 1998. In Final Form: June 25, 1998

The behavior of mixtures of a cationic polyelectrolyte of intermediate charge density (31%) and anionic surfactant both in bulk and at a negatively charged solid surface has been investigated. The polyelectrolyte employed was a random copolymer of the neutral acrylamide and cationic [3-(2-methylpropionamido)-propyl]trimethylammonium chloride, and the surfactant was sodium dodecyl sulfate (SDS). Measurements of flocculation and electrophoretic mobility in bulk solution clearly showed a phase separation with a maximum in turbidity corresponding roughly to charge neutralization of the polyelectrolyte/surfactant complex. Conductivity measured at low SDS concentrations showed a strong uptake of ions by the polyelectrolyte at a critical SDS concentration. The interferometric surface force apparatus was used to measure forces between muscovite mica surfaces onto which the polyelectrolyte was adsorbed from a 20 ppm, 10^{-4} M KBr solution. After the polymer solution was replaced with polymer-free 10^{-4} M KBr solution, a weak long range double-layer repulsion was observed between approaching surfaces, with a bridging attraction dominating at smaller separations. A weak adhesion was observed upon separating the surfaces. Addition of 4.2×10^{-4} M SDS caused a large swelling of the preadsorbed polymer layer due to formation of an associative complex between the polymer and surfactant. Further increasing the SDS concentration decreased the force and layer thickness due to screening of the electrostatic repulsion within the layers and some desorption of polymer molecules. That a slight desorption did occur was supported by electron spectroscopy for chemical analysis measurements. The results broaden the understanding of the effect of polyelectrolyte charge density on the interaction of preadsorbed polyelectrolyte layers with oppositely charged surfactants.

Introduction

Industry employs mixtures of oppositely charged polyelectrolytes and surfactants in a multitude of applications. For instance in paints, shampoos, and water and soil treatment and as rheology modifiers, emulsifiers, stabilizers, etc.¹ In most cases the processes were developed empirically. The principle approach of scientists to tackling these systems has been to measure bulk properties, which are now rather well understood. For instance, data for the phase behavior of some polyelectrolyte/surfactant mixtures are available.² Such mixtures are typically single phase at both low and high surfactant concentrations, while at intermediate concentrations a polymer-rich phase precipitates. The starting point for this behavior is an association step that occurs at a concentration (critical association concentration, cac) much lower than that at which micelle formation occurs (critical micelle concentration, cmc) in simple bulk surfactant solutions. It is well-known from the surfactant literature that micelle formation occurs at a particular ionic surfactant concentration due to a balance of the electrostatic repulsion between headgroups and hydrophobic and van der Waals attraction between tails. The cac and cmc are thus affected by such factors as temperature, salt type, and concentration. The condensation of

large polycounterions onto the micellar surface results in a much lower total entropy loss than the condensation of simple (nonpolymeric) counterions. This is accepted as an important reason for the reduced aggregation concentration of the surfactant in the presence of polyelectrolyte.³ Several different techniques pointed to the existence of this association step, but the measurement of a binding isotherm was necessary to quantify the thermodynamics. Initially, binding isotherms were measured by dialysis equilibrium.⁴ The development of membrane electrodes selective for ionic surfactants^{5,6} was a major step forward, allowing binding isotherm measurements to be performed quickly and efficiently. As a result, a number of features of polyelectrolyte/surfactant systems have been uncovered.^{7–16} The polyelectrolyte charge density, hydrophobicity, degree of branching, and stiffness have all been found to affect the polyelectrolyte/

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(1) Dautzenberg, H.; Jaeger, W.; Kötze, J.; Philipp, B.; Seidel, Ch.; Stscherbina, D. *Polyelectrolytes. Formation, Characterisation and Application*, 1st ed.; Carl Hanser Verlag: Munich, 1994; p 343.

(2) Thalberg, K.; Lindman, B.; Karlström, G. *J. Phys. Chem.* **1990**, *94*, 4289.

(3) Cabane, B. *J. Phys. Chem.* **1977**, *81*, 1639.

(4) Hill, R. M.; Briggs, D. R. *J. Am. Chem. Soc.* **1956**, *78*, 1590.

(5) Gavach, C. *Chim. Phys. Appl. Prat. Surf.* **1968**, *2*, 859.

(6) Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1982**, *86*, 3866.

(7) Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1983**, *87*, 506.

(8) Satake, I.; Yang, J. T. *Biopolymers* **1976**, *15*, 2263.

(9) Hayakawa, K.; Santerre, J. P.; Kwak, J. C. T. *Macromolecules* **1983**, *16*, 1642.

(10) Santerre, J. P.; Hayakawa, K.; Kwak, J. C. T. *Colloids Surf.* **1985**, *13*, 35.

(11) Lindman, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993.

(12) Malovikova, A.; Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1984**, *88*, 1930.

(13) Okuzaki, H.; Osada, Y. *Macromolecules* **1994**, *27*, 502.

(14) Satake, I.; Takahashi, T.; Hayakawa, K.; Maeda, T.; Aoyaki, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 926.

(15) Wallin, T.; Linse, P. *Langmuir* **1996**, *12*, 305.

surfactant association. The surfactant headgroup size and charge and tail group structure (i.e., branched, aromatic, aliphatic) are also important, as well as the background electrolyte type and strength, and finally the temperature.¹⁰ Due to the absence of appropriate experimental techniques before the 1970s, much speculation about the mechanism of association existed.¹⁷ The temperature dependence of the standard entropy and enthalpy of binding¹⁰ suggested the formation of surfactant clusters at the cac. This hypothesis was experimentally confirmed upon the advent of X-ray fluorescence,¹⁸ leading to the idea of a "bead and necklace" structure of surfactant aggregates along the polyelectrolyte chains. Many other types of measurements have been used to characterize bulk interactions (for examples see ref 16), some of which were employed in the current study. These techniques typically probe either the bulk solution properties or the dissolved polymer molecules. Examples are conductivity, electrophoretic mobility, static light scattering, turbidity (provides information on phase behavior), surface tension, and dye solubilization.

A particular aspect of the applied system that may be very important, particularly in colloidal systems, is conspicuous by its limited discussion in the literature. Namely, the influence of an interface.^{19,20} It has been amply demonstrated that both polyelectrolytes^{21,22} and surfactants²³ interact very strongly with interfaces and, in turn, that the interaction between two interfaces is strongly affected by the presence of these species. Work carried out in this laboratory has investigated the system cationic polyelectrolyte/negative surface/anionic surfactant. The principal aim of this work was to investigate the effect of polyelectrolyte charge density on the polyelectrolyte/surfactant interaction at the mica/water interface. However the effect of polymer concentration, background electrolyte, and dissolved polymer have also been considered. The most striking feature observed was the massive swelling of a preadsorbed polyelectrolyte layer as a result of associative adsorption of surfactant. This was manifested in the force measurements as a change from a long-range bridging attraction²¹ to an oscillatory force in the case of the 100% charged polymer due to regular distribution of surfactant aggregates.²⁴ With polymers having 10% charged groups,²⁵ a long-range and strong (nonoscillatory) repulsive force was observed. A 31% charged polymer has also been investigated, at an increased ionic strength of 10^{-2} M.²⁶ Here, light scattering and force measurements were used to investigate the influence of dissolved polymer on surface forces. Here, we report data on the behavior of preadsorbed layers of a 31% charged polyelectrolyte, interacting with sodium dodecyl sulfate at low ionic strength (10^{-4} M KBr). The

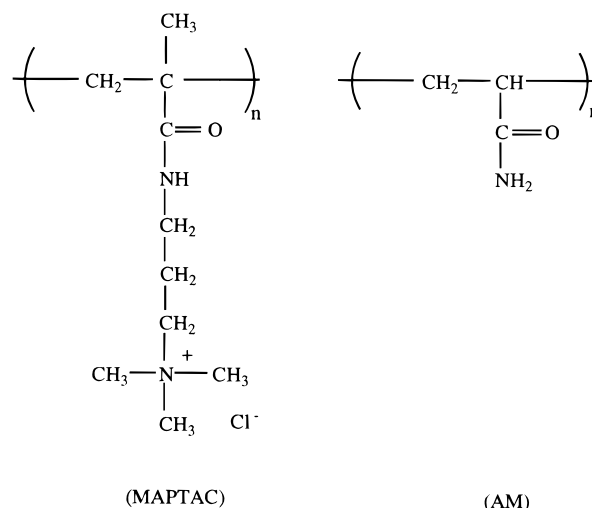


Figure 1. Chemical structure of AM and MAPTAC monomers.

intention of this work was to provide a full suite of results investigating the effect of polyelectrolyte charge density on the polymer/surfactant interaction in preadsorbed layers.

Experimental Section

The polyelectrolyte used in the current study was a copolymer of the neutral monomer acrylamide (AM) and the positively charged [3-(2-methylpropionamido)propyl]trimethylammonium chloride (MAPTAC) in the ratio 6.9:3.1 (Figure 1 shows the molecular structure of the monomers). The polymer was kindly provided by the late Professor Roland Audebert of Université Pierre et Marie Curie, Paris. The ratio of monomers employed means that the polymer has 31% of its monomer units charged (referred to in the remaining text as AM-MAPTAC-31). The molecular weight of the polymer is $780\,000\text{ g mol}^{-1}$. The molecular weight of the MAPTAC monomer is 221 g mol^{-1} and that of the AM monomer is 71.1 g mol^{-1} , so that the average polyelectrolyte molecule contains just over 2000 charges.

Sodium dodecyl sulfate (SDS, BDH, 99%) was used as received. Potassium bromide (KBr, Merck, pro analysis) was roasted at 500°C overnight before use. Water was prepared by passage through a Millipore Milli-RO plus system, followed by a Milli-Q 185 system. Immediately prior to the measurement, the water was degassed under vacuum using a water jet pump for at least 1 h.

All experiments were conducted at $21\text{--}24^\circ\text{C}$. The force measurements were conducted in a room thermostated at 21°C .

The conductivity of mixtures of AM-MAPTAC-31 and SDS in bulk was measured (CG 855 meter, LF 1100T electrode, Schott). The conductivity meter was calibrated first at $1000\text{ }\mu\text{S cm}^{-1}$. In this case, 50 mL of a 1000 ppm AM-MAPTAC-31 solution was titrated with a solution of 4.2×10^{-3} M SDS solution, which was dispensed from a 25 mL buret (Brand). The measurement was conducted in the absence of added electrolyte to enhance the sensitivity of the measurement. A calibration curve of pure SDS was also measured, where the initial conductivity was adjusted with NaCl to the same value as that initially measured in pure 1000 ppm AM-MAPTAC-31 solution. The difference between the two curves was calculated, providing some information about polyelectrolyte/surfactant association. Surface tension was measured via the Wilhelmy plate method (Krüss K122) at 22°C .

The assessment of flocculation and electrokinetic behavior of bulk polymer/surfactant solutions was conducted simultaneously. Twenty milliliter solutions were prepared in turbidity vials, each containing 200 ppm AM-MAPTAC-31 and 10^{-4} M KBr. A set of solutions was prepared, having SDS concentrations varying between 0 and 1.7×10^{-2} M (to mirror those used in the surface force apparatus (SFA) measurements, see below). The solutions were left to equilibrate for 20 min before measurements were performed. Flocculation of the polymer was first assessed by measuring the turbidity (Hach Ratio Turbidimeter 18900). The

(16) Ananthapadmanabhan, K. P. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D.; Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993.

(17) Saito, S. J. *J. Biochem.* **1957**, *154*, 21.

(18) Thalberg, K.; van Stam, J.; Lindblad, C.; Almgren, M.; Lindman, B. *J. Phys. Chem.* **1991**, *95*, 8975.

(19) Shubin, V. *Langmuir* **1994**, *10*, 1093.

(20) Shubin, V.; Petrov, P.; Lindman, B. *Colloid Polym. Sci.* **1994**, *272*, 1590.

(21) Dahlgren, M. A. G.; Waltermo, Å.; Blomberg, E.; Claesson, P. M. *J. Phys. Chem.* **1993**, *97*, 11769.

(22) Dahlgren, M. A. G.; Claesson, P. M.; Audebert, R. *J. Colloid Interface Sci.* **1994**, *166*, 343.

(23) Pashley, R. M.; McGuigan, P. M.; Ninham, B. W.; Evans, D. F. *Science* **1985**, *229*, 1088.

(24) Claesson, P. M.; Dedinaite, A.; Blomberg, E.; Sergeev, V. G. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1008.

(25) Kjellin, U. R. M.; Claesson, P. M.; Audebert, R. *J. Colloid Interface Sci.* **1997**, *190*, 476.

(26) Claesson, P. M.; Fielden, M. L.; Dedinaite, A.; Brown, W.; Fundin, J. *J. Phys. Chem. B* **1998**, *102*, 1270.

turbidimeter was calibrated using freshly prepared hydrazine sulfate/hexamethylene tetramine standards. In some cases the polymer flocculated in the form of large particles, visible to the naked eye, which settled rather quickly. In this case, the sample was agitated sufficiently to ensure a reasonably homogeneously dispersed suspension. The electrophoretic mobility was measured on a small volume of sample using a Malvern Zetasizer (Malvern Instruments). Using this apparatus the mobility of individual polymer molecules, as well as multimolecular aggregates could be determined.

Electron spectroscopy for chemical analysis (ESCA) measurements (Leybold-Heraeus LH 2000) were used to follow the adsorption of polymer onto mica and desorption from mica by SDS. All measurements were conducted using an Al K α X-ray source and a hemispherical analyzer. When weak signals were studied, multiple scans were used to improve the signal-to-noise ratio. A numerical integrator was used for calculating peak areas. The analysis exploited the measured ratio of K to N to provide a value of adsorbed amounts.²⁷ Sample solutions were prepared in 8 mL tubes, each containing 10^{-4} M KBr with [AM-MAPTAC-31] between 0 and 200 ppm. Mica pieces, 1×5 cm, were cut from the same sheet and cleaved just before being placed in the sample tubes. After 24 h of equilibration, the samples were immersed in 4×400 mL of 10^{-4} M KBr, and immediately afterward the mica surface was removed and blown dry with nitrogen. Some samples where the AM-MAPTAC-31 polymer was adsorbed from a 20 ppm solution were treated further in order to study the desorption of the polyelectrolyte by SDS. In this case the polyelectrolyte solution was first replaced with simple electrolyte by immersion in 4×400 mL of 10^{-4} M KBr, and then SDS was added to between 0 and 1.7×10^{-2} M. After a further 24 h the samples were diluted in 4×400 mL of water and the mica pieces were removed and blown dry with nitrogen. The polymer-coated mica samples were then ready for analysis.

All surface force measurements were conducted with a MK IV surface force apparatus.²⁸ The surfaces employed were negatively charged muscovite mica (New York Mica Corp., New York). Mica is an aluminosilicate material, which cleaves to form large molecularly smooth sheets. For use in the SFA, the mica was cleaved into $1\text{--}3$ μm thick squares of uniform thickness with an area of about 1 cm^2 . These squares were then coated on one side with a thin layer of silver using thermal deposition and glued silvered side down to two semicylindrical silica lenses of radius about 2 cm. The glue used was an epoxy resin (Shell Epikote 1004) that liquefies at increased temperature and has been shown²⁹ to be thermally and chemically inert.

The SFA is described in great detail elsewhere.^{28,30} In brief, the two mica surfaces are brought together in gas or liquid, using a piezoelectric crystal and/or a synchronous motor. White light is shone through the semicylindrical lenses, which are mounted in a crossed cylinder geometry. The light is multiply reflected between the silver layers and an interference pattern, fringes of equal chromatic order, is created. The separation between the surfaces can then be calculated from the wavelengths of the standing waves. The lower surface is attached to a spring. The distance that the spring deflects is quantified as the difference between the distance moved by the piezo/synchronous motor and the resulting change in separation between the surfaces. The force, $F(D)$, is then simply calculated by multiplying the measured deflection by the spring constant of the double cantilever spring (measured at the end of each experiment).

When the data are analyzed, the force is normalized by the local geometric mean radius, R , which is approximately 2 cm. According to the Derjaguin approximation³¹ this quantity is related to the free energy of interaction per unit area between flat surfaces, $G_f(D)$

$$\frac{F(D)}{R} = 2\pi G_f(D) \quad (1)$$

with the condition that $D \ll R$. Since D is of the order of 10^{-6} m or less, this condition is satisfied. Another requirement is that the radius of the surfaces should be independent of D , but this is not always the case since the surfaces deform under strong repulsive and attractive forces.³² When the gradient of an attractive force $\partial F/\partial D$ exceeds the spring constant of the double cantilever spring, the system becomes unstable and the surfaces jump together to the next stable region of the force curve.

In the current experiment, zero separation was assessed in 0.1 mM KBr. The shape of the fringes and the adhesion in air were used as indicators of cleanliness. Water was introduced into the box, followed by addition of a small amount of KBr to give the desired concentration. Proper mixing of the solution was ensured by extracting several milliliters with the syringe and reinjecting. This procedure was repeated at least five times and was followed by rapid movement of the lower surface for several minutes. When polyelectrolytes were introduced into the SFA, the system was left to equilibrate overnight before any force measurements or dilutions were carried out. Before SDS was added, the polyelectrolyte solution was replaced with polyelectrolyte-free 0.1 mM KBr solution. SDS solution was injected into the measuring chamber and mixed using the procedure described above. After each surfactant addition, the mixture was left to stand overnight before measuring force curves. Solutions of SDS with concentrations of 4.2×10^{-5} M ($0.005 \times$ cmc), 4.2×10^{-4} M ($0.05 \times$ cmc), 1.7×10^{-3} M ($0.2 \times$ cmc), and 1.7×10^{-2} M ($2 \times$ cmc) were investigated. SDS stock solutions were filtered with a $0.2\text{ }\mu\text{m}$ Gelman filter before injection into the SFA.

Results

Bulk Properties AM-MAPTAC-31/SDS in 10^{-4} M KBr. Before the investigation of how polyelectrolyte and surfactant interact at the mica surface, the association in bulk solution phase was assessed by measuring solution conductivity, particle electrophoretic mobility, suspension turbidity (resulting from flocculation of dissolved polymer), and surface tension. Considering results from conductivity measurements first, Figure 2 illustrates the change in specific conductivity as SDS is added in one case to a 1000 ppm solution of AM-MAPTAC-31 and in the other case to a solution of KBr of equivalent ionic strength. The small effective diffusion coefficient of the polyelectrolyte means that it has a very small influence on the conductivity compared to the monovalent surfactant and counterion species.³³ It is immediately obvious that free surfactant is removed from solution even at an added SDS concentration of 4×10^{-5} M ($\sim 0.005 \times$ cmc). If one makes the greatly simplified assumption that the inorganic counterions contribute equally to the conductivity in the surfactant solution and in the polyelectrolyte/surfactant mixture, it is possible to calculate a "binding isotherm" (Figure 3). The conductivity of SDS solutions as a function of concentration (Figure 2) was used as a calibration curve for determining free SDS concentration in the presence of polyelectrolyte. With this simplification, cooperative binding is deduced at a free SDS concentration of 7×10^{-5} M ($0.0084 \times$ cmc), which provides an indicator of the bulk association behavior. The finite slope of the curve above and below the steep section indicates that additional surfactant binds to the polyelectrolyte probably due to Coulombic interactions at low concentrations and Coulombic and hydrophobic interactions at high concentrations. The shape and magnitude of the binding isotherm are broadly consistent with those measured using sur-

(27) Claesson, P. M.; Herder, P.; Stenius, P.; Eriksson, J. C.; Pashley, R. M. *J. Colloid Interface Sci.* **1986**, *109*, 31.

(28) Parker, J. L.; Christenson, H. K.; Ninham, B. W. *Rev. Sci. Instrum.* **1989**, *60*, 3135.

(29) Pincet, F.; Perez, E.; Wolfe, J. *Langmuir* **1995**, *11*, 373.

(30) Israelachvili, J. N.; Adams, G. E. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 975.

(31) Derjaguin, B. V. *Kolloid-Z.* **1934**, *69*, 155.

(32) Parker, J. L.; Attard, P. *J. Phys. Chem.* **1992**, *96*, 10398.

(33) Rice, S. A.; Nagasawa, M. *Polyelectrolyte Solutions*, 1st ed.; Academic Press: New York, 1961.

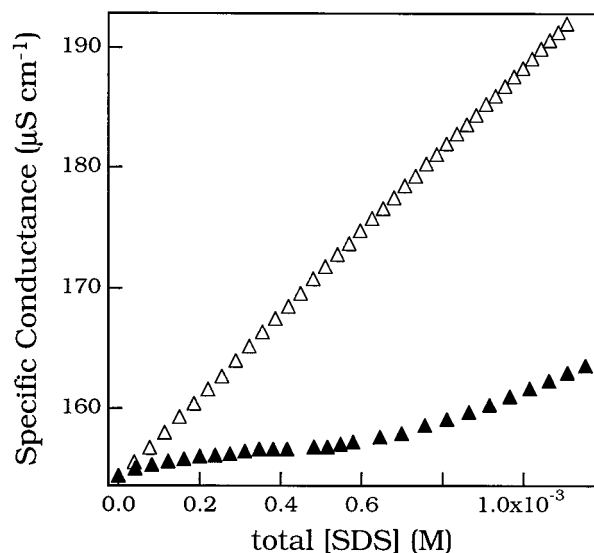


Figure 2. Specific conductance versus total [SDS] for both pure SDS solution (Δ) and SDS/AM-MAPTAC-31 mixtures (▲).

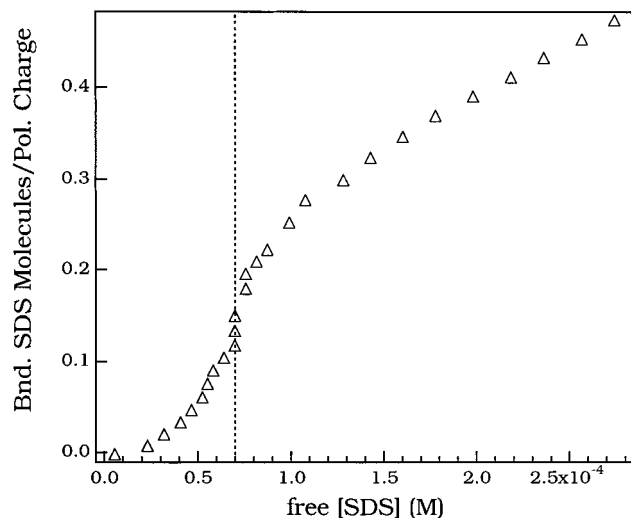


Figure 3. A "binding isotherm" of bound SDS molecules/polymer charge versus free [SDS] calculated from the conductivity data in Figure 2, assuming that the surfactant ion is the only one contributing to the conductivity changes.

factant-selective electrodes.⁶ The "steepness" of the profile may be decreased due to the liberation of counterions from the polyelectrolyte with increased surfactant binding.

The electrokinetic and flocculation behavior of 200 ppm AM-MAPTAC-31 solutions as a function of total SDS concentration (i.e., bound + free) is shown in Figure 4. The peak in turbidity as a function of [SDS] is caused by a phase separation at intermediate concentrations. The peak in turbidity did not coincide exactly with the charge neutralization concentration (abbreviated to cnc $\approx 1.7 \times 10^{-3}$ M) as determined by electrophoretic mobility because macroscopic flocculation at this concentration led to formation of particles large enough to sediment, hence reducing the optical density. The free SDS concentration at the cnc can be calculated assuming that each charged unit on the polyelectrolyte is neutralized by a surfactant molecule, so that $\text{cnc}_{\text{free}} = 1.2 \times 10^{-3}$ M, and approximately 29% of added SDS is bound to the polymer. Disappearance of the second phase with recharging above the cnc illustrates that nonelectrostatic attractive interactions are strong enough to overcome electrostatic repulsion between the negatively charged polymer-surfactant complex and

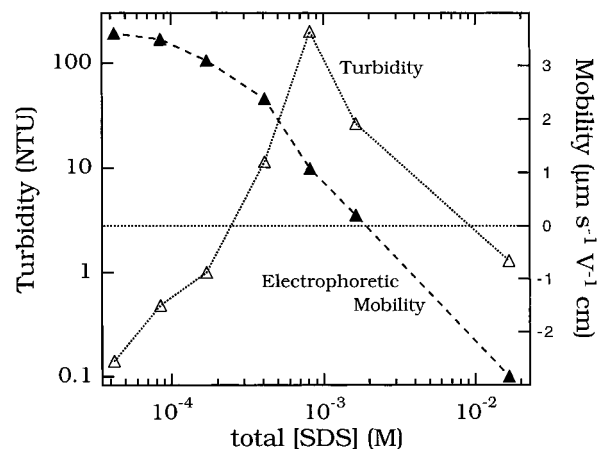


Figure 4. Turbidity and electrophoretic mobility of 200 ppm AM-MAPTAC-31 as a function of total [SDS].

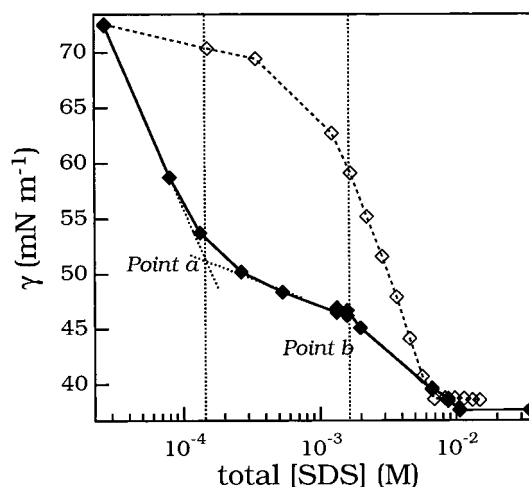


Figure 5. Surface tension (γ) versus total [SDS] for 200 ppm AM-MAPTAC-31/SDS mixtures (◆) and for pure SDS (◇).

dodecyl sulfate anions. These findings are broadly consistent with a comprehensive static light scattering study of mixtures of this polymer with SDS in 10^{-2} M NaCl solution.²⁶

Surface tension (γ) versus total [SDS] results for a 200 ppm AM-MAPTAC-31 solution are shown in Figure 5. The shape of the isotherm is characteristic for polymer-surfactant systems.³⁴ Below the cac, the nonpolar tails of the surfactant molecules are free to adsorb at the air-water interface, and the negative charges on the head-groups interact with the cationic polyelectrolyte, thus neutralizing them. This reduces the electrostatic penalty of bringing the surfactant to the interface and increases their surface activity. At this concentration, the polyelectrolyte/surfactant complex at the solution/air interface has some resemblance to a hydrophobically modified polymer. At the cac, the surfactant tails start to bind to each other in micelle-like structures stabilized by polyelectrolytes in bulk solution. Most of the added surfactant above the cac becomes included in these aggregates, which holds the bulk concentration rather constant, with the consequence that the surface tension is not strongly reduced between points a and b. Above point b (which is equivalent to charge neutralization), further adsorption to the polyelectrolyte is less favorable, and hence more surfactant is free to adsorb to the air-water interface. Above the cmc, γ remains constant due to incorporation

(34) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 301.

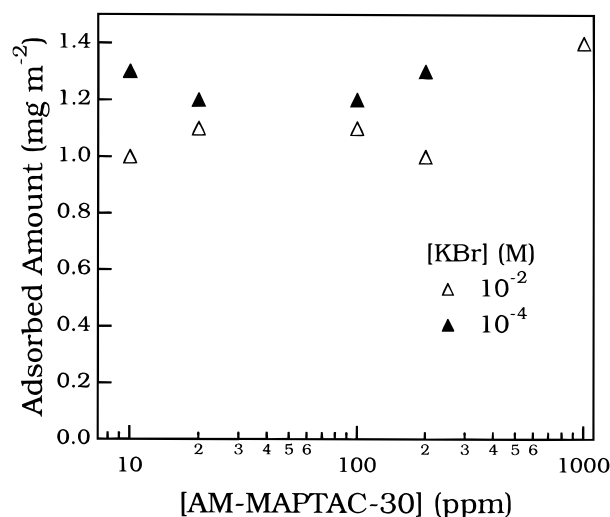


Figure 6. Adsorption isotherm for AM-MAPTAC-31 in 10^{-2} and 10^{-4} M background electrolyte, onto muscovite mica as determined by ESCA.

of further surfactant into free micelles. The increase in cmc in the polyelectrolyte solution allows the simple calculation of adsorbed amount at cmc. In this case, assuming a cmc for SDS (from ref 35) of 8 mM, 2 mM of the 10 mM added SDS is adsorbed to 200 ppm of polyelectrolyte. This is equivalent to 4.1 bound SDS molecules/polyelectrolyte charge. The strongly negative electrophoretic mobility measured at this concentration supports the hypothesis of a large uptake of SDS above the concentration required to neutralize the charge on the polymer. The phase separation observed at intermediate [SDS] may have had some effect on the surface tension measurement. It is assumed, however, that the system was at equilibrium and the polymer-rich phase did not accumulate at the air/water interface.

Adsorption of AM-MAPTAC-31 on Mica, ESCA Results. The adsorption isotherm of AM-MAPTAC-31 onto mica as determined by ESCA is shown in Figure 6. The observed behavior follows the expected pattern from theory and from previous studies on polyelectrolyte adsorption on mica,^{21,22} i.e., a high affinity adsorption reaching saturation at [polymer] < 20 ppm. The inert salt concentration, 10^{-4} or 10^{-2} M had only a weak effect with a slightly lower adsorption at the higher salt concentration.

Forces between Polyelectrolyte-Coated Surfaces in KBr Solutions. The interaction between mica surfaces coated with AM-MAPTAC-31 in polyelectrolyte-free 0.1 mM KBr solution is shown in Figure 7 (note the reduction in force compared with that measured between bare mica surfaces). The force is unchanged relative to that measured in the polyelectrolyte solution. A double-layer repulsion dominates the interaction at distances above ~ 20 nm. From this position an attractive force causes an inward jump into a "hard wall" located 3–4 nm from mica–mica contact. Also shown are DLVO fits to the data, employing a numerical solution to the Poisson–Boltzmann equation and nonretarded van der Waals force.³⁶ A Hamaker constant of 0.5×10^{-20} J (consistent with a hydrocarbon layer on each surface³⁷) was used to model the van der Waals force, and surface potentials of 70 mV for the

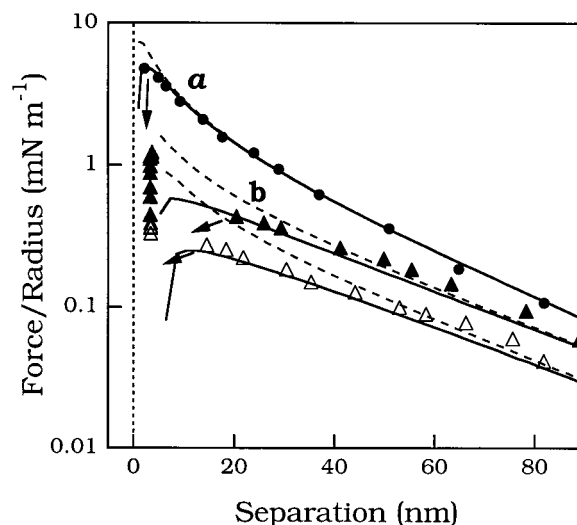


Figure 7. Force measured (a) between bare mica surfaces and (b) between surfaces bearing a layer of AM-MAPTAC-31 preadsorbed from a 20 ppm solution in 10^{-4} M KBr. Between uncoated mica surfaces (\bullet), a long-range repulsion was observed, followed by a jump into adhesive contact from ~ 2 nm (as indicated by the arrow). Forces calculated according to DLVO theory are shown, using constant charge (dashed lines) and constant potential (solid lines) boundary conditions. A Hamaker constant of 2.2×10^{-20} J was used to calculate a nonretarded van der Waals force.³⁰ Fitting parameters of $\Psi_0 = 150$ mV, $\sigma_0 = 51.76$ mC m $^{-2}$, and $1/\kappa = 26$ nm ($=1.37 \times 10^{-4}$ M) were extracted. The force between polyelectrolyte-coated surfaces (b) was measured both 2 h (day 1, \blacktriangle) and 17 h (day 2, \triangle) after replacing the polyelectrolyte solution with 10^{-4} M KBr. "Jump into contact" is indicated by the arrows. The dashed vertical line at zero separation represents the hard wall measured between bare mica surfaces in 10^{-4} M KBr solution (this convention is employed throughout the remaining force profiles). Comparison with DLVO theory provided fitting parameters of $\Psi_0 = 70$ mV and $\sigma_0 = 1.87$ mC m $^{-2}$ for day 1 and $\Psi_0 = 48$ mV and $\sigma_0 = 0.776$ mC m $^{-2}$ for day 2.

interaction measured on day 1 and 48 mV on day 2 were employed to optimize the fit at large separations where the electrical double-layer force is expected to dominate. Due to the low compressibility of the polymer layer, the origin of the double layer and van der Waals force was moved to 3.4 nm (the compressed layer thickness). The theoretical Debye length was used (30.4 nm). Both of the measured force curves correspond reasonably with the theoretical fit, but in both cases the distance at which the surfaces jumped together was greater than that expected from the van der Waals force. This is consistent with measurements using other polyelectrolytes,^{21,22} as well as Monte Carlo simulations on adsorbed polyelectrolytes,^{38–40} and it has been attributed to a bridging attraction. On separation, the surfaces adhered together requiring a force of 1 mN m $^{-1}$ to separate them. This was a significant reduction compared with that measured between uncoated mica surfaces in 10^{-4} M KBr (30 mN m $^{-1}$). The force minimum on separating the surfaces was located at a separation of 5.5 nm. It should be noted that there was considerable variation in the magnitude of the repulsive force between approaching surfaces before the jump into contact. However Figure 7 shows force curves that can be considered "representative". The magnitude

(35) Hines, J. D. *J. Colloid Interface Sci.* **1996**, *180*, 488.

(36) Chan, D. Y. C.; Pashley, R. M.; White, L. R. *J. Colloid Interface Sci.* **1980**, *77*, 283.

(37) Hough, D. B.; White, L. R. *Adv. Colloid Interface Sci.* **1980**, *14*, 3.

(38) Åkesson, T.; Woodward, C.; Jönsson, B. *J. Chem. Phys.* **1989**, *91*, 2461.

(39) Böhmer, M. R.; Evers, O. A.; Scheutjens, J. M. H. M. *Macromolecules* **1990**, *23*, 2288.

(40) Miklavic, S. J.; Woodward, C. E.; Jönsson, B.; Åkesson, T. *Macromolecules* **1990**, *23*, 4149.

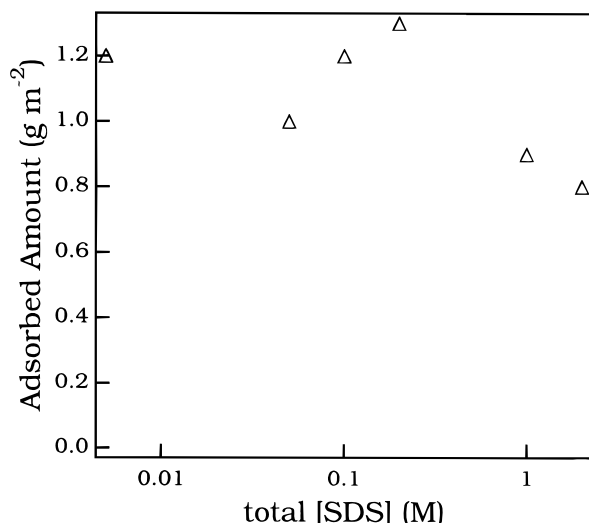


Figure 8. Desorption isotherm of preadsorbed AM-MAPTAC-31 from mica by SDS as a function of total SDS concentration, determined by means of ESCA.

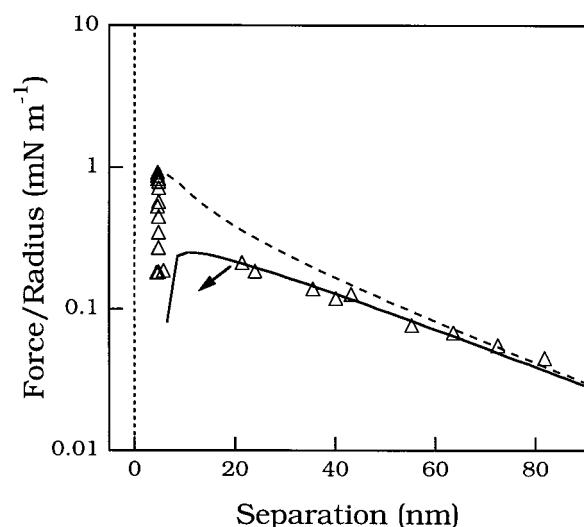


Figure 9. Force measured between mica surfaces bearing preadsorbed layers of AM-MAPTAC-31 after equilibration with 4.2×10^{-5} M SDS solution in 10^{-4} M KBr. The DLVO fit (constant σ_0 and constant Ψ_0 as per Figure 3) is shown, with $\Psi_0 = 45$ mV, $\sigma_0 = 0.688$ mC m $^{-2}$, layer thickness = 4.5 nm, $A = 0.5 \times 10^{-20}$ J, and the analytical Debye length.

of the charge density on the surface calculated from Poisson–Boltzmann theory is 0.8 mC m $^{-2}$, compared with 52 mC m $^{-2}$ for bare mica surfaces at the same salt concentration, i.e., a 66-fold decrease on coating the surface with the polyelectrolyte. We note that the negative lattice charge on mica corresponds to a charge density of 336 mC m $^{-2}$; i.e., ions such as H^+ and K^+ are adsorbed to the surface.

Desorption of Preadsorbed AM-MAPTAC-31 from Mica by SDS, ESCA Results. The desorption of polyelectrolyte by addition of SDS was followed by ESCA measurements (Figure 8). A slight, but significant, desorption was found at very high SDS concentrations (1.7×10^{-2} M).

Forces between Preadsorbed AM-MAPTAC-31 Layers on Mica Surfaces in the Presence of SDS. Equilibration of preadsorbed AM-MAPTAC-31 layers on mica overnight in the presence of 4.2×10^{-5} M ($0.005 \times$ cmc, Figure 9) caused no significant change in the force compared to that observed in simple electrolyte solution.

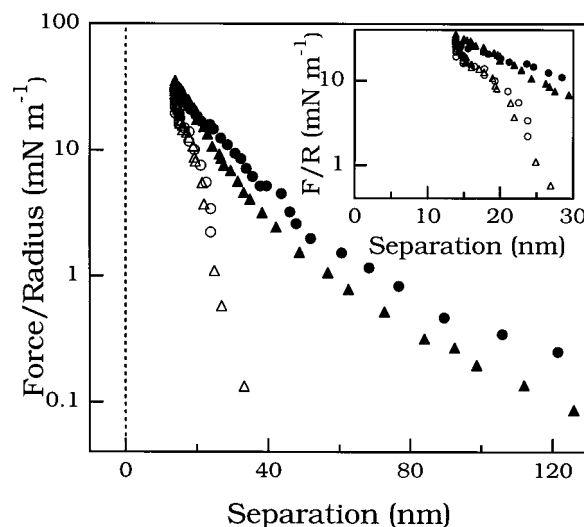


Figure 10. Force measured between mica surfaces bearing preadsorbed layers of AM-MAPTAC-31 after equilibration with 4.2×10^{-4} M SDS solution in 10^{-4} M KBr. The first (\bullet, \circ) and second ($\blacktriangle, \triangle$) approach and separation, respectively, are displayed. The inset magnifies the small separation regime to highlight the layer reexpansion between 12 and 20 nm.

An attractive force was again found to cause the surfaces to jump together from a distance of around 20 nm, close to the distance measured in the surfactant-free solution. The adhesion was also unchanged. The layer thickness was 4.5 nm after the jump into contact and at maximum compression, which is slightly higher than that observed without SDS present (3.4 nm). To ensure that interacting polymer layers did not induce a hydrodynamic force, a slow measurement rate was used, with each approach curve measured over approximately 20 min.

Increasing the SDS concentration to 4.2×10^{-4} M ($0.05 \times$ cmc, Figure 10) caused a dramatic swelling of the polyelectrolyte layer. This resulted in a strong increase in range and magnitude of the now purely repulsive force and an increased hard wall separation. Despite the large swelling of the layer, we found that the measured interaction was reproducible between consecutive force measurements to within the limits shown in Figure 9. A slightly lower reproducibility was observed between experiments using different mica sheets. Typically, the repulsion was first observed at a separation of 140 nm (corresponding to a layer thickness of 70 nm on each surface). At large separations the repulsion increased roughly exponentially with a decay constant of 25–30 nm. This is about twice the expected decay length of a double-layer force at the given ionic strength. Hence, we conclude that both steric and electrostatic forces contribute to the measured interaction. At separations below about 50 nm, the force becomes significantly steeper, but no clear hard wall is reached. A separation of about 12 nm (6 nm per surface) was reached under the highest force employed, 40 mN m $^{-1}$.

On separation, a change in state of the adsorbed layer appeared to occur between ~ 12 and 20 nm, possibly due to the expulsion (on compression) and readsorption of surfactant molecules within the polyelectrolyte layer. This effect has also been observed for a 10% charged polyelectrolyte.²⁵ An adhesion of -0.36 mN m $^{-1}$ was observed at a separation of 34 nm.

A further increase in SDS concentration to 1.7×10^{-3} M ($0.2 \times$ cmc, Figure 11) reduced the range and magnitude of the repulsive force. Under a high force, a hard wall

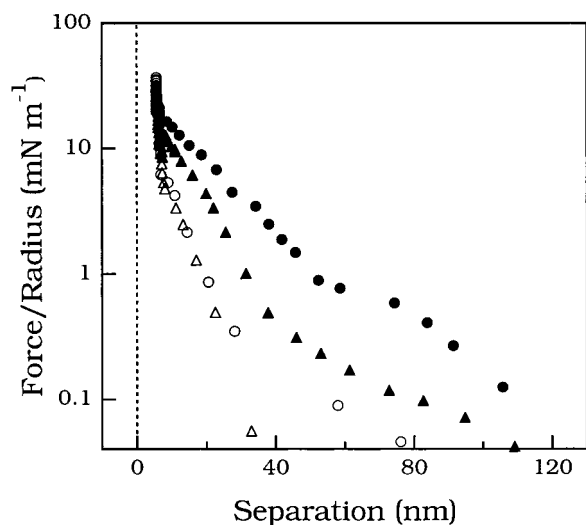


Figure 11. Force measured between mica surfaces bearing preadsorbed layers of AM-MAPTAC-31 after equilibration with 1.7×10^{-3} M SDS solution in 10^{-4} M KBr. The first (●,○) and second (▲,△) approach and separation are shown.

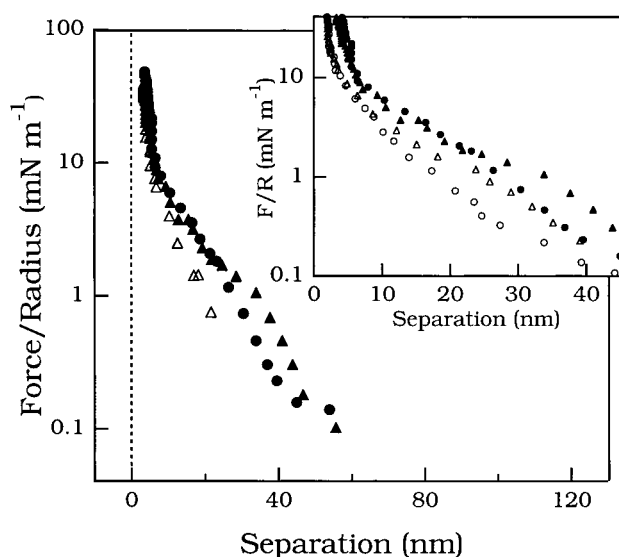


Figure 12. Force measured between mica surfaces bearing preadsorbed layers of AM-MAPTAC-31 after equilibration with 4.2×10^{-2} M SDS solution in 10^{-4} M KBr. The initial approach after 1 day (▲) and 2 days (●) and separation after 1 day (△) are shown. The inset displays first and second approaches after 1 day (●,○) and 2 days (▲,△).

was reached. It was located at a separation of 5–6 nm, approximately half that measured in $0.05 \times \text{cmc}$ SDS using the same compressive force. No adhesion was measured in this surfactant concentration, although a significantly lower repulsion was observed upon separating the surfaces. The magnitude of the force decreased more noticeably between the first and second approach compared with that measured in $0.05 \times \text{cmc}$ SDS.

A final increase in SDS concentration to 1.7×10^{-2} M ($2 \times \text{cmc}$, Figure 12) resulted in a decrease in the hard-wall separation, to 3.3 nm. The magnitude of the force at longer range was significantly reduced compared to that measured in $0.2 \times \text{cmc}$ SDS. It is interesting to note that when two force curves were measured consecutively, a reproducible reduction in force and layer thickness was observed on the second run (see the inset of Figure 11 for two examples of this behavior). At this stage we have no reasonable explanation for this observation. No adhesion

was measured at this SDS concentration. Some hysteresis was observed upon separating the surfaces, but less than that seen in $0.2 \times \text{cmc}$ SDS.

Discussion

The system under investigation is a mixture of anionic surfactant, cationic polyelectrolyte, and negatively charged solid surface. A quantitative study of this system should investigate the interplay between all components. The current study examines the behavior of bulk mixtures of polyelectrolyte and surfactant and also the surface forces between mica surfaces coated with AM-MAPTAC-31 as a result of interactions with surfactant. The full three-component system is subject to a number of interactions. Before addition of surfactant to the system, the equilibrium is simply between the polyelectrolyte in solution and that at the solid surface. The adsorption isotherm as measured using ESCA (Figure 6) shows a very high affinity of AM-MAPTAC-31 for the mica surface, with as little as 10 ppm resulting in saturation. Despite the strong Coulombic attraction to the interface, the adsorbed layer retains a finite conformational entropy. Theory³⁹ and previous experimental results²² for similar systems suggest a slight overcompensation of the surface charge. Force measurements performed in the current experiment (Figure 7) indeed showed a weak electrostatic repulsion, but it is impossible to state from the available evidence whether the surface charge was overcompensated or undercompensated. The attraction from $D \sim 20$ nm was a result of the dangling polymer tails attached to each surface experiencing an electrostatic attraction to the other surface.^{38,40} The reduction in double-layer repulsion with time observed between mica surfaces precoated with polyelectrolyte in simple 10^{-4} M KBr solution (Figure 7) is more difficult to explain given that dissolved polymer had been removed from the apparatus. The reduced range of the bridging attraction suggests that the polymer layer had become more compact. This factor in itself may have allowed a greater number of the charged groups on the polymer to come close to the mica surface permitting ion exchange and expulsion of simple cations, thus reducing the overall surface charge. The clarity of the effect is further evidence of the kinetic perils of working with polymers at solid interfaces (i.e., allow sufficient equilibration time!). It seems highly probable that the decrease in force with time can only occur if the surface is initially overcompensated. Of course, desorption of polyelectrolyte would also result in a decreased force; however, previous studies have shown this to be an extremely slow process.²² The measured adhesion (1 mN m^{-1}) was much smaller than that for 100% charged layers.²¹ This decrease is expected based on Monte Carlo simulations³⁹ and, considering the steeply increasing magnitude of the expected attractive force with decreasing separation, is related to the increased thickness of the adsorbed layer at the lower charge density.

Now considering the equilibrium between polymer and surfactant in bulk, the solution properties were investigated at a single polyelectrolyte concentration (Figure 4). The formation of a separate polymer-rich phase (i.e., aggregates) at intermediate surfactant concentrations is obvious, corresponding closely with the charge neutralization concentration ($[\text{SDS}]_{\text{free}} = 1.2 \times 10^{-3} \text{ M}$). The phase separation is simply a result of the decreased solvency of the polymer/surfactant complex due to a decreased net charge and increased hydrophobicity. The continued adsorption of surfactant after neutralization demonstrates the importance of non-Coulombic attractive forces—principally the hydrophobic attraction. The critical first

step in initiating aggregation is the formation of an associative complex at surfactant concentrations much lower than the cmc (Figure 3). The reason for the steep increase in adsorption is surfactant aggregation facilitated by the presence of the polyelectrolyte. The decrease in free energy inherent in removing surfactant tails from an aqueous environment is the driving force for this process, the formed micelles act as "sinks" for added surfactant. In the absence of polyelectrolyte, the charges of the surfactants in the micelles are neutralized by both a bound and a diffuse layer of inorganic counterions. When polyelectrolyte is present, the simple counterions are no longer required because the micelles can be stabilized much more efficiently by the polymer. The loss of conformational and translational entropy of binding the polymer to the surfactant aggregates is small compared to the increase in entropy of liberating small counterions from the polyelectrolyte as well as the simple ions that otherwise would have been associated with the micelles.³ We have not been able to measure a binding isotherm of the surfactant to the polymer directly. Surface tension measurements (Figure 5), however, provide a simple qualitative picture of what happens in solution. Above the cac, the surface tension remains rather constant (until charge neutralization), suggesting that most of the added surfactant is incorporated into the complex. The high gradient of the surface tension versus total [SDS] isotherm below the cac (point a) shows that the polyelectrolyte increases the surface activity of the surfactant at these low concentrations. The increase in slope above point b (which from mobility measurements (Figure 4) is the charge neutralization concentration) confirms that adsorption of surfactant ions is less favorable, which is expected due to the Coulombic repulsion. Conductivity measurements (Figure 2) also indicate that the free SDS concentration increases only slowly above the cac.

Equilibrium: Polymer/Surfactant/Surface. Polyelectrolyte/surfactant complexes become less charged with increasing [SDS] up to the charge neutralization concentration. Thus, considering only Coulombic forces, the adsorption strength onto mica should steadily decrease, whereas the adsorbed amount may vary in a nonmonotonic fashion. Surface force measurements (the principal investigative tool employed thus far) on this polymer conducted at 10^{-2} M²⁶ showed that the range of the force was steadily reduced, up to cac, indicating that the adsorbed layer became more compact. When complexes between cationic polyelectrolytes and anionic surfactants are allowed to adsorb onto negatively charged solid surfaces, one has to consider that the amount of surfactant in the complex may change upon adsorption. Slow changes in adsorbed layer structure may occur due to the polymer rearranging to decrease its free energy and also redistribution of surfactants in the layer. These effects have been discussed in a previous study,⁴¹ and it will be treated in more detail in a coming publication.⁴²

The presence of polymer in solution, although providing important information on the adsorption of polyelectrolyte-surfactant aggregates, does not provide information about direct association between surfactants and polyelectrolytes at the solid-liquid interface. In the current work, dissolved polymer was removed from solution before surfactant was added. The extent of desorption as a result of adding SDS was measured using ESCA (Figure 8). A slight desorption was apparent after 24 h in $2\times$ cmc

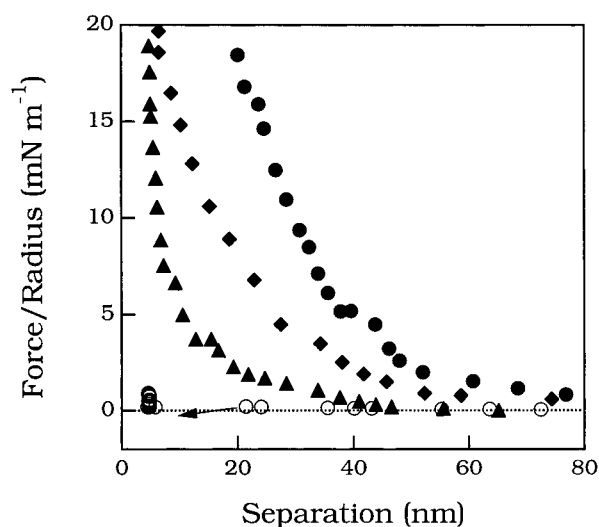


Figure 13. First approaches measured between mica surfaces precoated with AM-MAPTAC-31 across 10^{-4} M KBr: [SDS] = 4.2×10^{-5} (○), 4.2×10^{-4} (●), 1.7×10^{-3} (◆), and 1.7×10^{-2} M (▲). The arrow in the figure represents a jump into contact.

solution. The first force curve measured on approach at each SDS concentration has been replotted together in Figure 13 to allow better comparison. The force between preadsorbed surfactant layers measured in $0.005\times$ cmc (Figure 9) was very weakly repulsive at long range, with a bridging attraction at shorter range (20 nm), and was also basically unchanged with respect to that measured before SDS was added. The thickness of the compressed layer was slightly increased due to adsorbed SDS (4.5 nm, cf. 3.4 nm), consistent with the observed adsorption of surfactant below cac in bulk (Figure 3). That the force was basically unchanged at larger separations only suggests that the polymer did not undergo any major conformational changes. Increasing [SDS] to $0.05\times$ cmc caused a dramatic increase in the range and magnitude of the repulsive force. The increased force is due to a swelling of the adsorbed layer resulting from polymer/surfactant complex formation. That complex formation occurred between 0.005 and $0.05\times$ cmc is consistent with the bulk binding isotherm (Figure 3), which shows the former concentration to be below the cac and the latter above. The adsorbed surfactant aggregates should give the polymer layer an overall negative charge. Repulsion between surfactant aggregates and between the aggregates and the mica surface favors the formation of an extended layer. The force between the surfaces is a combination of an electrostatic repulsion, where the plane of charge depends on the intersurface separation⁴³ and a steric repulsion. The purely repulsive force measured in the current work contrasts strongly with the oscillatory force measured between mica surfaces coated with a polyelectrolyte having one positive charge per monomer in the presence of SDS.²⁴ This oscillatory force is persuasive evidence that the surfactant forms regularly sized and spaced aggregates within the layer. The absence of oscillations in the current measurements suggests a more disordered array of aggregates within the layer, which is entirely reasonable considering the reduced polyelectrolyte charge density. When the surfaces were separated, the layers were observed to undergo a sudden expansion when the applied force was still around 10 mN/m (inset Figure 10). Two conclusions can be drawn from this observation. The first is that some surfactant

(41) Claesson, P. M.; Dedinaite, A.; Fielden, M. L.; Kjellin, U. R. M. *Prog. Colloid Polym. Sci.* **1997**, *106*, 24.

(42) Dedinaite, A.; Claesson, P. M. In preparation.

(43) Miklavic, S. J.; Marcelja, S. J. *J. Phys. Chem.* **1988**, *92*, 6718.

was expelled from the layer under high compressive force, and the second is that the driving force for polymer/surfactant association is strong enough to allow readorption even under a high compressive force. The next concentration investigated, $0.2 \times \text{cmc}$ ($1.7 \times 10^{-3} \text{ M}$, Figure 11), was slightly higher than the cnc in bulk ($1.2 \times 10^{-3} \text{ M}$). It should be emphasized that the adsorbed layer should become negatively charged at $0.05 \times \text{cmc}$, due to the presence of the mica surface, in comparison with the much higher bulk cnc. It is therefore difficult to directly compare bulk properties with those of a preadsorbed layer. However in a mixed system where adsorption is allowed to occur from polymer/surfactant mixtures, the final adsorbed layer may be expected to have similar properties, although the adsorbed amount may be quite different. The principal effect of increasing the SDS concentration to $0.2 \times \text{cmc}$ and subsequently to $2 \times \text{cmc}$ (Figure 12) was to reduce the repulsive force and layer thickness (as illustrated in Figure 13). The decreasing repulsion can be due to a combination of effects. The increased ionic strength gives a smaller repulsion between surfactant aggregates and hence a smaller repulsive force. Further, some desorption of polymer may have occurred, at least at the highest SDS concentrations employed. Desorption is consistent with the single-phase solution observed in bulk polymer/surfactant mixtures at this surfactant concentration (Figure 4) and with ESCA measurements (Figure 8). The force measured on separating the surfaces was rather consistent with increasing SDS concentration. A possible explanation for this observation is that most of the surfactant was desorbed on squeezing the surfaces together and did not fully readorb during the time taken to measure the separation curve.

Finally we briefly discuss the influence of ionic strength. It is established that polymer layers adsorbed from a high ionic strength solution are much thicker than those adsorbed from a low ionic strength solution.²¹ Increasing the salt concentration after preadsorbing a polyelectrolyte from low ionic strength solution caused some layer swelling, but to a greatly reduced extent compared to the case where adsorption took place directly from a high ionic strength solution. The swelling of the adsorbed layer in an SDS solution of $4 \times 10^{-4} \text{ M}$ was much larger than that observed as a result of increasing the salt concentration to 10^{-2} M (cf. for a 100% charged polymer). The influence of SDS on AM-MAPTAC-31 layers deposited from a 10^{-2} M salt solution has been described in a previous publication.²⁶ The measurements made in the presence of both surfactant and polymer showed a decrease in layer thickness with increasing [SDS]. The polymer layer preadsorbed from a 1900 ppm polymer and 10^{-2} M KBr solution adopted a rather extended conformation even in the absence of SDS (Figure 14). The addition of SDS to $1 \times 10^{-4} \text{ M}$ did not affect the long range force, but caused a significant increase in layer thickness at maximum compression. The force measured on separating the surfaces showed that the layer did not reexpand immediately once the compression was removed, suggesting that aggregate formation may have occurred under high compressive force, temporarily binding the polymer layers into a more compact structure. The polymer layer swelled considerably after increasing [SDS] to $1 \times 10^{-3} \text{ M}$ SDS indicating significant polyelectrolyte-surfactant complex formation. The cac at the surface appears to lie in the same concentration range at both 10^{-4} and 10^{-2} M ionic strength. The rather dramatic differences in layer structure as a function of salt concentration is caused by

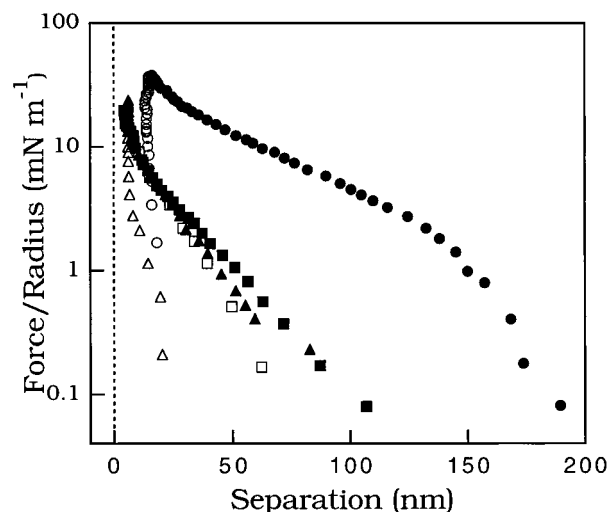


Figure 14. Forces measured between mica surfaces pre-coated with AM-MAPTAC-31 across 10^{-2} M KBr solution. The polymer was adsorbed from a 1900 ppm (w/v) solution in 10^{-2} M KBr. Forces were measured across 10^{-2} M KBr (■) also containing 10^{-4} M SDS (▲) and 10^{-3} M SDS (●). Approach and separation are represented by filled and hollow symbols, respectively.

a lower Coulombic driving force for both polymer/surface and also polymer/surfactant interaction at the higher ionic strength.

The work of Shubin^{19,20} is a special case worth discussing with respect to the current work. The polymer employed was a weakly charged polysaccharide having a longer nonelectrostatic persistence length than the polymer used in the current study. Swelling of an adsorbed layer on silica was observed on addition of SDS, similar to that observed in the current case; however, mixtures of polymer and surfactant were sequentially injected into the measuring chamber, so the starting point for the adsorption of polyelectrolyte/surfactant aggregates was not the bare surface for all but the first solution conditions employed. The results were, however, generally in agreement with the findings in this work.

The results presented in the current report describe the influence of SDS on various properties of dissolved and adsorbed AM-MAPTAC-31. To go further with the analysis and understanding of this system, the quantitative determination of species distribution is required. This not only would allow a quantitative comparison of different measurements but also would permit the correct mechanistic interpretation of the observed surface forces.

Conclusion

The solution and electrokinetic properties of AM-MAPTAC-31/SDS complexes in bulk solution were assessed by measuring the turbidity and electrophoretic mobility as a function of SDS concentration. An obvious phase separation occurred at intermediate surfactant concentrations, around the isoelectric point of the polyelectrolyte-surfactant complex, as expected for this type of system. The conductivity of SDS solutions in the presence of AM-MAPTAC-31 clearly illustrated an associative phenomena at a free SDS concentration of around $7 \times 10^{-5} \text{ M}$ ($0.008 \times \text{cmc}$).

Adsorption of the 31% charged polyelectrolyte AM-MAPTAC-31 onto mica from a 20 ppm solution in 0.1 mM KBr left the surface slightly charged, resulting in a weak electrostatic repulsion between the surfaces. Some polymer tails extend about 10 nm from the surface, as judged by the range of the attractive bridging force. The layers

could be compressed to around 1.5–2.0 nm. The small adhesion observed compared to that for more highly charged polyelectrolytes is consistent with theoretical expectations.

Addition of a small quantity of SDS ($0.005\times$ cmc) did not affect the surface forces. Increasing the SDS concentration to $0.05\times$ cmc caused a massive increase in repulsive force and layer thickness. This change was attributed to the formation of an associative complex between the surfactant molecules and the adsorbed polyelectrolyte. A slight adhesion was still present.

Increasing the polyelectrolyte concentration above $0.05\times$ cmc to 0.2 and then $2\times$ cmc saw a progressive decrease in the magnitude of the force and compressed layer thickness. This suggests either a progressive desorption of polyelectrolyte with increasing surfactant concentration, reduction of the electrostatic repulsion, or a combination of these effects. The relevance of these results when considering the effect of polyelectrolyte charge density was discussed.

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