Surface Deposition and Phase Behavior of Oppositely Charged Polyion−Surfactant Ion Complexes. Delivery of Silicone Oil Emulsions to Hydrophobic and Hydrophilic Surfaces

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Ⓢ Supporting Information

ABSTRACT: The adsorption from mixed polyelectrolyte− surfactant solutions at hydrophobized silica surfaces was investigated by in situ null-ellipsometry, and compared to similar measurements for hydrophilic silica surfaces. Three synthetic cationic copolymers of varying hydrophobicity and one cationic hydroxyethyl cellulose were compared in mixtures with the anionic surfactant sodium dodecylsulfate (SDS) in the absence or presence of a dilute silicone oil emulsion. The adsorption behavior was mapped while stepwise increasing the concentration of SDS to a polyelectrolyte solution of constant concentration. The effect on the deposition of dilution of the bulk solution in contact with the surface was also investigated by gradual replacement of the bulk solution with 1 mM aqueous NaCl. An adsorbed layer remained after complete exchange of the polyelectrolyte/surfactant solution for aqueous NaCl. In most cases, there was a codeposition of silicone oil droplets, if such droplets were present in the formulation before dilution. The overall features of the deposition were similar at hydrophobic and hydrophilic surfaces, but there were also notable differences. SDS molecules adsorbed selectively at the hydrophobized silica surface, but not at the hydrophilic silica, which influenced the coadsorption of the cationic polymers. The largest amount of deposited material after dilution was found for hydrophilic silica and for the least-hydrophobic cationic polymers. For the least-hydrophobic polyions, no significant codeposition of silicone oil was detected at hydrophobized silica after dilution if the initial SDS concentration was high.
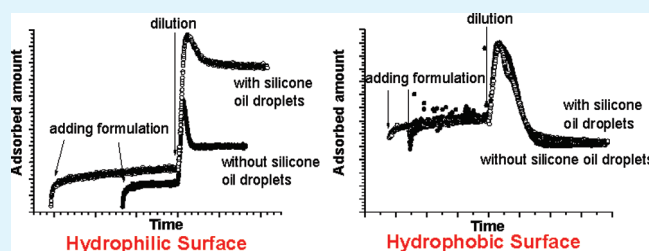
KEYWORDS: oil emulsion, surfactant−polyion complexes, adsorption, interfaces, phase behavior

INTRODUCTION

Aqueous mixtures of oppositely charged polyelectrolytes and surfactants are widely studied because they provide easy and versatile ways to control the properties of solutions and interfaces owing to their association behavior.[1−7] On progressively increasing the concentration of ionic surfactant added to a solution of an oppositely charged polyelectrolyte, surfactant micelles start to form at the polyions at the so-called critical aggregation concentration (cac), which is usually several decades lower than the critical micellar concentration (cmc) of the surfactant alone. The cac and the surfactant aggregation number are affected by the polyelectrolyte concentration and by the charge density, the hydrophobicity, and the flexibility of the polyion chain.[8−12] This strong attraction between the oppositely charged polyions and surfactant aggregates typically leads to an associative phase separation where a phase concentrated in the polyions and surfactant ions separates out from a dilute solution.[13] If the polyion contains hydrophobic functionalities, so that there is an

additional hydrophobic attraction between the polyion chain and the surfactant aggregates, an additional cooperative binding of excess micelles to the polyion can occur near the surfactant cmc, leading eventually to a redissolution of overcharged polyion−surfactant ion complexes.[14,15]

The adsorption of polyion−surfactant ion complexes at solid−liquid interfaces is of special importance for many industrial products, such as detergents and personal care products.[16,17] In order to further modify the properties of the surfaces, one can use the associating mixture as a deposition vector for some other component added to the formulation.[18] In a conditioning hair shampoo, for example, a cationic polyelectrolyte is typically mixed with the anionic surfactant. To enhance the softness, and/or to repair hairs, a silicone emulsion is often added and the
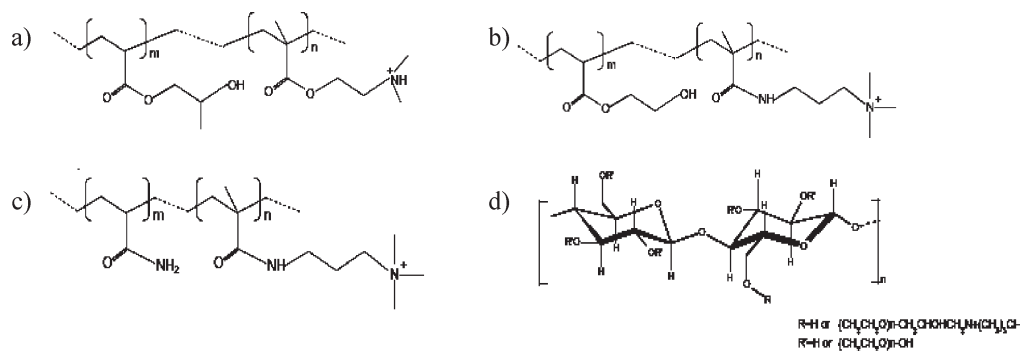
Figure 1. Schematic pictures of the repeating units of (a) HPA/DMAM, (b) HEA/MAPTAC, (c) AA/MAPTAC, and (d) cat-HEC.

silicone droplets should then be codeposited with the polyion—surfactant ion complexes. In typical shampoo formulations, the polyion—surfactant ion complexes are "redissolved" by a large excess of bound surfactant in the formulation. As the shampoo is diluted during the rinsing stage, surfactant molecules leave the complex, which loses its excess charge, and eventually a coacervate is formed.

Research on the adsorption of polyelectrolyte/surfactant complexes at solid surfaces has intensified during the last 20 years, involving a number of different laboratories and methods.[4,19−29] In a series of joint studies from our laboratories, we are currently systematically investigating surface deposition from aqueous mixtures of oppositely charged polymers and surfactants, where we vary both the composition of the aqueous mixtures and the protocol to achive the surface deposion. The studies published so far have involved cationic polysaccharide derivatives,[30,31] or synthetic copolymers of cationic monomers with neutral monomers of varying hydrophobicity,[14] depositing as complexes with anionic surfactants on hydrophilic silica surfaces. The stoichiometries of the adsorbed polyion—surfactant ion complexes have been varied by two different protocols. Either surfactant was added progressively to a solution initially containing only the polyelectrolyte, or a dilution experiment was performed to simulate the deposition-by-rinsing protocol used in applications. In one of the studies, droplets of emulsified silicone oil were included, and the codeposition of the droplets at the silica surface was studied.[31] These previous studies have invariably demonstrated a strong correlation between the conditions for phase separation in the bulk, as evidenced by bulk turbidity, and conditions for an enhanced adsorption on hydrophilic silica, when the free surfactant concentration was varied in dilute solutions of the polyelectrolyte. Moreover, both the cac and the surfactant concentration required for redissolution of the complexes varied strongly with the hydrophobicity of the cationic polymer. With an increasing hydrophobic character of the polyion, both the cac and the ultimate redissolution of the polyion—surfactant ion complex occurred at lower surfactant concentrations.

The aim of the present study is to extend our previous studies to include hydrophobic surfaces. The key questions addressed here are: How do hydrophobic interactions affect the delivery of polyion—surfactant ion complexes alone, and the codelivery of silicone oil emulsion droplets, to surfaces? Do we find substrate specificity/selectivity in such a deposition, and does this depend on the choice of polyion? To that end, we have here studied four cationic polymers: three synthetics, selected on the basis of previous experiments to represent a range of hydrophobicities,

Table 1. Polyelectrolyte Characteristics[14,30]

polyelectrolyte	M_w (kg/mol)	polydispersity	charge content (meq/g)
HPA/DMAM	525	2.2	1.3
HEA/MAPTAC	935	5.9	1.1
AA/MAPTAC	699	8.8	1.1
cat-HEC	1000	n/a	0.6

and a well-studied polysaccharide derivative. Studies have been performed by in situ null ellipsometry to understand and follow with fine kinetic records the deposition and the behavior of mixtures of the cationic polyelectrolytes with the anionic surfactant SDS on both hydrophilic and hydrophobized silica surfaces, and to investigate the delivery of a silicone emulsion by the mixtures on the surfaces. Results for systems with and without emulsion and on different surfaces are compared in detail.

■ MATERIALS AND METHODS

Materials. Three cationic copolymer samples of varying hydrophobicity, synthesized by Procter & Gamble, were selected from a previous study[14] and used without further purification, namely, hydroxypropylacrylate/dimethylaminoethyl methacrylate (HPA/DMAM), hydroxyethyl acrylate/methacrylamidopropyl trimethylammonium chloride (HEA/MAPTAC) and acrylamide/methacrylamidopropyl trimethylammonium chloride (AA/MAPTAC). Hydroxyethylcellulose UCARE LR-30 M grafted with hydroxyethyl trimethylammonium chloride (cat-HEC LR30M) was supplied by Amerchol Corporation and purified as described elsewhere.[30]

Schematic pictures of the repeating units are shown in Figure 1 and molecular weights, polydispersities and charge densities of the polyelectrolytes are presented in Table 1. The polyelectrolytes were dissolved in 1 mM NaCl at a concentration of 1000 ppm.

The surfactant sodium dodecylsulfate (SDS) was purchased from BDH and used without further purification. Its *cmc* in water is 8.1 mM.[32] Sodium chloride (Supra pur, 99.99) was from Merck. A silicone oil emulsion (with the detailed composition shown in the Supporting Information) was provided by Dow Corning. The silicone oil droplets are stabilized by anionic and nonionic surfactants and have a hydrodynamic radius of 18 nm as determined by dynamic light scattering.[31] All solutions were prepared in degassed Milli-Q water (Millipore).

In situ Null Ellipsometry. This technique is based on measurements of changes in the state of polarization when polarized light is reflected against a surface, given by the relative change in amplitude, Ψ, and phase shift, Δ. The measured parameters, Ψ and Δ, can be used to calculate the thickness and the refractive index of a layer formed on a macroscopic surface. From these two parameters the adsorbed amount

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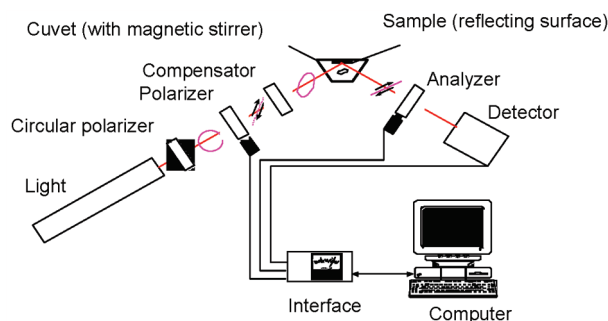
Figure 2. Schematic representation of the automated Rudolph Research thin-film null ellipsometer type 43603−200E. The method is based on measurement of the changes in the state of polarization of light. The polarized light from the laser is depolarized with a circular polarizer. After the polarizer, the emerging linearly polarized light is transformed into elliptically polarized light when passing through the compensator, which is a quarter wave plate. The ellipticity can be varied by rotating the polarizer. As the reflection against the surface of the sample also changes the ellipticity of the light, the polarizer can be rotated in such a way that the light after reflection again is linearly polarized. The relative rotation of this light is measured by using another polarizer, the analyzer, which is rotated until a minima in light intensity as measured by the detector.

of a material can be calculated. In this study we used an automated Rudolph Research thin-film null ellipsometer type 43603−200E, where the light first passes a polarizer followed by a quarter wave plate (compensator) and then is reflected against the sample. Finally, after passing another polarizer (analyzer), the light intensity is monitored with a detector as shown in Figure 2. A xenon arc lamp was used as the light source and a filter for a wavelength of 401.5 nm was placed just before the detector. The measurements were performed at an angle of incidence of 68°, using a trapezoid glass cuvette with a sample volume of about 5 mL. The solution in the cuvette was agitated by means of a magnetic stirrer at a speed of 300 rpm. Continuous exchange of the bulk solution (dilution or "rinse" experiment) was achieved by means of two Teflon tubes, which were inserted into the cuvette and connected to a multichannel peristaltic pump set at a flow rate of 5 mL/min. The inlet to the cuvette was connected to a container with salt or SDS solution and the outlet from the cuvette was connected to the drain. All experiments were performed at 25 ± 0.1 °C, the temperature being regulated by a thermostatted bath. The setup allows measurements with a time resolution of 2−3 s.

To accurately determine the refractive index and the thickness of the adsorbed film, we have to determine the optical characteristics of the substrate in two media, since the substrate is composed bulk silicone of complex refractive index $N_2 = n_2 − jk_2$ and a silicon oxide, SiO_2, layer (refractive index n_1, thickness d_1). We therefore performed measurements in air and in 1 mM NaCl to characterize the substrate. Typical values are $n_2 = 5.50 ± 0.01$, $k_2 = −0.35 ± 0.03$, $d_1 = 300 ± 20$ Å, $n_1 = 1.480 ± 0.005$, but may vary slightly from batch to batch. This substrate characterization procedure is fully described in reference.[33] Four-zone measurements were used at the beginning of each experiment to correct for imperfections of the optical components.[34]

The effect of surfactant concentration on the adsorption from polyelectrolyte/surfactant mixtures was mapped by first injecting 0.5 mL of the polyelectrolyte solution inside the ellipsometry cuvette initially filled with 4.5 mL of the 1 mM NaCl solution to get a final polyelectrolyte concentration of 100 ppm. The ellipsometric angles were recorded until steady state had been reached. Known amounts of SDS solutions (0.1 or 1 M) were then sequentially added into the cuvette and the system was equilibrated until steady state values of ψ and Δ were recorded before the next addition of SDS. In the experiments where the

effect of diluting the initial polyelectrolyte/surfactant mixtures (with or without 400 ppm of the silicone emulsion) was studied, the appropriate mixed solution was equilibrated for at least one day under agitation with a magnetic stirrer before it was added to the sample cell. After steady state was reached, the exchange of the bulk solution for pure salt or SDS solution was initiated by starting the peristaltic pump.

The data were analyzed according to a four-layer optical model: silicon, silicon oxide, adsorbed layer with a refractive index n_f and a thickness d_f, and the bulk solution, assuming isotropic media and planar interfaces. The numerical procedure is described in detail in ref 33. The adsorbed amount is calculated according to the so-called Feijter's formula[34]

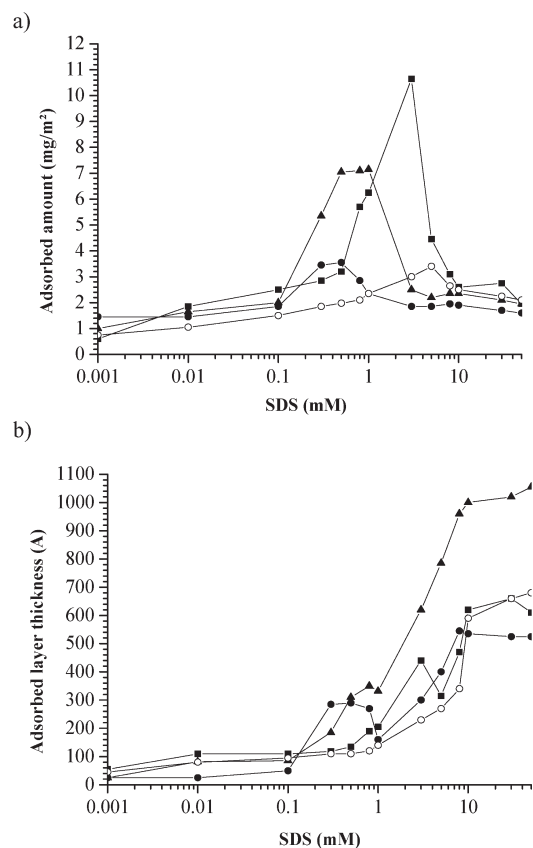$$\Gamma = \frac{d_f(n_f − n_0)}{dn/dc} \tag{1}$$

Here n_0 is the refractive index of the bulk solution and dn/dc is the refractive index increment of the adsorbing substance, where a value of 0.15 was used as described in previous studies[14,20,28−31] for both the pure polyelectrolytes and the mixed layer with surfactant.

All experiments were repeated at least twice, and the deviation between replicates was within 10%.

Surface Preparation. Silicon wafers were provided by Stefan Klintström (Department of Chemistry, IFM, Linköping University, Sweden). The silicon wafers (p-type, boron-doped, resistivity 1−20 Ω.cm) were thermally oxidized in an oxygen atmosphere at 920 °C for about 1 h, followed by annealing and cooling in an argon flow. This procedure yields a SiO_2 layer of about 300 Å thickness. The wafers, which where cut into 12 × 25 mm pieces, were cleaned first in a mixture of 25% NH_4OH (pro analysis, Merck), 30% H_2O_2 (pro analysis, Merck), and water (1/1/5, by volume) at 80 °C for 5 min, and then with 32% HCl (pro analysis, Merck), 30% H_2O_2 and water (1/1/5, by volume) at 80 °C for 10 min, followed by extensive rinsing with water and ethanol. The wafers were stored in ethanol. Before use, they were rinsed with ethanol, dried under nitrogen flow, and cleaned in a plasma cleaner (Harrick Scientific Corp., model PDC-3XG) at a pressure of 0.0001 mbar for 5 min. The surface charge density of silica at pH 6.5 in 1 mM electrolyte solution (KCl) has been determined to ca. −0.3 $\mu C/cm^2$.[35] This corresponds to ca. 3 × $10^{−9}$ meq anionic charges/cm^2, or a surface area of 5000 $Å^2$/charge. Hydrophobic surfaces were obtained by silanization under vacuum of plasma cleaned hydrophilic surfaces. The surfaces were placed in a 2 L desiccator connected to a vacuum pump. About 2 mL of dimethyloctylchlorosilane (purum, Flucka) was added inside the desiccator and silanization was performed overnight. Cleaning of the surfaces was carried out by 3 cycles of rinsing first with tetrahydrofuran and then with ethanol, with 20 min of sonication between each rinsing step. The hydrophobicity was checked before use and the water contact angle was 90 ± 1°. The wafers were stored in ethanol and dried under nitrogen flow before use. To avoid gas bubbles on the hydrophobic surface, ethanol was pumped through the ellipsometry cuvette before the aqueous solution was added.

■ RESULTS

Adsorption from Polyelectrolyte/Surfactant Mixtures to Hydrophobic Silica Surfaces. The adsorption behavior of a particular polyion−surfactant ion combination at a selected surface can be conveniently mapped by following the adsorbed amount (and thickness) while sequentially increasing the surfactant concentration in a polyelectrolyte solution of constant concentration (titration experiment).[14,28−31] The results of such experiments for SDS complexes of the various polyions of this study adsorbing to hydrophobized silica are displayed in panels a and b in Figure 3, showing adsorbed amount and layer thickness,

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a)

b)

Figure 3. (a) Adsorbed amount and (b) layer thickness on hydrophobic silica surfaces as a function of the bulk SDS concentration as SDS is sequentially added to a 100 ppm solution of HPA/DMAM (filled circles), HEA/MAPTAC (filled triangles), AA/MAPTAC (filled squares), or cat-HEC (open circles).

Table 2. Steady-state adsorption at hydrophobic surfaces from 100 ppm solutions of the polyelectrolytes in 1 mM NaCl

polymer	Γ (mg/m^2)	d (Å)
HPA/DMAM	1.45	25
HEA/MAPTAC	1.00	25
AA/MAPTAC	0.60	55
Cat-HEC LR30M	0.75	45

could be identified where the adsorbed amount began to increase sharply with the concentration to finally reach Γ_{max}. We here refer to the latter SDS concentration, which is related to the critical association concentration (cac) for SDS at the polyion, as the peak onset concentration, c_{onset}. For the synthetic polyions, the values of c_{onset} and c_{max} were, within experimental uncertainty, the same for hydrophobized and hydrophilic silica (Table 3), and both concentrations decreased with an increasing hydrophobicity of the synthetic polyion. For cat-HEC, the situation was slightly different, as we discuss in more detail below. In our previous works the bulk solution turbidity, monitoring bulk phase separation, was also recorded for the various systems at increasing SDS concentration.[14,30] For each system, a peak in turbidity was recorded on such a titration, and the characteristic surfactant concentrations c_{onset} and c_{max} for the turbidity peak were found to be the same, or nearly the same, as for the surface adsorption peak. That is, the surface adsorption behavior mirrors the bulk phase separation behavior.

The thickness of the adsorbed layer also increased with added SDS above c_{onset} in a similar fashion on hydrophobized silica (Figure 3) as was previously found on hydrophilic silica; this increase is due to the swelling of the adsorbed layer as its net charge increases due to an excess of polyion-bound surfactant micelles.[14,30] A local maximum in thickness appeared at the peak in adsorption for some systems, and the layer thickness continued to increase with increasing SDS concentration to reach a plateau above ca. 10 mM SDS. This is past the maximum in adsorbed amount suggesting a highly swollen layer at high SDS concentrations.

A closer comparison reveals, however, some significant differences in the results for hydophobized and hydrophilic silica surfaces. Even below c_{onset} a significant increase of the adsorbed amount (by 0.5−1 mg/m^2) with increasing SDS concentration was observed for all polyions at hydrophobized silica (Figure 3a). Such an increase below c_{onset} was absent at hydrophilic silica.[14,30] For cat-HEC, we found in the present study a very gradual increase of the adsorbed amount, with no distinct c_{onset}, all the way up to c_{max} = 5 mM at hydrophobized silica (Figure 3a), while a distinct onset at c_{onset} = 0.5 mM and a maximum at c_{max} = 2 mM was seen on hydrophilic silica.[30] There were also significant differences in the adsorbed amounts, see Table 3. The synthetic polyions all gave similar maximum adsorbed amounts at hydrophilic silica, but showed large differences at hydrophobized silica, with the maximum adsorbed amount increasing in the order HPA/DMAM < HE/MAPTAC < AA/MAPTAC. Of the investigated polyions, cat-HEC gave the lowest adsorbed amount at both surfaces.

Surface Deposition and Codeposition of Emulsified Silicone Oil by Dilution. Previous experiments on hydrophilic silica have shown that it is possible to obtain a surface deposition of polyion-surfactant ion complexes by diluting a polyelectrolyte/surfactant mixture in contact with the surface.[28,31] Such a strategy is employed extensively in hair-care and fabric-care applications.

respectively. Results for the same systems adsorbing at hydrophilic silica surfaces have been presented in previous work.[14,30]

The properties of the adsorbed layer of the polyions without SDS are summarized in Table 2. The observed increasing adsorbed amount of the polyions alone in the order AA/MAPTAC < HEA/MAPTAC < HPA/DMAM for the synthetic polyions is in agreement with previous measurements for the same polyions,[14] and corroborates the previous conclusions that an increasing adsorbed amount on a hydrophobic surface reflects an increasing hydrophobicity in a series of otherwise comparable polyions. Quantitatively, the present investigation gave lower adsorbed amounts, compared to ref 14 for HEA/MAPTAC and HPA/DMAM, possibly due to different batches of hydrophobized silica. The adsorbed amount for cat-HEC agrees well with previous results.[30]

The sequential addition of SDS to a polyelectrolyte of constant concentration gave similar effects on adsorbed amount at hydrophobized silica (Figure 3a,b) as those previously observed for hydrophilic silica.[14,30] A pronounced peak in the adsorbed amount as a function of SDS concentration was seen in all cases, but the position and magnitude of the peak varied for the different polyions; see Table 3, where we have included the corresponding data for hydrophilic silica from the previous investigations. The adsorbed amount and the concentration of SDS at the peak maximum are here referred to as Γ_{max} and c_{max}, respectively. In most cases, a characteristic concentration of SDS

Table 3. Characteristics of the Peaks in Adsorbed Amounts (see text) for Various Polyelectrolyte/SDS Combinations at Hydrophobic and Hydrophilic Surfaces. Values for Hydrophilic Surfaces Are Taken from Ref 14 and 30

| polyelectrolyte	hydrophobic			hydrophilic		
	c_{onset} (mM)	c_{max} (mM)	Γ_{max} (mg/m²)	c_h (mM)	c_{max} (mM)	Γ_{max} (mg/m²)
HPA/DMAM	0.1	0.5	3.5	<0.1	0.5	5.7
HEA/MAPTAC	0.1	0.5–1	7.2	0.1	0.8	5
AA/MAPTAC	0.5	3	10.6	0.5	3	6.2
cat-HEC		5	3.4	0.5	2	1.8

Table 4. Initial SDS Concentrations (mM) in the Experiments Where the Bulk Solution Was Diluted with 1 mM Aqueous NaCl

polyelectrolyte	c_{max}	c_{rediss}	far above c_{rediss}
HPA/DMAM	0.5	1	
HEA/MAPTAC	0.8	3	
AA/MAPTAC	3	10	
cat-HEC	5	10	20

Initially a one-phase formulation at high surfactant concentrations is applied and this solution is then diluted. The effect is basically as predicted when moving from high to low surfactant concentrations in the surfactant titration map in, e.g. Figure 3, by dilution with a low ionic strength salt solution (or rinsing with tap water in applications). Generally, the deposition after dilution is observed to decrease with increasing initial surfactant concentration, provided that the initial surfactant concentration is above c_{max}.[14,31] Ellipsometry experiments have further shown that the same dilution strategy can be used to co-deposit silicone oil droplets from an emulsion included in formulations of cat-guar or cat-HEC mixed with SDS, on a hydrophilic silica surface.[31]

In the present study we have compared the deposition with and without silicone oil emulsion, at hydrophobic and hydrophobized silica surfaces, for the various polyions complexed with SDS. For each polyion, we have chosen two initial SDS concentrations. One was equal to c_{max}, and the second SDS concentration was selected to be situated just above the phase separation zone, as inferred from surface adsorption and bulk turbidity data from sequential addition of SDS to a polyelectrolyte solution in the present work and in ref 14. We will refer to the latter SDS concentration as the redissolution concentration, c_{rediss}. For cat-HEC, one additional initial SDS concentration was included, significantly above c_{rediss}. Table 4 summarizes the starting surfactant concentrations chosen in this study for the various polyions. The evolution of an adsorbed layer during dilution of the mixed polyelectrolyte/surfactant bulk solution depended strongly on the surfactant concentration, as described in the following.

Monotonically Decreasing Deposition When Diluting from c_{max}. Figure 4 displays typical features for formulations where the surfactant concentration before dilution was at c_{max}. Specifically, the figure shows the time-dependent adsorption at a hydrophobic surface for an emulsion-free formulation of AA/MAPTAC in 3 mM SDS. Immediately after adding the formulation to the cuvette, there was a very rapid increase in adsorbed amount, followed by a more gradual build-up over a significant time period. The relative variation in thickness of the adsorbed layer during the slow build-up phase was smaller than the variation in
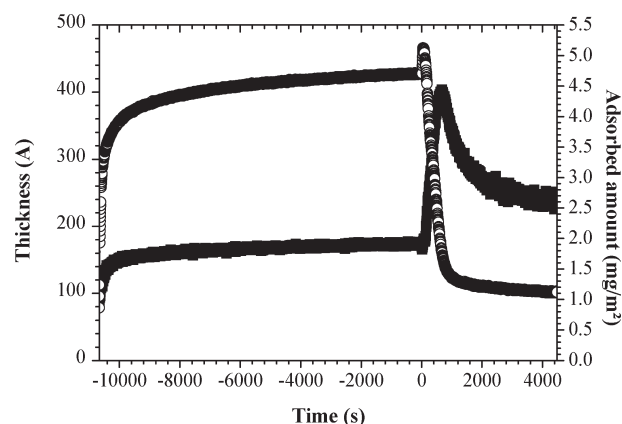
Figure 4. Evolution of the adsorbed amount (open circles) and thickness (filled squares) of the layer adsorbed on hydrophobized silica from 100 ppm AA/MAPTAC dissolved in 3 mM SDS, 1 mM NaCl during dilution of the bulk solution. Dilution with 1 mM NaCl started at $t = 0$.

the adsorbed amount. For some systems, a constant thickness was reached immediately after the initial steep increase.

Directly after the start of the dilution of the bulk solution, the adsorbed layer of polyion-surfactant ion complexes swelled rapidly, with a concomitant sharp decrease in adsorbed amount. While the adsorbed amount decreased rapidly and monotonically on rinsing (sometimes a small overshoot was seen), a more-or-less pronounced maximum in thickness would thus appear, followed by a slow compacting of the layer with time. The adsorbed amount leveled off more or less rapidly after the rinsing, but the compacting of the layer had not leveled off completely within the time of the experiment (2000–5000 s after rinsing). Thus, on dilution of the solution, material rapidly left the adsorbed layer, and during this process the layer first swelled rapidly and then contracted slowly. These features agree with limited data from dilution experiments at comparable initial conditions in a previous investigation.[14] Cat-HEC did not behave exactly according to the scenario exemplified in Figure 4. For cat-HEC the change in thickness typically would parallel the adsorbed amount when the bulk solution was diluted, that is, there was a gradual build-up of both adsorbed amount and thickness on injecting the formulation at c_{max} (5 mM) followed by a more-or-less monotonic decrease.

Different Patterns of Deposition Are Seen When Diluting from c_{rediss} or above. For systems with initial surfactant concentrations at or above c_{rediss}, a transient peak in adsorbed amount was generally observed on dilution of the bulk solution. This feature was also observed in previous investigations, where

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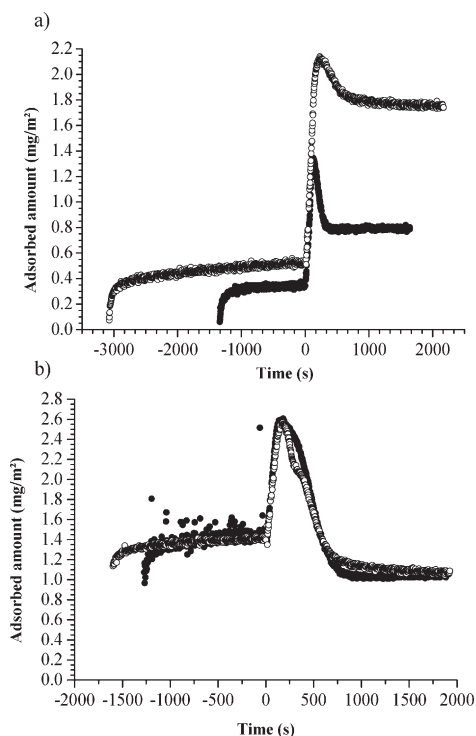
Figure 5. Effect of diluting a formulation of 100 ppm AA/MAPTAC,10 mM of SDS and 1 mM NaCl, without (filled circles) or with (open circles) 400 ppm silicone emulsion on the deposition onto (a) hydrophilic and (b) hydrophobized silica. Time zero corresponds to the beginning of the dilution process with 1 mM NaCl at a rate of 5 mL/min, for a cuvette volume of 5 mL and a stirring rate of 300 rpm.


Figure 6. Effect of diluting a formulation of 100 ppm cat-HEC, 20 mM SDS and 1 mM NaCl, without (filled circles) and with (open circles) 400 ppm silicone emulsion on the adsorption at a) hydrophilic and b) hydrophobized silica. Time zero corresponds to the beginning of dilution with 1 mM NaCl at a rate of 5 mL/min, for a cuvette volume of 5 mL and a stirring rate of 300 rpm.

it was also found that the magnitude of the transient peak decreased if the surfactant concentration was increased above c_{rediss}.[14,31] Figure 5 shows examples of pronounced transient peaks for AA/MAPTAC in 10 mM SDS, in the presence or absence of 400 ppm silicone emulsion, both on hydrophilic and hydrophobized silica surfaces. The results in Figure 5 highlight a new feature, compared to previous investigations, namely, that the dilution-induced deposition may be quite different on hydrophilic and hydrophobic surfaces. On the hydrophilic surface, there was initially only a low adsorbed amount (0.3–0.5 mg/m^2), with a net increase resulting from the dilution of the bulk solution in contact with the surface. There was a much higher final adsorbed amount after dilution from the formulation with silicone oil emulsion (1.8 mg/m^2) than from the one without (0.8 mg/m^2). On hydrophobized silica, however, there was no difference in adsorbed amount, neither before nor after diluting the formulations with or without emulsion. Moreover, in both cases, there was a net decrease in adsorbed amount on rinsing, from 1.4 mg/m^2 to 1.1 mg/m^2. Interestingly, however, a large transient adsorption peak appeared on rinsing from these mixtures, reaching as high as 2.6 mg/m^2. The fine structures of the transient peaks indicate that there was a difference in the transient deposition from mixtures with or without emulsion. This transient difference was even more evident in the thicknesses of the adsorbed layers (not shown).

Figure 6 shows the results for cat-HEC with SDS when the solution was diluted from a surfactant concentration of 20 mM, far above c_{rediss}. Here, there was no initial adsorption to hydrophilic silica, but a thin adsorbed layer developed immediately on
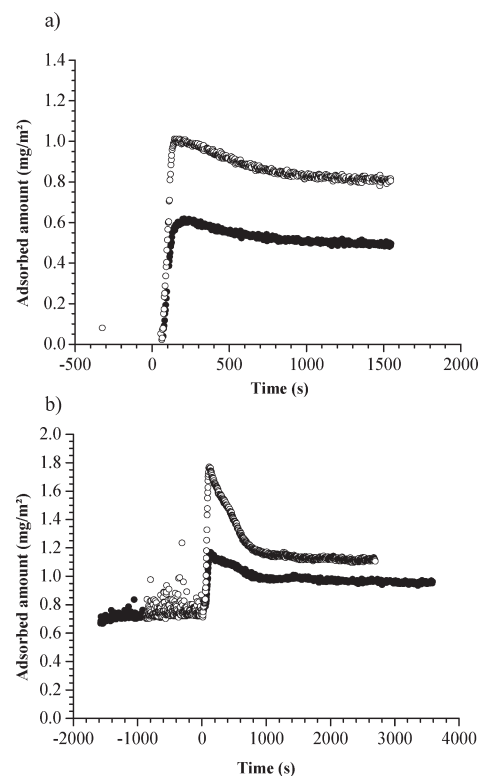
hydrophobized silica. Diluting the bulk solution led to a net increase in deposition after a transient maximum that was quite weak except for the mixture including emulsion at hydrophobized silica. As in Figure 5, the net increase in adsorbed amount upon further dilution, from the mixture including emulsion was significant on hydrophilic silica, but insignificant on hydrophobized silica.

Deposition Induced by Diluting the Bulk Solution Can Be Controlled by Surface Properties and Formulation Composition. The effect on deposition when diluting the formulation (data corresponding to those shown in Figure 4) are shown in detail for all investigated mixtures in the Supporting Information. To obtain an overview of the quantitative variations and trends in these experiments, we have summarized data on adsorbed amounts immediately before diluting the bulk solution and at steady state after dilution in Figures 7 and 8, respectively. Each panel shows results for one polyion, at two or more initial surfactant concentrations, comparing hydrophilic and hydrophobic surfaces with and without added emulsion droplets. The observed considerable variation in adsorbed amount is interesting from the point of view of applications, and it must ultimately reflect the molecular interactions responsible for deposition. We will now walk through this multidimensional parameter set by considering one parameter at a time.

Increasing the Initial Surfactant Concentration above c_{max} Typically Resulted in a Decreasing Adsorbed Amount. We note that the variation in adsorbed amount with increasing initial surfactant concentration was much larger before diluting the bulk
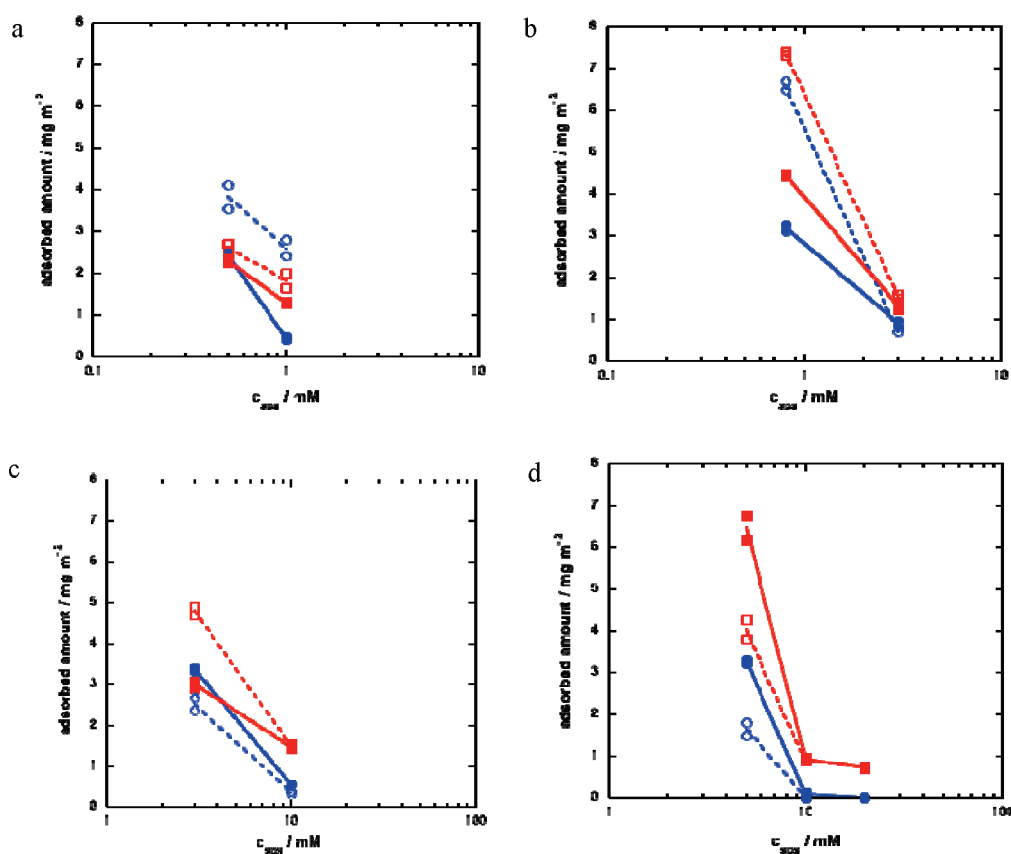
Figure 7. Summary of adsorbed amounts from mixed polyelectrolyte/SDS solutions before dilution (see text) for (a) HPA/DMAM, (b) HEA/MAPTAC, (c) AA/MAPTAC, and (d) catHEC. Conditions were 100 ppm polyelectrolyte, 400 ppm emulsion (when present), SDS as indicated. Empty symbols = without emulsion, filled symbols = with emulsion. Hydrophobic surfaces are indicated by red color and square symbols, and hydrophobized surfaces by blue color and circles. Lines (guides to the eye) connect average values for formulations with (solid) or w/o (dashed) emulsion.

solution ($0-7.5$ mg/m^2; see Figure 7) than after ($0.5-3$ mg/m^2; see Figure 8). This might be expected since the bulk solution conditions vary greatly before dilution whereas, ultimately as the bulk solution is diluted, all surfaces end up contacting a bulk solution of essentially 1 mM NaCl. Interestingly, there was always a deposited layer after diluting the bulk solution, even in the cases (hydrophilic silica, high SDS concentrations) where there was no adsorption before dilution.

Significant differences in adsorbed amount at hydrophobic and hydrophilic surfaces. In most cases, the addition of the formulation led to a larger adsorption on hydrophobic surfaces. The only case where there was significantly more adsorption on hydrophilic than on hydrophobized silica was for HPA/DMAM formulations without added emulsion (Figure 7a). At the highest investigated surfactant concentrations, 10 and 20 mM, there was little or no adsorption at all on hydrophilic silica before dilution, see panels c and d in Figure 7. On hydrophobized silica, however, there was always an adsorbed layer, leveling off at approximately 0.7 mg/m^2 at the highest surfactant concentrations (Figure 7d). Here it should be noted that SDS on its own does not adsorb to the bare hydrophilic silica surface, but does adsorb to a hydrophobic surface. It is therefore likely that the 0.7 mg/m^2 at the highest surfactant concentrations on the hydrophobic surface mainly consists of surfactant. The deposition on hydrophilic and hydrophobized silica after dilution of bulk solution was much more dependent on the formulation. Here two of the polyions, HEA/MAPTAC and AA/MAPTAC, gave significantly higher

adsorbed amounts on hydrophilic silica compared to hydrophobic silica.

Presence of Silicone Oil Droplets Affects Deposition in a Systematic Way. Low surfactant concentrations with the synthetic polyions surprisingly gave a lower adsorbed amount when silicone oil emulsion droplets were present. However, at low surfactant concentrations, one cannot neglect the contribution from the dodecylbenzene sulfonate originating from the emulsion (0.26 mM) to the total anionic surfactant concentration. Hence, the total initial anionic surfactant concentration with emulsion present is actually higher than the c_{max} calculated from the amount added SDS, which may explain the comparatively low adsorbed amount.

More interesting is the fact that at the highest initial surfactant concentrations, the adsorbed amounts approach the same limiting values with and without emulsion for all systems except HPA/DMAM. When the bulk solution was diluted, however, there was—as might be expected—in most cases a larger adsorbed amount from the formulations containing emulsion. This additional amount should correspond to codeposition of silicone oil droplets. However, the final adsorbed amount from the emulsion-containing formulation was not significantly higher than without the silicone oil for the more hydrophilic copolymers, AA/MAPTAC (Figure 5) and cat-HEC, on hydrophobized silica after dilution from high initial surfactant concentrations.

Polyion Properties Are Important for Deposition. If we limit the comparison to the synthetic polyions, which seems reasonable
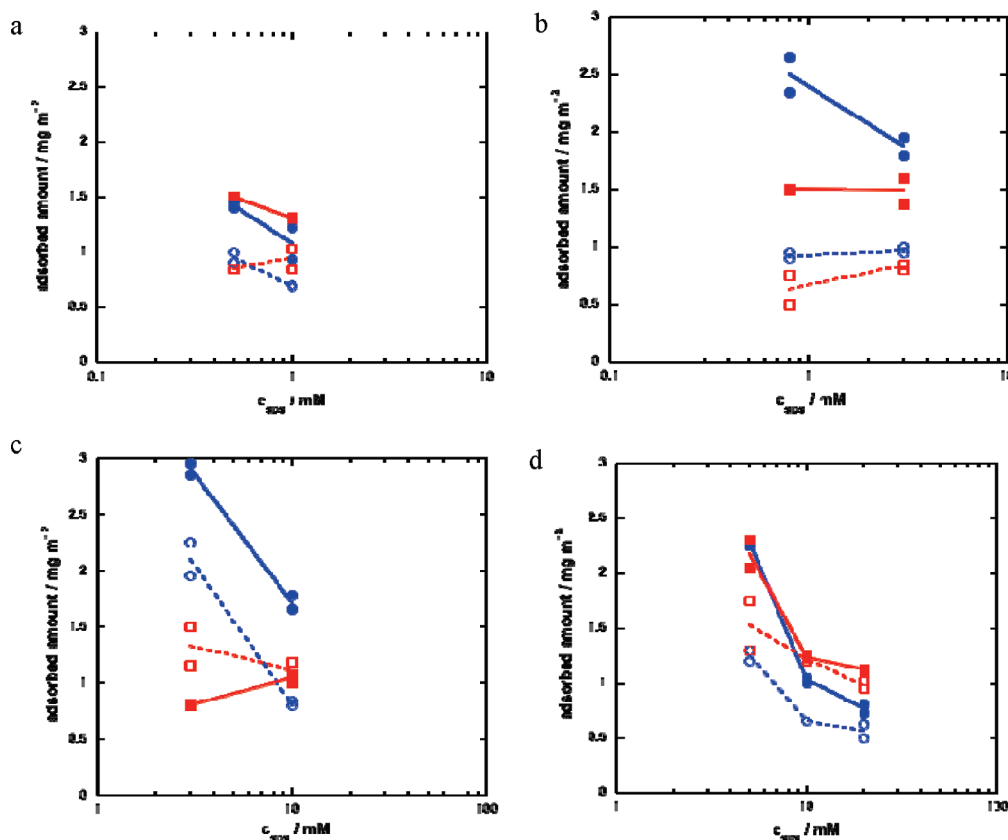
Figure 8. Deposited amounts after the bulk solution had been completely diluted with 1 mM aqueous NaCl (see text) for (a) HPA/DMAM, (b) HEA/MAPTAC, (c) AA/MAPTAC, and (d) catHEC. The surfactant concentration refers to the initial content of SDS before diluting the bulk solution. All data are shown. Symbols as in Figure 7; note that the y-axis scale here is more expanded.

in view of their similar chemical structure, a consistent picture emerges: After dilution of the bulk solution, the adsorbed amount on hydrophilic silica increased with decreasing polyion hydrophobicity, both with and without emulsion droplets present. On hydrophobic silica, there was no clear trend in adsorption behavior as a function of polyion hydrophobicity. Consequently, with a decreasing hydrophobicity among the synthetic polyions there was an increasingly larger additional deposition at hydrophilic silica compared to hydrophobized silica. HPA/MAPTAC gave equal deposition to both surfaces, but both HEA/MAPTAC and AA/MAPTAC deposited more material on the hydrophilic surface. Cat-HEC did not conform to the pattern shown by the synthetic copolymers; it stood out by consistently showing a larger adsorbed amount after rinsing on hydrophobic surfaces.

Intermediate Dilution with a Surfactant Solution Affects the Deposition. The results presented in Figures 7 and 8 show that a substantial deposition on a surface can be obtained from a polyelectrolyte–surfactant formulation initially at c_{max}, but that much, sometimes most, of the material layer will be removed on subsequent dilution with the pure aqueous sodium chloride solution. The removal is indeed predicted by maps of the adsorption behavior from experiments where the surfactant concentration is sequentially increased at constant polyelectrolyte concentration (Figure 3). From the latter behavior we would infer that the main reason for removal of the layer is that we lower the bulk surfactant concentration from c_{max} to effectively zero. On the other hand, we also observe (Figure 8) that the final deposition resulting from dilution is dependent on the initial
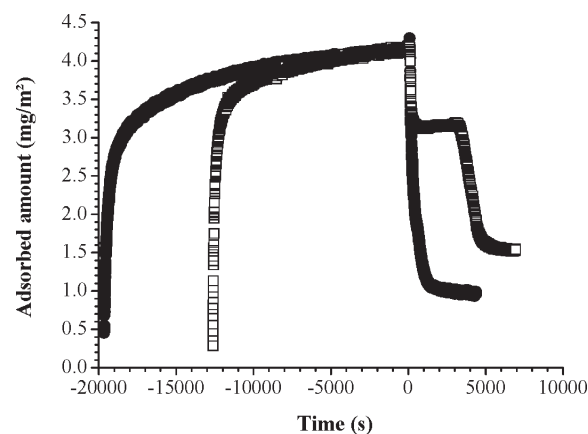
Figure 9. Evolution of layers adsorbed on hydrophilic silica from 100 ppm HPA/DMAM dissolved in 0.5 mM SDS, 1 mM NaCl subjected to different dilution procedures. The bulk solution was diluted directly with 1 mM NaCl (filled circles), or by sequential dilution with 0.5 mM SDS, 1 mM NaCl followed by 1 mM NaCl (open squares). The first dilution step defines $t = 0$.

surfactant concentration. This indicates a history-dependent deposition, where intermediate processes may trap complex at the surface before and during dilution. Based on these considerations, we chose to investigate formulations, with or without emulsion, of HPA/DMAM at c_{max} (= 0.5 mM SDS), and introduce a step where we diluted with a solution of 0.5 mM

SDS and 1 mM NaCl before diluting with 1 mM NaCl. This means that we initially only diluted the polyelectrolyte in the bulk solution. Figure 9 illustrates the results obtained for an emulsion-free system and hydrophilic silica, where we also compare with the results for directly diluting with 1 mM NaCl. Clearly, diluting with 0.5 mM SDS removed much less material from the surfaces than rinsing with 1 mM NaCl. A subsequent dilution with 1 mM NaCl removed additional material from the surface, but the final adsorbed amount was higher than on directly diluting the bulk solution with 1 mM NaCl. The same protocol, with an intermediate dilution step with surfactant solution, was applied with and without added emulsion for both surfaces. We generally found (see the Supporting Information for details) that the intermediate dilution protocol gave rise to a significant increase in the final adsorbed amount after rinsing, especially for the formulation without added emulsion.

■ DISCUSSION

Adsorption from Polyelectrolyte−Surfactant Mixtures at a Hydrophobic Surface on Increasing the Surfactant Concentration. Figure 3 shows the resulting changes in adsorption at hydrophobized silica when stepwise increasing the surfactant concentration in emulsion-free solutions of the various polyelectrolytes. The overall trends are very similar to those previously obtained for the same systems at hydrophilic silica. The observed maximum in adsorbed amount occurs at a surfactant concentration, c_{max}, which is the same or similar as on hydrophilic silica and generally increases with decreasing polyion hydrophobicity. We conclude that also at hydrophobic surfaces, the adsorption isotherm on surfactant titration mainly reflects the binding isotherm of the surfactant ion to the polyion.

Nevertheless, there are some important quantitative differences in deposition on hydrophilic and hydrophobized silica. On hydrophobized silica, we observed a continuous gradual binding also below c_{onset} (Figure 3). This shows that there was an adsorption of surfactant ions to the hydrophobic surface even before the surfactant ions started to form micelles at the polyion at the cac. A synergism can be expected, where the adsorption of negatively charged surfactant induces further adsorption of polycations. Interestingly, the increase in adsorbed amount before c_{onset} varied with the polyion. If we compare only the chemically similar synthetic polyions, we see that already on addition of very small amounts of SDS, the order of increasing adsorption is reversed compared to the surfactant-free systems: An decreasing polyion hydrophobicity gives an increasing adsorbed amount in the mixtures with SDS. This ranking of the adsorbed amount persisted at all SDS concentrations, and the differences were very pronounced at the respective adsorption maxima, see also Table 3. By contrast, no significant differences in adsorbed amount at c_{max} was seen among the synthetic polyions at hydrophilic silica. A possible explanation for this trend is a stronger direct adsorption to the hydrophobized surface for a more hydrophobic polyion. Due to its larger size a hydrophobic polyion can interact more favorably with the hydrophobic surface (large reduction in free energy) than a surfactant molecule, that is, the polyion can partially replace the surfactant. A further consequence is that also the capacity of the polyion to bind surfactant becomes less if some of its potential surfactant binding sites are already blocked by the polyion adsorbing to the surface.

A very gradual increase in adsorption at hydrophobized silica was seen from the cat-HEC solution on increasing the SDS concentration.

Here, no distinct c_{onset} appeared from the measurements, probably because the maximum height of the adsorption peak was, by comparison, quite low for this polyion. This indicates that the effect of surfactant adsorbed directly to the surface was comparatively large for cat-HEC. Presumably, this is also the reason why c_{max} for cat-HEC was significantly different on hydrophobized and hydrophilic silica, see Table 3.

It is clear that even high concentrations of added SDS did not remove all preadsorbed polyions from the two types of surface. A layer of surfactant-swollen polyions remained in all cases. The thickness of this layer was of the order of a surfactant-swollen polyion coil,[30,31] and the picture of a monolayer of adsorbed swollen coils at high surfactant concentrations is supported by the fact that the thickness of the layer increased with increasing molecular weight of polyion (cf. Table 1 and Figure 3), if we again restrict the comparison to include only the chemically similar synthetic polyions.

Adsorption from Premixed Solutions (before Dilution). Clearly, the adsorbed amount resulting from adding a premixed formulation was different from that obtained on sequentially increasing the surfactant concentration. Similar observations illustrating the history-dependent, nonequilibrium nature of adsorbed layers from aqueous polyelectrolyte−surfactant mixtures have been made and discussed previously.[14,20,23,28−31] Here we are especially interested in the consequences of the fact that negatively charged surfactant ions adsorb to hydrophobized silica, but not to negatively charged hydrophilic silica.

An additional direct adsorption of surfactant molecules to hydrophobized silica, as discussed above, is the simplest explanation for the result that the initial adsorbed amount from a given formulation was generally higher to hydrophobized silica than to hydrophilic silica (Figure 7). The difference is most clearly seen at high surfactant concentrations, and the kinetics of adsorption gives additional information. In Figure 6 we see that there was no initial adsorption from cat-HEC in 20 mM SDS to hydrophilic silica, but an effectively instantaneous (on the time scale resolvable by ellipsometry) development of a thin layer of ca. 0.7 mg m^{-2} of material at hydrophobized silica. There can be little doubt that the latter layer was essentially pure SDS that rapidly adsorbed to the hydrophobic surface. At this high initial surfactant concentrations, no adsorption of polyion-surfactant ion complexes occurred at any surface, since these complexes were sufficiently negatively charged by excess surfactant to be repelled by either hydrophilic silica or hydrophobized silica covered by adsorbed surfactant. Assuming that the layer obtained under the these conditions was essentially only SDS, we can calculate an area of ≤ 70 Å^2 per adsorbed surfactant molecule, which is of the expected order of magnitude.

A similar effectively instantaneous adsorption of ca. 1 mg m^{-2} of material at hydrophobic silica was observed for all formulations; an example is seen in Figure 5. This observation suggests that for kinetic reasons a layer of adsorbed surfactant always developed initially on hydrophobized silica. However, for formulations at low initial surfactant concentrations, at c_{max} in particular, the rapid initial adsorption was followed by a much slower increase of adsorbed amount, because of adsorption of polyion−surfactant ion complexes. An example is seen in Figure 4. Presumably, the slow additional build-up of surface-adsorbed material involved a number of processes: A comparatively rapid transport of polyion−surfactant ion complexes to the surface, an attachment to the surface, and a reorganization

of the composite adsorbed layer including also displacement of the initially adsorbed surfactant with the polyion.

The kinetics of transport of polyion—surfactant ion complexes to the surface can be obtained from the initial linearly increasing adsorption to hydrophilic silica, where no initial fast adsorption of surfactant occurred. For a diffusion-controlled process, the initial rate of adsorption can be described by the following simple model[35,36]

$$\frac{d\Gamma}{dt} = \frac{D}{\delta} c \qquad (2)$$

Here $d\Gamma/dt$ is the initial adsorption rate, D the diffusion coefficient, δ the thickness of the unstirred layer, estimated to 0.1 mm with the cuvette and the agitation rate used in this study,[37] and c the concentration of the component for which the adsorption rate is calculated. For cat-HEC in 5 mM SDS with our without emulsion, we found an experimental initial rate of adsorption of 0.0073 ± 0.0009 mg m^{-2} s^{-1} Using a concentration c of 100 ppm and a diffusion coefficient of the complex calculated from the Stokes—Einstein equation for an average hydrodynamic radius of about 40 nm,[30] we obtain $d\Gamma/dt = 0.006$ mg m^{-2} s^{-1}. The latter value agrees well with the experimental value, suggesting that the adsorption of the polyion was diffusion controlled.

We may use eq 2 to also calculate the adsorption rate of SDS to a hydrophobic surface. With $D = 4 \times 10^{-10}$ m^2 s^{-1} for an SDS unimer,[38] we obtain an adsorption rate of ca. 1 mg m^{-2} s^{-1} at an SDS concentration of 1 mM, confirming that the transport of SDS molecules was too fast to be captured by the ellipsometry measurements (time resolution 2—3 s).

Transient Processes during Dilution Depend on Initial Conditions and on Dilution Protocol. The dilution of the bulk solution in contact with the surface generally induced a rapid change in adsorbed amount and thickness of the adsorbed layer, followed by a slower leveling off to some new "final" state. The overall features of the transient changes occurring during rinsing are most easily understood with reference to the map of the adsorption behavior in Figure 3, because dilution ("rinsing") corresponds to a decrease in the surfactant concentration. Thus, dilution from an initial surfactant concentration at c_{max} should give a monotonic decrease in adsorbed amount, whereas dilution from c_{rediss} or higher should give an initial increase followed by a decrease. However, it is clear from our results that both the details of the transient changes and the final adsorbed amount depend on both the initial conditions and the actual concentration in the bulk solution when we perform the adsorption measurement. For instance, we observed in Figures 4b and 5b that silicone oil droplets seemed to transiently co-deposit at hydrophobized silica during dilution from comparatively high initial surfactant concentrations, but would not remain in the adsorbed layer on continued dilution. Extensive dilution then seems to represent a "missed opportunity" for codeposition of silicone oil droplets to hydrophobic surfaces.

We also observed that diluting only the polyelectrolyte, as in Figure 9, could give rise to a significantly higher final adsorbed amount. Dilution with surfactant solution at a concentration equal to c_{max} did not remove very much of the adsorbed layer, which is consistent with the adsorption isotherm in Figure 3. From this, we may conclude that a significant depletion of surfactant in the adsorbed layer occurs when diluting the bulk solution with a surfactant-free dilute salt solution, and that a consequence of this depletion isa desorption also of polyions.

Surface Deposition Remaining after Dilution Can Be Tuned in Many Ways. One of the most interesting observations of this study is that the properties of the adsorbed layer remaining after the bulk solution had been completely replaced by dilute salt solution vary widely with the initial surfactant concentration, the nature of the cationic polyion, and the nature of the surface. This remaining layer, which we in the following will refer to as the dilution-deposited layer, may contain a mixture of polyions, surfactant ions and, when present in the formulation, silicone oil droplets. Since the proportions of the various components cannot be determined by ellipsometry at a single wavelength, we have to rely on more indirect information on the layer composition. The thickness of the dilution-deposited layer was typically at least 100 Å; for layers deposited from formulations initially at c_{max}, dilution-deposited layer thicknesses of several hundreds of Å were often observed. This relatively large thickness clearly indicates that the dilution-deposited layers generally contained polyions that were not adsorbed flatly to the substrate surface. Indeed, as illustrated in Figure 4, layers deposited from formulations initially at c_{max} often expanded when the bulk solution was diluted, although a large proportion of the adsorbed material was lost in the process. The adsorbed amounts in dilution-deposited layers formed from emulsion-free formulation on hydrophobized silica varied in the range 0.5—1.5 mg/m^2 (Figure 8) similarly to the adsorbed amount from solutions of only polyelectrolytes (Table 2), but the results for the individual systems varied for the two processes.

As a rule (the important exceptions will be discussed below), formulations with emulsion droplets gave a larger adsorbed amount than the corresponding formulations without emulsion droplets. Similar results have been obtained in a study of deposition from formulations of cat-HEC and cat-guar with SDS in a previous study.[31] There can be little doubt that this additional deposition was due to a codeposition of silicone oil droplets. Using a simple subtraction of the results in Figure 8, we conclude that the codeposited amount of silicone oil is estimated to vary in the range 0—1.5 mg/m^2.

Of the investigated polyions, HEA/MAPTAC had the best capacity to co-deposit silicone oil droplets to both hydrophobized and hydrophilic silica, according to the results in Figure 8. Except for HPA/DMAM, there was generally more silicone oil codeposition to hydrophilic silica than to hydrophobized silica. AA/MAPTAC delivered silicone oil efficiently to hydrophilic silica, but not at all to hydrophobized silica; see also Figure 5. The same held true for cat-HEC at high surfactant concentrations; see also Figure 6. The latter results have important implications for applications, since they show that there exist certain polyions that, when mixed with SDS at an appropriate concentration, can be used to specifically co-deposit silicone oil droplets to some surfaces (here hydrophilic silica) but not others (here hydrophobized silica). This might be interesting for practical applications like hair shampoos, because damaged hairs that benefit from deposited silicone oil are hydrophilic, whereas virgin hairs are hydrophobic. It is interesting that the surface selectivity was found only for the two most hydrophilic polyions of our investigation, AA/MAPTAC and cat-HEC.

Because the bulk composition of the various aggregates to be deposited must be the same, the reason for a selective surface deposition must lie in the differences between the substrate surfaces. Here we can suggest one possibility. Both polyions and surfactant ions probably attach in a similar fashion to hydrophobic

silicone oil droplets as to hydrophobized silica. The polyions will be attached to a hydrophobic surface primarily via hydrophobic interactions. Thus, as soon as the adsorbed polyion-surfactant ion complexes carry a charge, the complexes adsorbed on droplets should be similarly charged as those on hydrophobized silica and, hence, repel each other. For dissimilar surfaces, the situation should be different. A polyion adsorbed to hydrophilic silica should use primarily its positively charged groups as anchors at the negatively charged groups silica surface. Hydrophobic functionalities might then still be available to interact with a silicone oil droplet. Conversely, a polyion adsorbed by its hydrophobic funcional groups to a silicone oil droplet would have exposed charged groups available for binding to a hydrophilic surface. In essence, the combination of unlike functionalities on the polyion might make the polyion an efficient linker of unlike particles and surfaces, but less suitable to link like particles and surfaces.

Deposition of silicone oil droplets on hydrophobic surfaces by diluting polyelectrolyte/surfactant solutions at high initial surfactant concentrations thus seems difficult. We may here recall also that the results in Figure 7 generally show very small differences in adsorbed amounts, before diluting the bulk solution, between systems with and without silicone oil at high surfactant concentrations. This indicates that at high surfactant concentrations, no silicone oil was codeposited before dilution. However, at low initial surfactant concentrations, the results in Figure 8 indicate that silicone oil droplets could be successfully codeposited also on hydrophobic surfaces. It seems likely that the droplets were here deposited in the initial surface layer already before dilution. To remove such already embedded droplets by exposing the layer to aqueous NaCl might be difficult, compared to removing the quite loose layers of droplet-containing material that transiently developed during dilution from mixtures at high surfactant concentrations.

One remaining trend to discuss is the observation that the deposited amount in dilution-deposited layers formed on hydrophilic silica from initial formulations containing silicone oil increased monotonically with decreasing polyion hydrophobicity. We note that this trend is the same as seen in the adsorption of the various polyion—surfactant ion complexes at hydrophobized silica in Figure 3. Thus, this observation supports the notion of a similarity in the adsorption at hydrophobic silica and at hydrophobic silicone oil droplets for the polyion—surfactant ion complexes.

■ CONCLUSIONS

In this study, we have compared the adsorption of oppositely charged polyion-surfactant ion complexes at hydrophobic and hydrophilic silica using different protocols: A stepwise increase of the surfactant concentration in a bulk solution containing the polyion (titration experiment) or addition of a premixed formulation to the cuvette, followed by dilution with 1 mM NaCl, simulating rinsing with water that occurs in the use of consumer products such as shampoo.

The overall features of the titration experiment were similar for hydrophobic and hydrophilic surfaces, and for the various cationic polyions investigated. There was a maximum in adsorbed amount for conditions corresponding to, or nearly to, the conditions for maximum bulk coacervation. Thus, the adsorption peak shifted to lower surfactant concentrations with an increasing hydrophobicity of the polyion.

Regardless of the experimental protocol, there were quantitative differences in the adsorbed amount between hydrophobized and hydrophilic surfaces. Most of the differences observed in titration experiments, or on adding the premixed formulation to the cuvette, can be understood as consequences of a selective adsorption of surfactant ions to hydrophobized silica, but not to hydrophilic silica.

The dilution experiments generally showed that a layer of adsorbed material remained when the initial formulation was completely replaced by dilute aqueous NaCl, and that the amount of material contained in such a dilution-deposited layer depended on the nature of the substrate surface, the hydrophobicity of the polyion, and the concentration of surfactant present in the solution before dilution. A significant codeposition of silicone oil droplets occurred after dilution of the bulk solution for most, but not all, initial conditions. For the synthetic polyions, the amount of deposited material increased with decreasing initial surfactant concentration and decreasing polyion hydrophobicity. The most efficient codeposition of silicone oil was obtained on hydrophilic silica and for the more hydrophilic copolymer. Little or no codeposition on hydrophobized silica was obtained with hydrophilic polyions and at high initial surfactant concentrations.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.**   Full time-resolved recordings of all rinsing experiments performed as described in the main article, a table detailing the composition of the silicone oil emulsion, and a table with adsorbed amounts for the experiments with intermediate dilution with surfactant solution (PDF). This material is available free of charge via the Internet at http://pubs. acs.org.

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■ ACKNOWLEDGMENT

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