Adsorption and Viscoelastic Analysis of Polyelectrolyte–Surfactant Complexes on Charged Hydrophilic Surfaces

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Supporting Information

ABSTRACT: The aggregation of surfactants around oppositely charged polyelectrolytes brings about a peculiar bulk phase behavior of the complex, known as coacervation, and can control the extent of adsorption of the polyelectrolyte at an aqueous–solid interface. Adsorption kinetics from turbid premixed polyelectrolyte–surfactant mixtures have been difficult to measure using optical techniques such as ellipsometry and reflectometry, thus limiting the correlation between bulk phases and interfacial adsorption. Here, we investigated the adsorption from premixed solutions of a cationic polysaccharide (PQ10) and the anionic surfactant sodium dodecyl sulfate (SDS) on an amphoteric alumina surface using quartz crystal microbalance with dissipation (QCMD). The surface charge on the alumina was tuned by changing the pH of the premixed solutions, allowing us to assess the role of electrostatic interactions by studying the adsorption on both negatively and positively charged surfaces. We observed a maximum extent of adsorption on both negatively and positively charged surfaces from a solution corresponding to the maximum turbidity. Enhanced adsorption upon diluting the redissolved complexes at a high SDS concentration was seen only on the negatively charged surface, and not on the positively charged one, confirming the importance of electrostatic interactions in controlling the adsorption on a hydrophilic charged surface. Using the Voigt based viscoelastic model, QCMD also provided information on the effective viscosity, effective shear modulus, and thickness of the adsorbed polymeric complex. The findings of viscoelastic analysis, corroborated by atomic force microscopy measurements, suggest that PQ10 by itself forms a flat, uniform layer, rigidly attached to the surface. The PQ10–SDS complex shows a heterogeneous surface structure, where the underlayer is relatively compact and tightly attached and the top is a loosely bound diffused overlayer, accounting for most of the adsorbate, which gets washed away upon rinsing. Understanding of the surface structure will have important implications toward understanding lubrication.

INTRODUCTION

Aqueous mixtures of polyelectrolytes and oppositely charged surfactants have been the focus of several scientific studies in the past few decades because of their diverse applications in paper making, latex paints, minerals and mining, detergents, fabric softeners, personal care, and health care formulations. The bulk phase behavior of polyelectrolyte–surfactant mixtures has been studied extensively and typically there exist three regimes in the phase diagram. In general, for a clear solution at a given polyelectrolyte concentration, the turbidity increases with increasing surfactant concentration; the upper boundary of Regime 1 is identified when the turbidity reaches a maximum value. In Regime 2, the association of the polyelectrolyte–surfactant complex results in the precipitation of the coacervates. At higher surfactant concentrations (in Regime 3), resolubilization occurs (a single phase clear solution forms again) owing to the cooperative association of excess surfactant molecules around the polyelectrolyte chains. This bulk phase behavior of a polyelectrolyte–surfactant mixture, governed by Coulombic and hydrophobic interactions, is strongly affected by polymer charge density, hydrophobicity of the polymer, rigidity of the polymer, surfactant tail length, and ionic strength of the solution. Despite several bulk phase studies, very few investigations have studied the adsorption of a polymer–surfactant complex at the aqueous–solid interface. In this case, the adsorption process is challenging to study because of the simultaneous interactions between surface/polymer, surface/surfactant, and surface/polymer–surfactant complex.

Effects of surfactant addition on the preadsorbed polyelectrolyte on mica surface was first studied using the surface force apparatus (SFA), where swelling of the adsorbed polymer layer was observed with increased surfactant incorporation. However, surface force measurements do not provide direct information on surface excess, limiting the interpretation of the experimental data. Swelling of the preadsorbed polyelectrolyte layers by penetration of surfactant was also suggested, two decades later, by neutron reflectivity (NR) measurements. In situ null ellipsometry was used to quantify the adsorption; an
enhancement in the adsorbed mass was seen after surfactant addition, only above the critical aggregate concentration (CAC), to the preadsorbed polymer layer.24,25 The increase in adsorption above the CAC is due to the cooperative association of surfactant molecules around polymer chains forming complex aggregates, as indicated by reduced electrophoretic mobility in the bulk solution.21,22 Chemical composition of the adsorbed layer was analyzed by X-ray photoelectron spectroscopy (XPS) to understand the relative contribution of the cationic polymer and the anionic surfactant in the adsorbed layer.23 It was found that at a low surfactant concentration the adsorption was predominantly due to polymer. Complexation in bulk with a surfactant concentration above CAC resulted in a higher adsorbed amount, consisting of both the polymer and the surfactant. Higher surfactant concentration in Regime 3 resulted in diminished adsorption over the negative surface. Although the authors attempted to correlate the complex formation in bulk and the extent of adsorption, the XPS measurements were performed ex situ under a high vacuum in a non-native state of the adsorbed layer and it is important to study the effect of in situ compositional changes on the adsorption.

Prior work on the adsorption of polyelectrolyte–surfactant complexes has provided important insights, but substantial gaps have not been addressed. For example, the ellipsometry study by Terada et al.24 measured the highest adsorption before the phase separation for a polymer (JR400) that was preadsorbed on silica, when sodium dodecyl sulfate (SDS) was added sequentially. However, high turbidity from the premixed JR400-SDS solutions at higher SDS concentrations, even before the phase separation, prevented them from measuring the adsorbed amount using ellipsometry. Bulk phases and surface adsorption were previously correlated for the case of preadsorbed cationic polysaccharide by sequential addition of SDS.25,26 Because the relaxation time of the preadsorbed polymer chains could be long, it is not clear whether similar results would be obtained if the premixed polymer–surfactant solutions would be exposed to a fresh surface. To overcome the experimental limitation from turbidity, quartz crystal microbalance with dissipation (QCMD) was used to study the adsorption from premixed poly(vinyl amine)–SDS solutions on a hydrophobic polystyrene surface.27 However, the authors considered a rigid structure for the adsorbed layer, which may not be correct for a hydrated viscoelastic polyelectrolyte complex in an aqueous medium. The authors acknowledged the need for a sophisticated analysis to quantify the adsorption and to characterize the viscoelastic properties of the adsorbed complexes.

It is important to identify a correlation between the complexation behavior in bulk phases and the adsorption at the interface. If a correlation is established then the adsorption at an interface could be optimized in a predictable manner, simply by tailoring the bulk phase composition. Such predictability is of interest to many technological applications, such as personal care and home-care products, where the adsorption of polyelectrolyte–surfactant complexes occurs in situ on a solid surface from a bulk formulation. Polymer–surfactant systems also act as a carrier for a hydrophobic active agent, which needs to be delivered to the solid surface in an aqueous environment. Hence, identifying the conditions under which optimum adsorption occurs from the bulk solution is crucial. Additionally, it is imperative to study the structure and conformation of the adsorbed mass, which has a direct implication on surface texture and friction. Taylor et al.28 have elaborated the use of NR to directly determine the density profile of the adsorbed layer at the air–water interface. These studies shed light on the characteristic discontinuities in surface tension curves that correlated with the bulk phase transitions. Adsorption at a fluid air–water interface is reversible in contrast to polyelectrolyte adsorption at charged solid–water interface where the pseudoequilibrium state dictates the conformation of polyelectrolyte–surfactant complex. Interpretation of the NR results at the solid–liquid interface is challenging, and not many studies have elucidated the structural information at this interface.29 The conformation of the adsorbed polymer–surfactant complex has been suggested as extended, swollen, and loopy, in contrast to the flat structure of the adsorbed polyelectrolyte, by SFA, small-angle neutron scattering, and NR analysis.30,31 However, to the best of our knowledge, no study has investigated the density and viscoelastic properties of the adsorbed polymer–surfactant complex that have direct ramifications toward tribology and surface lubrication.

Although electrostatics has been proven to control the adsorption of the unmodified, hydrophilic polyelectrolyte–surfactant complex on a hydrophilic charged surface,21,31 all the prior adsorption studies were performed on negatively charged surfaces, such as silica and mica. To verify the importance of electrostatic interactions, adsorption experiments should also be done on a positively charged surface. Here, we investigate the adsorption from premixed cationic quaternized hydroxethyl cellulose (PQ10) and SDS mixtures onto an amphoteric aluminum oxide surface. The surface charge of the alumina surface can be tuned using pH. The QCMD was used to monitor the adsorption process from the solutions across the bulk phase regimes in order study the influence of the complexity in bulk on the interfacial adsorption. A viscoelastic Voigt model was used to model the QCMD data to calculate the thickness, shear viscosity, shear elastic modulus, and density of the adsorbed layer. Atomic force microscopy (AFM) was also used to directly image the adsorbed layer from the PQ10–SDS solutions on a SiO2 coated silicon substrate, to compare with the thickness and surface coverage of the adsorbed layer determined using the QCMD measurements.

### MATERIALS AND METHODS

**Materials.** The cationic polymer quaternized hydroxethyl cellulose ethoxylate, PQ10, was purchased from Sigma-Aldrich (Figure 1). This high molecular weight cationic polysaccharide was purified by tangential flow filtration (TFF) process using a KrosFlo Research TFF system. First, a polysulfone membrane with a molecular weight cutoff (MWCO) of 100 kDa was used to remove salts and relatively shorter polymer chains. A poly(ether sulfone) membrane of 0.5 μm porosity was used to remove very high molecular weight fractions. After freeze-drying, the purified polymer was characterized by aqueous gel permeation

![Figure 1. Schematic of the chemical structure PQ10. τ is the degree of quaternization.](image)
chromatography with a light scattering detector to estimate the absolute molecular weight without relying on uncharged polysaccharides as standards. Using a mobile phase containing 0.5 M NaNO₃, the molecular weights were determined to be $M_0 = 194$ kDa and $M_0 = 555$ kDa, with a PDI of 2.86. Although these samples still have a broad polydispersity, they are comparable with a well characterized standard cationic hydroxyethyl cellulose: JR400 (a Dow product).32 Elemental analysis for PQ10 showed a nitrogen number of 3.59%, corresponding to a charge density of 2.3 meq/g and a degree of quaternization $\tau = 35\%$, suggesting the presence of one positive charge per 830 Da of PQ10 average molecular weight.

The anionic surfactant SDS (Sigma-Aldrich) was recrystallized in ethanol three times. Its purity was characterized by surface tension measurements of solutions containing 10 mM NaCl (Fisher Scientific, 99% purity). Using the Gibb’s adsorption isotherm, a surface excess of $1.9 \times 10^{-10}$ mol/cm² was determined, a value close to that ($2.2 \times 10^{-10}$ mol/cm²) measured previously by Chari and Hossain.33 The 10 mM NaCl concentration was used for all the adsorption studies. Millipore water (resistivity $= 18$ MΩ-cm) was used to make solutions of PQ10, SDS, and NaCl. After mixing all the of components to their respective concentrations, solutions were shaken for a few minutes and equilibrated for at least 24 h. All the measurements were done within 48 h of solution preparation.

Characterization of the Bulk Solution. The regimes in the bulk phase diagram for the PQ10–SDS complex were identified by turbidimetry and zeta-potential measurements. A PQ10 concentration of 100 ppm and a NaCl of 10 mM were kept constant and SDS concentration was varied to identify the three regimes of PQ10–SDS complex solutions. It is important to note that the concentration of SDS was not sequentially increased in the same solution. Different samples were used for each of SDS concentrations studied here. Turbidity of the complex solutions was measured using a HF Scientific Inc. Micro100 turbidimeter. Net charge on the complex was determined by zeta-potential measurements using a Malvern Zetasizer nano-ZS90 instrument. Electrophoretic mobility was determined by measuring the direction and velocity of the complex at 25 °C under the applied electric field, and the Zetasizer software converted the electrophoretic measurements into $\zeta$-potential values by using Smoluchowsky model.34

Zeta Potential of Al₂O₃. Al₂O₃ (aluina) nanoparticles of standard grade 150 mesh (58 Å, Aldrich) were suspended in aqueous solutions (0.5 wt %) by ultrasonication for 30 min. Particle suspensions at different pHs were analyzed for zeta potential. In another experiment, the Al₂O₃ particles were suspended in PQ10 (100 ppm) solution by rapid magnetic stirring. Ultrasonication was not used in this case to avoid possible polymer disintegration. After stirring for 1 h, the suspensions were centrifuged to separate the supernatant solution containing unadsorbed PQ10. The precipitated alumina particles were again suspended in Millipore water, adjusted to pH 9, in order to analyze the net zeta potential after PQ10 adsorption.

Quartz Crystal Microbalance with Dissipation (QCMD). Adsorption of PQ10 and PQ10–SDS complex onto the charged solid surface was investigated by QCMD (Q-Sense Model E4, Q-Sense AB, Sweden). The sensors used were AT-cut quartz crystals with a fundamental frequency of 5 MHz. The sensors were coated with Al₂O₃ (Q-Sense). The charge on the Al₂O₃ coating can be tuned by changing the pH above or below the isoelectric point. Prior to an experiment, the quartz sensors were cleaned by sonication in 2 wt % SDS solution and finally with an ethanol wash. After drying under a N₂ stream, the sensors were cleaned using an air plasma (Harrick Scientific, PDC 32G) for 10 min. The cleaned sensors were placed in flow cells, and solutions were injected into the flow cells at a flow rate of 0.150 mL/min using a cartridge pump (ISIMATEC-ISM935). By changing the environment of the sensors from air to water, a large change in frequency $(F)$ and dissipation $(D)$ was always observed. For studying adsorption from aqueous solutions, it is important to establish a baseline with respect to water. In the beginning of each experiment, the sensors were equilibrated under a stock solution containing only 10 mM NaCl at respective pH until a stable baseline was obtained for 15–20 min. Then PQ10 or PQ10–SDS solutions were injected and a sudden change in $F$ and $D$ was observed due to the adsorption. The flow was stopped after the rapid change was over. An equilibrium state was declared when no change in the values of $F$ and $D$ was observed as a function of time. For PQ10 alone, the equilibrium was achieved much more quickly compared to the PQ10–SDS complex. The adsorption of polymer–surfactant complex is slow, and a steady state is achieved over a period of several days.28,35 For practical reasons, an equilibrium was considered to be achieved when the rate of change of $F$ was less than $2$ Hz/h,36 which occurred over 24–30 h for some of the PQ10–SDS solutions.

After the steady state was achieved, excess chains of PQ10 were removed by rinsing the QCMD cell using the stock solution of 10 mM NaCl. When the steady state was achieved after rinsing, this state was analyzed and is referred to hereafter as “after wash”. Four sensors were used simultaneously to provide the average values and standard deviations, and these experiments were repeated at least twice. Since the noise is particularly high at the fundamental frequency (5 MHz), only the higher overtones $(n=5, 7, and 9)$ were analyzed, as practiced by many others previously.37–39

Analysis of QCMD Data. The Sauerbray equation,40 which is used to model thin compact films, was not suitable for analyzing the adsorption of a PQ10–SDS complex layer. One can see in Figure 2 that the change in frequencies for the three overtones is different and that the dissipation values are far greater than 1, indicating that the adsorbate does not obey the Sauerbray equation. For the PQ10–SDS adsorbed layer, the QCMD response is dependent on the viscoelastic properties of the adsorbed layer. To capture the viscoelastic response, we have used the Voigt model to analyze the QCMD data based on the contact or proposed by Voitov and coworkers.41

In this model, the quartz crystal is treated as a loss-less generator of known thickness, surface area, density, and shear modulus. In contact with the quartz resonator, a two-layer model for the adsorbed layer is used. The two-layer adsorbate is in contact with a semi-infinite bulk solution having the same density and viscosity as water at 25 °C. The Voigt model is valid under a no-slip boundary condition where the layers are uniform in thickness and in viscoelastic properties. The changes in the resonant frequency $(\Delta F)$ and the dissipation factor $(\Delta D)$ are calculated as follows:

$$
\Delta F \approx \frac{1}{2 \pi \rho_0 h_0} \left[ \sum_{j=1,2} h_0 \rho_j \omega_0 - 2 h_0 \left( \frac{\eta_j}{\omega_j} + \frac{\eta_{oo}}{\omega_0^2} \right) \right]
$$

(1)
In eqs 1 and 2, $\rho_0$ is the density of the crystal; $h_0$ is the thickness of the crystal; $f_i$ is the resonant frequency; $\eta_j$ is the viscosity of the bulk liquid; $\delta_i$ = $(2\eta_j/\rho_j)^0.5$ is the viscous penetration depth of the shear wave in the bulk liquid; $\rho_j$ is the density of bulk liquid; and $\omega$ is the angular frequency of oscillation. The thickness, density, viscosity, and elastic shear modulus of the adsorbed layer are represented by $h_j$, $\rho_j$, $\eta_j$, and $\mu_j$ respectively. To account for the inhomogeneity of the adsorbed layer, as explained in the AFM subsection later in the paper, we are referring to the viscosity and shear modulus as “effective viscosity” and “effective shear modulus”. The QTools software and eqs 1 and 2 were used to model the experimental data. The fittings were done using upper and lower bounds for all the parameters, and a Simplex algorithm was used to find the optimum solution with the least scaled error. A two-layer model was chosen for modeling the QCMD data. The first layer is modeled as a tightly attached layer, with low dissipation and a high shear modulus. The second layer was considered as a thick layer with high dissipation and a low shear modulus. The upper and lower limits used in modeling the data are shown in Table 1. “L1” and “L2” refer to the layers 1 and 2, respectively.

### Table 1. Limiting Values for Viscoelastic Parameters (Effective Viscosity ($\eta$), Effective Shear Modulus ($\mu$), Thickness ($h$), and Density ($\rho$)) Used for Fitting QCMD Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>L1 min</th>
<th>L1 max</th>
<th>L2 min</th>
<th>L2 max</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$ (Pa·s)</td>
<td>0.001</td>
<td>0.1</td>
<td>0.001</td>
<td>0.01</td>
</tr>
<tr>
<td>$\mu$ (Pa)</td>
<td>5000</td>
<td>$1 \times 10^6$</td>
<td>100</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>$h$ (nm)</td>
<td>1</td>
<td>40</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>$\rho$ (kg/m$^3$)</td>
<td>1250</td>
<td>1400</td>
<td>1000</td>
<td>1050</td>
</tr>
</tbody>
</table>

Depending on the response of each solution, these limits were changed locally to obtain the best fit with minimum cumulative square error, $\Sigma \xi^2$. Since the QCMD response also accounts for the coupled water (because of hydration of the film) including viscous drag during oscillations and entrapment in the cavities of the adsorbed film, the appropriate term to describe adsorption would be hydrodynamic surface concentration ($\Gamma$) instead of adsorbed mass. Note that the thickness ($h_j$) and density ($\rho_j$) were not independent variables within this model. The density of each layer was optimized during the fitting iterations, and $h_j$ was changed to match the best fit for the experimental data. From the values of $h_j$ at any instance and $\rho_j$ (constant with time), the hydrodynamic surface concentrations ($\hat{\Gamma}$), in ng/cm$^2$, at equilibrium were calculated using the following equation:

$$\hat{\Gamma} = h_j/\rho_j$$

### AFM Imaging

The AFM investigation was performed using an Agilent 5420 AFM instrument. Image acquisition was performed by Agilent PicoView 1.14 software. The aqueous image was done for PQ10 and PQ10–SDS complex adsorbed over smooth silicon surfaces that have a layer of SiO$_2$. Imaging of the adsorbed structures over alumina would have been ideal for a comparison with QCMD measurements, however alumina surfaces are not as smooth as silicon wafers which is a prerequisite for topography sensitive AFM measurements. Under the experimental conditions, the charge on the silica-coated silicon wafer was negative, allowing comparison of these results with those of the negatively charged alumina surface used in QCMD. The silicon wafers were cleaned thoroughly using (2 wt %) SDS solution, followed by piranha treatment (70:30 H$_2$SO$_4$/H$_2$O$_2$, 100 °C), rinsing with Millipore DI water, and oxygen plasma for 5 min. The silicon wafers were soaked with solutions for at least 24 h before imaging. The aqueous AFM imaging was done on silicon wafers after the adsorption process was complete. A drop of the same PQ10/PQ10–SDS solution was added on the AFM cantilever to ensure that the AFM cantilever and the substrate were covered by the corresponding aqueous solution. The AFM images were obtained in an intermittent contact mode (acoustically driven AC mode or tapping mode) using soft Si tips with a spring constant of $k = 7.4$ N/m. The acquired images were analyzed for root-mean-square (RMS) roughness and volume adsorbed by Agilent Pico Image 6.2 software.

### RESULTS AND DISCUSSION

#### Characterization of Bulk Phase Behavior

Figure 3 shows turbidity of the solutions and zeta potential of the complex for a series of mixtures with a fixed PQ10 concentration (100 ppm) and a varying SDS concentration. PQ10 alone (no SDS) forms a clear solution with a low turbidity value (0.22 NTU (nephelometric turbidity units)) and a positive zeta potential of 27.5 ± 5 mV. At low concentrations of SDS in Regime 1, the solutions are clear, showing a minimal turbidity. There is a slight reduction in the zeta potential, suggesting a reduction in the cationic charge of PQ10 due to binding of SDS, forming a complex. It is possible that the free/unbound SDS in the solution may affect the zeta potential measurements. However, we have also observed a significant drop in the surface tension for PQ10–SDS solutions at the corresponding SDS concentrations, where both PQ10 and SDS by themselves are not surface active (Supporting Information, Figure S1). This synergistic reduction in surface tension confirms the formation of a surface active complex between PQ10 and SDS.

A dramatic increase in turbidity is observed after 0.3 mM SDS, and a maximum turbidity is recorded at 0.8 mM SDS in Regime 1. In this concentration range, a steady decrease in the zeta potential is also observed. With diminishing cationic charge, due to binding with SDS, PQ10 chains tend to associate in bulk as a result of reduced interchain repulsions and form multichain aggregates. The aggregation of the complex chains is suggested by an increase in the turbidity of the solutions, known as Tyndall effect. Interestingly, the onset of the decrease in zeta potential (0.1 mM SDS) coincides with the critical aggregate concentration (CAC ~ 0.09 mM SDS) determined from the surface tension measurements (Supporting Information, Figure S1). Formation of larger aggregates, leading to increase in turbidity, was also reported by Zhou et al. using dynamic light scattering. A systematic increase in hydrodynamic radius was observed in their study due to complexation between cationic hydroxyethyl cellulose and SDS before the phase separation occurred. Our zeta potential measurements suggest the formation of a neutral complex at 1 mM SDS. Surface tension data (Supporting Information, Figure S1) also shows a second inflection near 1

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**Figure 3.** ζ-Potential (squares) of the complex and turbidity (circles) of the premixed solutions of PQ10 (100 ppm) with varying SDS concentration in the presence of 10 mM NaCl. Regimes are indicated by arrows. Dashed lines are due to the uncertainty about the exact location of the boundaries between the regimes.
mM SDS, which is understood as the saturation of the direct binding of surfactant aggregates to the polymer chains. The concentration of 1 mM is also the point at which macroscopic phase separation is observed, marking the onset of Regime 2. Zeta potential, turbidimetry, and surface tension measurements suggest that 1 mM SDS corresponds to the concentration at which SDS molecules compensate the cationic charges of 100 ppm PQ10 in 10 mM concentration of NaCl. The range of Regime 2 extends to 2 mM SDS. In a surface tension curve (Supporting Information, Figure S1) a plateau is seen between the CAC and the second inflection at 1 mM SDS. A recent theoretical investigation by Bahramian et al. has used the Butler analysis using a Langmuir isotherm to explain the formation of a plateau, which is observed for a dissociable polyelectrolyte—surfactant complex. In comparison some strongly interacting polyelectrolyte-surfactant complexes show a surface tension peak due to the depletion of both the polyelectrolyte and surfactant from the surface layer because of precipitation or phase separation.

At 3 mM SDS, a clear single-phase solution is observed. The zeta potential measurement indicates that the PQ10–SDS complex has a net negative charge at this point, implying an overcompensation of the charge of the polymer chains. The continued cooperative association of excess surfactant molecules around the polymer chains, mediated by hydrophobic interactions, results in the net negative charge on the complex, as suggested by the pearl-necklace model. For concentrations higher than 4 mM SDS, increasing negative ζ-potential is seen, forming clear solutions with zero turbidity. The complex coacervates break into smaller particles due to interchain Coulombic repulsions, thus forming a single-phase solutions labeled as Regime 3.

**PQ10 Adsorption on Alumina.** Zeta potentials for 100 ppm PQ10 and 0.5 wt % Al₂O₃ particles dispersed in the aqueous solutions at varying pH are shown in Figure 4. The zeta potential for PQ10 is approximately constant at 25 ± 5 mV over a pH range of 4–11. This pH-independent zeta potential for PQ10 is consistent with the previous observation that PQ10 is a strong polyelectrolyte and that the charge of PQ10 does not change with pH. In comparison, the Al₂O₃ particles show a strong pH dependence of surface charge. The positive zeta potential seen at pH 4 decreases with increasing pH and an isoelectric point is observed around pH 8. From pH 9 onward, the zeta potential continues to decrease with increasing pH. The isoelectric point for spherical Al₂O₃ particles could be different than that for the flat surface coated with Al₂O₃ used in our QCMD measurements. The study by Lutzenkirchen et al. suggested that the isoelectric point for Al₂O₃ can be between pH 5 and 8 depending on the crystal face exposed on the surface. For this study, only pH 4 and 9 are considered, the values at which the surface is expected to be positively and negatively charged, respectively. Figure 4 also shows the hydrodynamic surface concentration (Γ) over an Al₂O₃ coated quartz surface from PQ10 solutions with varying pH. As expected, cationic PQ10 does not adsorb on a positively charged surface at pH 4. Γ shows a steady increase with increasing pH and the maximum Γ is seen at pH 11, where the surface presumably has a maximum negative charge density in the given range of pH.

At a fixed bulk concentration of 100 ppm, a continuous increase in the Γ at equilibrium with increasing negative surface charge density highlights a well-known fact that polyelectrolyte adsorption continues to occur until the surface charge inversion takes place. To validate this claim, in a parallel experiment, Al₂O₃ particles were dispersed in PQ10 (100 ppm, 10 mM NaCl) solution at pH 9 for the polymer to adsorb on the surface of particles. Later, the zeta potential for the Al₂O₃ particles was measured separately in an aqueous solution (10 mM NaCl, pH 9) devoid of any unadsorbed PQ10 chains. Zeta potential for this suspension of particles coated by PQ10 is found to be 1.2 ± 6 mV (datum point not shown here). The change in zeta potential for Al₂O₃ particles from −11.1 to +1.2 mV at pH 9 after PQ10 adsorption proves that the polyelectrolyte adsorption on an oppositely charged surface results in surface charge overcompensation. Charge reversal has also been demonstrated to modify the negatively charged surface of hydrophilic silica by a thin adsorbed layer of cationic polyelectrolytes, inducing adsorption of anionic SDS onto the otherwise unfavorable bare substrate.

Figure 5 shows the values of Γ for PQ10 solutions as a function of bulk concentration at pH 9. Γ is almost the same for solutions ranging in concentration between 5 and 700 ppm. Similar results have been observed for the adsorption of cationic cellulose derivative (JR400) on silica and cationic acrylamide copolymer (AM-MAPTAC) on mica. The concentration-independent adsorption is a characteristic of a strong polyelectrolyte, and once the surface charge of the substrate is slightly compensated, further adsorption is prevented due to electrostatic repulsion. This phenomenon is evident from the zeta potential measurements where a slight positive charge on Al₂O₃ particles at pH 9 is observed after adsorption of PQ10.

**Adsorption of PQ10–SDS Premixed Solutions on Alumina.** After understanding bulk phase behavior of the
complex, now we can analyze its effect on surface adsorption. For the experiments with premixed PQ10–SDS solutions, PQ10 concentration is kept constant at 100 ppm and only the SDS concentration is varied over a series of solutions to analyze the three regimes in the bulk phase diagram. Figure 6 shows the hydrodynamic surface concentration of the premixed complexes on a negatively charged alumina surface at pH 9. The inset in Figure 6 shows adsorption of PQ10 alone at pH 9. Both \( \Gamma \) before and after washing are approximately 1000 ± 240 ng/cm\(^2\), indicating that the PQ10 chains are adsorbed irreversibly on the negatively charged alumina surface. This irreversible adsorption of a polyelectrolyte is energetically favored due to a tremendous gain in entropy upon adsorption by release of counterions from both polyelectrolyte and the surface, as compared to the smaller conformational entropic penalty incurred by polyelectrolyte chains.\(^{47,48}\) For low SDS concentrations (less than CAC), the adsorption of PQ10–SDS complex is quantitatively similar to that of PQ10. This is consistent with the observations from the zeta potential measurements that the charge on the complex is relatively unchanged due to a limited binding of SDS to PQ10 below CAC, and hence the adsorption is typically controlled by polymer–surface interaction as also suggested by Dedinaite and Claesson.\(^{23}\)

From 0.3 mM SDS onward (above CAC), a significant increase in \( \Gamma \) is observed, ranging from approximately 1800 ± 70 ng/cm\(^2\) at 0.3 mM SDS to the maximum value of ~8900 ± 60 ng/cm\(^2\) at 0.8 mM SDS. It is an interesting observation that the onset of increase in \( \Gamma \) coincided with the increase in turbidity after 0.3 mM SDS, and also that the maximum \( \Gamma \) is observed when the turbidity reaches the maximum value at 0.8 mM SDS in Regime 1. We believe that the diminishing cationic charge on PQ10 with increasing SDS binding above CAC, as shown by the zeta potential measurements, leads to increase in the adsorption that is limited by surface charge overcompensation. The highest adsorption takes place from a solution in which the net charge on the PQ10–SDS complex is close to zero. After washing, \( \Gamma \) reduces significantly and attains values statistically similar to the postwash \( \Gamma \) observed from the solutions below CAC. This result suggests that only a certain amount of the complex is strongly attached to the surface from the solutions in Regime 1 and that the loosely bound PQ10–SDS complex gets washed off. We will provide more evidence to support this hypothesis later in this paper. For Regime 2 solutions ranging from 1 to 2 mM SDS, a macroscopic phase separation was observed and no adsorption data were measured.

In Regime 3, when the complexes are negatively charged, a minimal adsorption is observed due to the repulsion between the negatively charged complex and negatively charged alumina surface at pH 9. In contrast to Regime 1, upon washing there is an increase in \( \Gamma \) for solutions with SDS concentration of 3 and 4 mM. This observation can again be understood based on the net complex charge. The washing of excess bound SDS results in charge reversal of the complex, causing adsorption of the cationic complex to be favored. This conjecture is supported by zeta potential measurement results for the PQ10 (100 ppm)/SDS (3 mM) solution. The zeta potential for this complex is \(-17 ± 5\) mV, and after dilution by a factor of 10 (the same as the washing volume in QCMD experiment), the zeta potential reverses to 13 ± 4 mV. The reversal of the complex charge justifies the increased adsorption after washing. A similar observation of increasing adsorption with rinsing was reported by Terada et al.\(^{24}\) for a premixed solution in Regime 3 of JR-400/SDS on a negative silica surface.

A complementary experiment is conducted on positively charged alumina surface at pH 4 to illustrate that the adsorption is controlled by electrostatic interactions. Figure 7 shows the results for \( \Gamma \) for premixed PQ10–SDS solutions as a function of SDS concentration, on the alumina surface at pH 4. In Regime 1, below CAC, small but a nonzero values of \( \Gamma \) (\(-500 ± 70\) ng/cm\(^2\)\) are observed. Surface tension measurements show that even with concentrations as small as 0.05 mM SDS, PQ10–SDS complexes are formed, potentially leading to adsorption on positively charged surfaces, which is otherwise forbidden for PQ10 alone. Washing results in a significant desorption of the adsorbed complex even below CAC, unlike the behavior of corresponding solutions at pH 9. This observation suggests that the binding to the surface is not strong, due to the unfavorable complex charge and surface charge interactions.

From 0.3 mM SDS onward, above CAC, the adsorption increases sharply with reducing cationic charges on the complex (as shown by zeta potential measurements) and a maximum \( \Gamma \) of 7000 ± 200 ng/cm\(^2\) is observed, corresponding to the most turbid solution at 0.8 mM SDS. A large reduction in \( \Gamma \) after washing suggests the removal of loosely attached PQ10–SDS complex chains, an observation similar to that for the corresponding solutions over the negatively charged surface at pH 9. In Regime 3, negatively charged complexes have favorable conditions to adsorb on a positively charged surface, and hence
significantly higher $\Gamma$ ($\sim 4600 \pm 300$ ng/cm$^2$) is seen for a solution with 3 mM SDS, as opposed to the same solution at pH 9. With increasing SDS loading from 3 to 5 mM, the increasing negative charges on the complex result in the lower $\Gamma$ values required for overcompensation of the positive surface charge. $\Gamma$ decreases after washing because of the reversal of the complex charge, as demonstrated earlier, which results in repulsion from the positive surface.

On a positively charged alumina surface, there is a possibility of free SDS adsorbing in competition with the PQ10–SDS complex. When SDS solutions at different concentrations (no PQ10) at pH 4 are flowed over the alumina coated quartz crystal, we observe the Sauerbrey type adsorption, where the responses for harmonics 5, 7, and 9 are overlapped with a low dissipation value ($\leq 1 \times 10^{-3}$). The calculated masses are 10 ng/cm$^2$ for 0.8 mM SDS and $\sim 30$ ng/cm$^2$ for 3 and 4 mM SDS. Assuming a surface coverage with a SDS monolayer, then for all-trans SDS molecules with height of $\sim 1.8$ nm$^{49}$ and density of 1000 kg/m$^3$ the calculated adsorbed mass would be 180 ng/cm$^2$ (product of length of a molecular layer and density). For a more thermodynamically stable SDS bilayer, the mass would be $\sim 360$ ng/cm$^2$. Both of these values are larger than the numbers obtained from the QCMD measurements for SDS. Thus, the SDS adsorption by itself, on the positively charged alumina coated quartz crystal, is minimal and is not sufficient to modify the nature of the surface.

There is no crossing-over of the prewash and postwash curves for $\Gamma$ from Regime 3 solutions over a positive surface. However, such a crossover is observed for Regime 3 solutions on a negative surface. From Regime 3 solutions, the cationic complexes formed in situ after washing are attracted to a negatively charged surface and repelled from a positively charged surface. This observation underlines the importance of electrostatic interactions in governing the adsorption of an unmodified polyelectrolyte–surfactant complex on a hydrophilic charged surface. Moreover, even for the premixed polymer–surfactant solutions, an increase in the adsorption with the commencement of bulk aggregation and the concurrence of the $\Gamma$ maximum with the turbidity maximum, on surfaces with either charge, highlight the correlation between the bulk phase and interfacial adsorption.

**Viscoelastic Properties of Layers.** Using the Voight-based viscoelastic model considering two layers of the adsorbate, the viscoelastic properties of the layers adsorbed on a negatively charged surface are determined after obtaining the best fit for the QCMD data. Viscoelastic analysis for the mass adsorbed on a positively charged surface is not discussed here, because the secondary verification using AFM is practically not possible on a positively charged silica coated silicon wafer, due to its very low isoelectric point. The values of the parameters before and after washing are as shown in Figure 8. “L1” refers to the layer next to the solid surface, and “L2” refers to the layer above L1. The effective viscosity of PQ10 L1 is $1.8 \pm 0.05$ mPa·s, twice the viscosity of water (0.9 mPa·s), whereas the effective viscosity of L2 is similar to that of water. After washing, the effective viscosity of PQ10 L1 does not show much change ($1.6 \pm 0.01$ mPa·s), and the effective viscosity of L2 remains close to that of water. The higher effective viscosity of L1 may suggest the presence of polymeric mass predominantly in L1, whereas L2 appears to be similar to an aqueous layer. For 0.8SDS complex, both L1 and L2 show significantly higher effective viscosities ($1.9 \pm 0.01$ and $1.7 \pm 0.05$ mPa·s, respectively) than that of the bulk water, suggesting presence of a viscoelastic complex in both the layers. With washing, there is little decrease in the L1 effective viscosity (to $1.5 \pm 0.04$ mPa·s), while the L2 effective viscosity drops down to that of water. For 3SDS, the effective viscosities of both L1 and L2 appear comparable to that of water and do not show a significant change after washing. For a complex bearing a net negative charge, without much adsorption on a negative surface, waterlike effective viscosity values are not surprising. Although after washing, an increase in $\Gamma$ is seen, effective viscosity values are observed to be similar to that of water, suggesting a highly hydrated nature of the adsorbed mass.

The bulk viscosity values reported for cationic HEC–SDS complexes were as high as 100 mPa·s, for a comparable molecular weight of the polymer.$^{17}$ In our case, the measured viscosity by QCMD for PQ10–SDS complex, along with the trapped water, is two orders of magnitude lower. This phenomenon could be because of the shear rate dependence of the viscosity of complex non-Newtonian fluids. The viscosity measured by the bulk rheometers (operated at $\leq 10^2$ Hz) could be irrelevant for the QCMD measurements, where the shear wave is generated at a megahertz frequency.$^{57}$ At such a high shear rate, the elastic component of the complex dynamic modulus dominates the viscous component, and hence the apparent viscosity is the same order of magnitude as that of water. Water, being a Newtonian fluid, does not exhibit any shear rate dependence of viscosity, and hence, the viscosity measured by QCMD is the same as that of the bulk viscosity of water.

![Figure 8. Parameters for the two layers considered in Voigt-based viscoelastic modeling: (A) effective viscosity; (B) shear modulus; (C) thickness; before and after washing: “L1” and “L2” refer to layer 1 and layer 2 adsorbed on a negatively charged surface, respectively; “PQ10” refers to PQ10 only; “0.8SDS” refers to PQ10–SDS complex at 0.8 mM SDS corresponding to maximum adsorption; “3SDS” refers to the PQ10–SDS solution in Regime 3 at 3 mM SDS.](image-url)
Figure 8B shows a chart for the effective shear moduli for different layers from all three solutions. The higher the effective shear modulus, the more elastic the nature of the adsorbate. PQ10 L1 shows a high value of effective shear modulus (∼0.84 ± 0.01 MPa), exhibiting a strong vibrational coupling between the elastic mass and the quartz crystal underneath which is also evident from a low dissipation value. PQ10 L2 is mostly waterlike, showing a very low effective shear modulus (∼400 Pa).

After washing, there is an increase in L1μ to 0.91 ± 0.02 MPa, implying a more compact arrangement on the surface. This hypothesis is supported by the thickness values, as shown in Figure 8C. The thickness of a tightly attached layer 1 of PQ10 is 13 ± 0.5 nm which becomes more compact (9 ± 0.3 nm), as indicated by an increase in effective shear modulus and a decrease in thickness, after washing. However, PQ10 L2 does not show any perceivable thickness.

Figure 9. AFM intermittent contact mode topography images of PQ10−0.8SDS complex before-wash trace and retrace scans (A and B); after-wash trace and retrace scans (C and D); PQ10-3SDS after-wash trace and retrace (E and F) (scan range 8 × 8 μm²); and PQ10 only trace and retrace scans (G and H) (scan range 4 × 4 μm²) on silicon wafer with SiO₂ coating. All the images were acquired under aqueous solutions.
For the 0.8SDS complex, effective shear modulus L1μ (0.40 ± 0.03 MPa) is higher than L2μ (0.09 ± 0.001 MPa), suggesting the structural differences among the two layers. After washing, L1μ does not change much (0.37 ± 0.03 MPa), but L2μ changes drastically from 0.09 to 0.007 MPa. The thickness of the L1 of the 0.8SDS complex is determined to be 11 ± 1 nm, very similar to the thickness of PQ10 L1, and after washing reduces to 4 ± 0.3 nm. A highly hydrated and barely elastic L2 of 0.8SDS complex forms a diffused layer, as indicated by the higher thickness of 91 ± 4 nm. After washing, the thickness reduces to 28 ± 4 nm, indicating the removal of hydrated, loosely attached layer. For 3SDS complex, a very low effective shear modulus is observed (ranging between 0.003–0.03 MPa) for both the layers confirming their hydrated and viscous nature. Low thickness values of 3 ± 0.2 nm for L1 and 15 ± 3 nm for L2 correspond to a minimal adsorption on a negative surface. After washing, an observed increase in adsorption is supported by the increased thickness values of 19 ± 0.9 and 71 ± 6 nm for L1 and L2, respectively.

**AFM Imaging.** Topography of the adsorbed PQ10–0.8SDS complex on a SiO2 coated silicon wafer from a solution corresponding to 0.8 mM SDS and the effective shear modulus is observed (Supporting Information Figure S2). The RMS roughness is measured to be 14.9 ± 4.4 nm with a maximum height of 211 ± 15 nm. Skewed adsorbed patches are observed along the direction of the moving tip, with trace and retrace images showing opposite directionality of the patches. Images obtained after washing (Figure 9C and D) also show a heterogeneous surface coverage, but with a reduced RMS surface roughness of 8.5 ± 0.1 nm and a maximum height of 76 ± 8 nm. In this case, the patches have relatively sharper boundaries with no directionality along the scanning tip.

Topography images for the SiO2 coated silicon wafer in PQ10-3SDS solution show no features (Supporting Information Figure S3). Images acquired after washing (Figure 9E and F) show a few patches that are skewed along the direction of the scanning tip and opposite directionality of the trace and retrace images. The RMS roughness is 0.78 nm with the maximum peak height of 34 nm. Figure 9G and H shows trace and retrace images of the adsorbed PQ10 alone which appear uniformly spread over the entire surface. The lower height scale and lack of features in the images suggest a smooth surface with minimal roughness. The RMS roughness is only 0.22 nm, and the maximum peak height is 4 ± 2 nm. Height profiles along the cross sections (Supporting Information Figure S3) show a decrease in the size of the aggregates adsorbed from the PQ10–0.8SDS solution, after washing. Distinct topography is seen in the cross section images from the PQ10–3SDS solution, obtained after washing, for which hardly any features are perceived before wash. A cross section profile for PQ10 alone shows nominal topographic features throughout the scanned length, suggesting a uniform and smooth surface structure.

Agilent Pico Image 6.2 advanced image processing software allowed calculation of the total surface area covered by the adsorbate from the topography images. Additionally, the total volume of the islands are also calculated from the height and the area corresponding to every pixel. The key consideration in this treatment is to select the baseline, with respect to which the topographic roughness is determined. The baseline is adjusted in such a way that, while the darkest or lowest spots in the topography images are omitted, the adsorbate is still perceived as a single island. The baseline is set at the boundary where one coherent island is on the verge of splitting into two or many islands. This protocol makes sure that the baseline is actually set at the boundary between the uncovered spots on silicon wafer and an underlayer, on top of which distinct patches exist. A significant baseline adjustment had to be done for PQ10–0.8SDS complex to satisfy the protocol, whereas as for PQ10 baseline adjustment was minimal, perhaps because of the uniform surface coverage.

Images shown in Supporting Information Figure S4 are provided to represent the analysis involved. Several such images acquired over different locations on the substrate, with different scan areas and over multiple samples were considered for the following analysis. For the PQ10–0.8SDS complex the volume of the adsorbate is 4.2 ± 1.6 μm3 over the net area of 62.8 ± 1.0 μm2 for the scan area of 8 × 8 μm2. To calculate the surface concentration of the adsorbate from the volume analysis of the images, an average density of 1100 kg/m3 is used, obtained from the two layer model best-fit for the QCMD data. The average surface concentration is calculated to be 8500 ± 2400 ng/cm2 for the PQ10–0.8SDS complex. On washing, the adsorbed volume decreases to 1.1 ± 0.3 μm3 spread over an area of 62.6 ± 0.9 μm2. Thus, after washing, there is only a small decrease in the surface area covered by the adsorbed complex. However, the adsorbed volume reduces almost 7.5 times. The corresponding surface concentration after washing is 1800 ± 470 ng/cm2. The adsorbed volume, after washing, from PQ10–3SDS solution is 0.14 μm3 over the area of 63.8 μm2, resulting in the calculated surface concentration of 235 ng/cm2. For PQ10 alone, the adsorbed volume is 0.009 μm3 over the area of 15.8 μm2 (4 × 4 μm2 scan area) and the surface concentration is 60 ng/cm2.

**Physical Model of the Complex Adsorption.** Based on the results presented, we propose a physical model for the adsorbed layers. As depicted in a sketch in Figure 10, PQ10 by itself appears to adsorb on the surface rigidly, with uniform surface coverage, as indicated by the high effective shear modulus and low RMS surface observed in the AFM image. Charged polyelectrolyte chains uniformly covering the surface implies a flat attachment parallel to the surface in a trainlike conformation.47,50 PQ10 chains with higher cationic charge density than PQ10–SDS complex attach irreversibly on the surface and can compensate the negative surface charge with only a few chains present at the interface, as shown by a minimum Γ value. The surface concentration, determined from AFM calculations, is nearly 16 times lower than the QCMD

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Figure 10. Schematic of the structures of adsorbed PQ10 and PQ10–SDS complex on a negatively charged surface. Void spaces on the surface (if any) are not depicted in the sketch.
measurements (60 ± 10 v/s 1000 ± 200 ng/cm²). This is due to the flat attachment of PQ10, resulting in minimal surface roughness; thus, the AFM tip could not perceive the true adsorbed volume. Within our model, PQ10 appears to adsorb as a single, thin uniform layer and layer 2 is mostly water.

For PQ10–0.8SDS complex, two distinct layers with dissimilar viscoelastic properties are seen from our analysis and are depicted in Figure 10. The higher effective shear modulus of layer 1 suggests more elasticlike behavior. Additionally, only a little perturbation in the viscoelastic properties of layer 1, with washing, implies a rigid attachment. Layer 2 appears more viscous, as indicated by a low effective shear modulus. With rinsing, drops in effective viscosity, effective shear modulus, and the thickness of layer 2 indicate removal of a loosely attached fluid which accounts for almost 80% of the Γ. Such a disordered structure for a near neutrally charged complex has been suggested based on absence of any characteristic fringes in the neutron reflectivity data obtained by Yanetz Arjeta et al., wherein typically a fringe has been seen when the sequentially added surfactant to the preadsorbed polymer forms a bilayer or expanded micelle like structures. The viscous nature of such aggregates is also seen from the AFM images. An opposite directionality of patches in the trace and retrace images (Figure 9A and B) suggests movement of the adsorbed structures with the moving tip. These movements imply floppy structures getting deformed by the shearing action of the scanning probe. Images obtained after washing show reduced RMS roughness, with distinct boundaries of the patches, where the trace and retrace images perfectly overlap (Figure 9C and D). Volume and surface area analysis of the images showed that, after washing, there is a significant change in the volume of the adsorbate but not in the surface area. These observations imply a loss of the viscous overlayer that accounts for change in the volume, leaving behind an underlying layer that is thin, strongly attached to the surface, and hence conserves the covered area. A reduced cationic charge density of the PQ10–SDS complex, although the initial attachment to the bare surface is relatively stiff and compact, may not be sufficient to compensate the negative surface charges. Also, the reduced solubility of polymer–surfactant aggregates in bulk may facilitate surface deposition. Hence, adsorption continues on top of layer 1, leading to the formation of a multilayer adsorbate by virtue of interchain associations, corresponding to a higher Γ.

For a hydrated, negatively charged PQ10–3SDS complex, a minimal Γ is seen with chains probably extended into the bulk away from the surface due to the electrostatic repulsions. A very low effective shear modulus and a water like viscosity suggest hindered surface attachment. This observation is reflected by absence of any topographic features in the AFM images obtained before washing. After washing (dilution), the reversal of the complex charge, likely due to the removal of the excess bound surfactants to satisfy the binding isotherm, results in a rise in adsorption on the negative surface. Low density and low effective elastic modulus of both layers imply the viscous nature of both layers adsorbed after dilution. An observation of floppy structures, showing opposite directionality in trace and retrace images, supports our hypothesis of a viscous and highly hydrated nature of the mass adsorbed after washing. This observation is of particular interest to technological applications where in situ dilutions of stable formulations would result in adsorption of a viscous, floppy layer, perhaps beneficial for surface lubrication. AFM measures only the topographic differences in height and is not sensitive to the amount of water in the adsorbed layer.

Therefore, the hydrodynamic surface concentration calculated using AFM is not accurate and these values for uniformly smooth adsorbed layer are expected to be different from the QCMD results.

It should be noted that, for the PQ10-0.8SDS complex, the calculated surface concentrations from AFM image analysis, both before and after wash (8500 ± 2400 and 1800 ± 470 ng/cm², respectively), are quite comparable to that obtained from the QCMD analysis (8900 ± 60 and 2000 ± 140 ng/cm², respectively). The QCMD analysis involved in this work assumes the presence of a homogeneous surface layer. The AFM measurements clearly show that this condition is not correct and that the second layer is patchy. Therefore, the agreement between these two techniques suggests that the calculation of surface coverage by QCMD analysis accurately captures the adsorption of the second patchy layer. However, this observation needs to be confirmed with a better QCMD model that accounts for heterogeneous surface layers.

SUMMARY

In our investigation, we have analyzed the adsorption of a cationic polysaccharide, PQ10 and the premixed solutions of PQ10–SDS on an amphoteric aluminum oxide surface using QCMD. The extent of adsorption of PQ10 on an amphoteric alumina surface is strongly dependent on the surface charge density since the adsorption is limited by the surface charge overcompensation. For premixed polymer–surfactant mixtures, a close correlation between the bulk phase behavior and the surface adsorption is seen. The maximum adsorption occurs before the macroscopic phase separation regardless of the charge on the surface. Enhanced adsorption on dilution from the redissolved complexes in Regime 3 solutions is observed on the negatively charged surface, but not on the positively charged surface. This result confirms that the electrostatic interactions dominate the adsorption of an unmodified polymer/surfactant complex on a charged hydrophilic surface. Based on the analysis of QCMD data and the AFM measurements, fundamental differences are found in the structure and in the viscoelastic properties of the adsorbed layers for PQ10 versus the PQ10–SDS complex. PQ10 adsorbs rigidly as a uniform layer over the surface with a flat conformation. The PQ10–SDS complex shows orthogonal heterogeneity in the adsorbate, where the layer next to the surface is relatively compact and rigidly attached, upon which there is a loosely adsorbed, diffuse overlaver extended away from the surface. The layer adsorbed after dilution of the redissolved solution appears viscous and highly hydrated. Such conformational differences at the surface will have important implications toward friction and lubrication, which will be topic for future studies.

ASSOCIATED CONTENT

Supporting Information

Density values used in calculation of the hydrodynamic surface excess, surface tension plots for polymer–surfactant mixtures, AFM topography images, height profiles along line sections, and volume analysis from the topography images. This material is available free of charge via the Internet at http://pubs.acs.org.

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