

Mixtures of Cationic Copolymers and Oppositely Charged Surfactants: Effect of Polymer Charge Density and Ionic Strength on the Adsorption Behavior at the Silica–Aqueous Interface

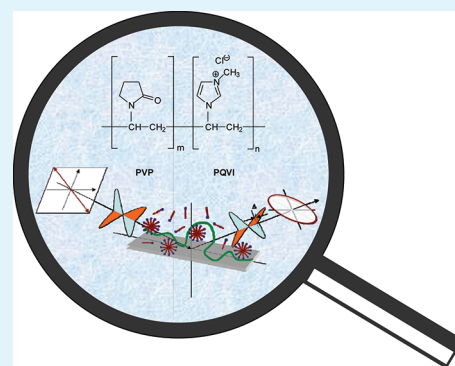
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ABSTRACT: This study addresses polymer–surfactant interactions at solid–liquid interfaces and how these can be manipulated by modulating the association between ionic surfactant and oppositely charged polymer, with a particular focus on electrostatic interactions. For this purpose, the interaction of a series of cationic copolymers of vinylpyrrolidone and quaternized vinylimidazol with sodium dodecyl sulfate (SDS) at the silica–aqueous interface was followed by in situ ellipsometry. To reveal the nature of the interaction, we performed measurements for different copolyion charge densities, in the absence and presence of added salt. The path-dependence of the interaction was studied by comparing the adsorption under two different conditions, adsorption from premixed solutions and sequential addition of surfactant to the polymer solution, but the same end state. The reversibility of the adsorption process was studied by following the effect of dilution on the adsorbed layer. All copolyions adsorbed to both silica and hydrophobized silica, revealing the importance of both hydrophobic and electrostatic attractive interactions. On both types of surface, an increase in adsorbed amount was found on lowering the fraction of charged units. An increased ionic strength gave an increased adsorbed amount in all cases, but especially on hydrophobic surfaces. The adsorbed amount on silica from mixtures of the copolyions with SDS peaked at an SDS concentration corresponding closely to the concentration of cationic charges of the different polyions. Around the region of charge equivalence, there was also a phase separation in the bulk. At higher concentrations of SDS, a redissolution in the bulk, and a decrease in adsorbed amount, occurred as a result of excess SDS binding to the complexes. For the most highly charged polyions, we observed a decrease in adsorbed amount, and a shift in the adsorption maxima to lower SDS concentrations, with increasing ionic strength.

KEYWORDS: polymer surfactant interactions, cationic copolymers, oppositely charged surfactants, null ellipsometry, silica surface, effect of rinsing



1. INTRODUCTION

Functional polymers and their mixtures with surfactants are of major practical importance in a variety of applications, ranging from paints and coatings, to food processing, personal care formulations, and biotechnology. Cationic copolymers are of particular interest in the formulation of hair care and styling products because of their ability to change the physical properties of the hair.^{1–3} It has been recognized that cationic polymers permit control over the rheology of shampoo compositions. Furthermore, these polyions have been demonstrated to improve hair conditions such as combability, texture, softness, hair shine, resistance to damage, and reduction of split ends. During the past decades, a number of polyions have been developed in particular for performance enhancement. The design of new functional cationic polymers is a subject of current intensive research, and this study was undertaken in this perspective.

The development of new polymers has been aided by the significant number of studies that has been carried out during

the past decade. These studies have increased our understanding of the formation and properties of polymer–surfactant complexes.^{4–9} Polymer–surfactant interactions in bulk solution have been studied extensively, whereas the association behavior at interfaces as a consequence of the adsorption/formation of complexes between ionic surfactant and oppositely charged polymer at solid–liquid interfaces is less well understood.^{10–20} Solid–liquid interfaces are of particular relevance in a number of industrial processes such as stabilization of colloids, mineral beneficiation, and oil recovery.²¹

Different methods have been adopted to study the adsorption behavior of surfactants and polymers at the solid–liquid interface.²² Most commonly, optical reflection and scattering techniques are used, for instance, ellipsometry,¹¹ small angle neutron scattering (SANS),^{23–25} neutron reflectivity

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ity,^{25,26} atomic force microscopy (AFM),^{27,28} and surface force measurements.^{11,29} Likewise, spectroscopic techniques such as electron spin resonance (EPR),³⁰ nuclear magnetic resonance (NMR),²⁴ photon correlation spectroscopy (PCS),^{23,24} infrared,³¹ and fluorescence.³⁰

In previous work from our laboratory, we have studied various cationic polymers interacting with SDS at interfaces, using ellipsometry and complementary bulk experiments. Some of the key results from our earlier studies regarding both adsorption of the cationic polyelectrolytes on oppositely charged silica surface and the adsorption from mixtures with anionic surfactants have been summarized in a recent review.²⁰ We have compared various cationic polysaccharide derivatives,^{17,18,32} and we have also systematically studied the effect of the hydrophobicity of the cationic polymer for a series of synthetic copolymers.³³ Those previous studies have highlighted the importance of both hydrophobic and electrostatic interactions for the performance of the cationic polymer–surfactant formulations at solid surfaces. However, the effect of varying the electrostatic interactions was not addressed in a systematic way. This is the main purpose of the present study, where we investigate the interaction of a homologues series of cationic copolymers, vinylpyrrolidone and quaternized vinylimidazol (PVP/PQVI) of different charge densities (Figure 1),

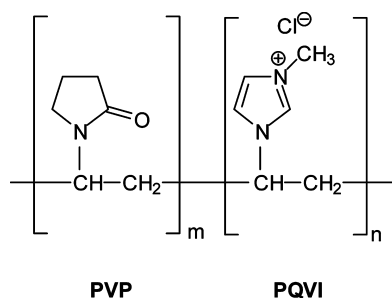


Figure 1. Monomer structures of the cationic copolymers. The three polymers used contained 25, 50, and 75 wt % quaternized vinylimidazol monomers, respectively.

with sodium dodecyl sulfate (SDS) at the silica–aqueous interface. The measurements were performed in the absence and presence of salt. The path-dependence of the interaction was studied by comparing the adsorption using two different protocols: (1) adsorption from premixed solutions and (2) sequential addition of surfactant to the polymer solution, both resulting in the same final composition in the bulk. The reversibility of the adsorption process was studied by following the effect of dilution of the bulk solution on the adsorbed layer.

2. EXPERIMENTAL SECTION

2.1. Materials. In the following, we denote the polymers according to the ratio of the cationic monomers: 75VP/25QVI, 50VP/50QVI, and 25VP/75QVI contain 25, 50, and 75 wt % quaternized vinylimidazol monomers, respectively. Monomer subunits are oriented randomly. To remove salts and low-molecular-mass impurities, we dialyzed all polymers extensively against pure water and then freeze-dried them. All polymers were products of BASF, Germany. The properties of the copolymers are summarized in Table 1.

Sodium chloride and sodium dodecyl sulfate (SDS) were obtained from Fluka (>99% purity) and used without further purification. Ethanol of spectroscopic grade was purchased from Kemetyl, Sweden, and used in all cleaning procedures.

Water of Millipore quality (resistivity $\approx 18 \text{ M}\Omega \text{ cm}^{-1}$, pH 5.6 ± 0.2) was used in all experiments and for preparation of all samples.

Table 1. Properties of the PVP/PQVI Copolymers Used in This Study^a

polymer	mol wt M_w (kD)	z average diameter (nm) ^b	charge density (meq/g) ^c
75VP/ 25QVI	165	21.6	1.20
50VP/ 50QVI	160	20.1	3.32
25VP/ 75QVI	120	14.7	4.18

^aChloride counterion. ^b0.5 M NaCl. ^c ± 0.02 meq/g.

The cleanliness of the water and vessels used to store the solution was tested by shaking the water in the vessel and low bubble persistence (<1 s) was used as a criteria for low content of surface-active organic compounds. Measurements were carried out with freshly prepared solutions at 25 °C.

Adsorption studies were performed on both hydrophilic and hydrophobized silicon wafers. The silicon wafer (p-type, boron-doped, resistivity 1–20 $\Omega \text{ cm}$) were thermally oxidized in an oxygen atmosphere at 920 °C for about 1 h, followed by annealing and cooling in an argon flow (Department of Chemistry, IFM, Linköping University, Sweden). This procedure finally yields a SiO_2 layer of around 300 Å thickness. The oxidized wafers were cut into slides with dimensions of about 40 × 12 mm. The silicon slides were cleaned by first treating them for five minutes in a mixture of 25% NH_4OH , 30% H_2O_2 and water (1:1:5 by volume) at 80 °C, followed by boiling for 10 min in a mixture of concentrated hydrochloric acid, 30% H_2O_2 and water (1:1:5 by volume) at 80 °C. The slides were then rinsed with water and ethanol and stored in absolute ethanol until use. Prior to the measurement, the surfaces were blown dry with nitrogen and treated for 5 min in a plasma cleaner (Harrick Scientific Corp. model PDC–3XG). In order to obtain hydrophobized silica surfaces the plasma-treated slides were further exposed to a low-pressure atmosphere of octyldimethylchlorosilane for at least 12 h. After the reaction, the hydrophobic surfaces were sonicated in ethanol and tetrahydrofuran (THF) five times each. In a final step, they were cleaned with ethanol again and kept in absolute ethanol prior to the measurements.

2.2. Ellipsometry. Ellipsometry is an optical technique, based on the change of polarized light upon reflection against an interface, that allows to in situ follow the adsorption of polymers and surfactants at solid–liquid interfaces.³⁴ Polarized light can be considered to consist of two components, the parallel and the perpendicular wave. By measuring the polarization of light reflected parallel and perpendicular to the plane of incidence, the relative phase change (Δ) and relative amplitude change (Ψ) from the reflected surface can be determined. In this way it is possible to deduce information about the properties of the surface, e.g., film thickness and refractive index, which can be used to calculate the adsorbed amount. To get an accurate measure of the adsorbed layer thickness and refractive index, we evaluated the recorded values of Ψ and Δ as a function of time by using the optical four-layer model.^{35,36} The silicon substrate is assumed to consist of bulk silicon (layer 1) covered with an silicon oxide layer with an approximate thickness of 300 Å (layer 2), on which the adsorbed layer is formed (layer 3) surrounded by the bulk solution (layer 4). These layers are assumed to have uniform thickness and composition and form planar interfaces. The complex refractive index $n_1 - jk_1$ of bulk silicon as well as the thickness d_2 and refractive index of the oxide layer n_2 was obtained by characterizing the bare silica substrates in air and in aqueous solutions. The mean refractive index of the adsorbed layer, n_3 , and thickness, d_3 , were then calculated using a numerical procedure originally devised by McCrackin et al.³⁷ as described by Tiberg, Jönsson, and Landgren.³⁵ To calculate the adsorbed amount, we applied the formula of de Feijter et al.³⁸

$$\Gamma = d_3(n_3 - n_4)/(dn/dc) \quad (1)$$

where dn/dc is the refractive index increment of the polymers and n_4 is the refractive index of the ambient bulk solution. For the treatment of

Table 2. Values of the Adsorbed Amount Γ of the Steady-State Adsorption Process of 75VP/25QVI, 50VP/50QVI, and 25VP/75QVI onto Silica and Hydrophobized Silica Surface^a

polymer	Γ (mg/m ²) in water		Γ (mg/m ²) in 10 mM NaCl ^b		Γ (mg/m ²) in 100 mM NaCl ^c	
	silica	hydrophob. silica	silica	hydrophob. silica	silica	hydrophob. silica
75VP/25QVI	0.60 ± 0.03 (≤5)	1.00 ± 0.05 (≤5)	0.55 ± 0.03 (50 ± 5)	1.04 ± 0.05 (100 ± 10)	0.69 ± 0.04 (100 ± 10)	1.09 ± 0.05 (100 ± 10)
50VP/50QVI	0.40 ± 0.04 (≤5)	0.86 ± 0.06 (≤5)	0.44 ± 0.04 (≤5)	0.98 ± 0.05 (100 ± 10)	0.65 ± 0.04 (≤5)	1.04 ± 0.05 (120 ± 10)
25VP/75QVI	0.44 ± 0.04 (≤5)	0.27 ± 0.03 ^d (≤5)	0.44 ± 0.04 (≤5)	0.65 ± 0.04 ^d (45 ± 5)	0.53 ± 0.04 (≤5)	0.92 ± 0.05 ^d (150 ± 10)

^aNumbers in parentheses are thickness values d , in Å. When it is not possible to resolve the layer thickness (thin adsorbed layer), the thickness is given as ≤5 Å. [polymer] = 100 ppm. ^bAdsorption from 10 mM NaCl aqueous solution. ^cAdsorption from 100 mM NaCl aqueous solution. ^dA gradual increase in the adsorbed amount is observed. Therefore, a higher polymer concentration is required to reach the plateau value.

the ellipsometric data, we used $dn/dc = 0.155$. Typical values of n_1 , k_1 , d_2 , and n_2 are $n_1 = 5.50 \pm 0.01$, $k_1 = -0.35 \pm 0.03$, $d_2 = 300 \pm 20$ Å, and $n_2 = 1.485 \pm 0.005$, respectively, which may vary somewhat from batch to batch. It should be noted that the optical slab model applied assumes homogeneous layers with sharp interfaces, which is important to bear in mind when interpreting the ellipsometry data. There are two situations that have to be taken into account here. First, it is highly unlikely that the adsorbed layer is homogeneous, but the surface is likely to be inhomogeneous with an varying density profile orthogonal to interfaces; second, lateral inhomogeneity of the layer is likely to occur in the mixed polymer/surfactant system. In both cases, the determined thickness represent an average optical thickness, which is smaller than the size of the aggregates. Here, it should be noted that the ellipsometry measurements are averaged over about 1 mm², i.e., the size of the light spot. We have previously discussed these challenges in interpreting the layer thickness from ellipsometry measurements with respect to the formation of brush like polymer layers³⁹ as well as for lateral inhomogeneous layers in terms of the adsorption of lipid liquid crystalline nanoparticles at interfaces.⁴⁰ As the ellipsometer measures only two parameters, Δ and Ψ , a more rigorous modeling requires additional parameters. These can be obtained by measuring in another media with different refractive index as we have demonstrated by combining measurements in H₂O and D₂O⁴¹ or by using multiwavelength ellipsometry.⁴² However, such measurements are very tedious and by no means trivial. In our opinion the more fruitful approach is to do spectroscopic ellipsometry (in particular in the UV–near UV range), although this requires detailed knowledge of the wavelength dependence of all the components. Such measurements are in progress and will be used in future studies, but further modeling is needed before they can be applied to more heterogeneous systems like the one in the present study. An additional aspect is that for low adsorbed amount, thin layers, and low optical contrasts, the refractive index of the layer and the layer thickness becomes coupled, so it is only possible to determine the adsorbed amount.⁴³ It has, however, been shown that the amount adsorbed (to a first approximation the product of the thickness and refractive index) is a reliability quantity that is in most cases independent of the optical model applied.^{35,43} In this study, we have focused on the evaluation of the adsorbed amount for adsorption from the neat polymer solution, which show relatively low adsorbed amount and thin polymer layers. However, for the mixtures with SDS, the adsorbed amount is generally higher and it is therefore possible to also evaluate the thickness of the layer. When the thickness is presented, it should be regarded as an average optical thickness.

2.3. Ellipsometry Measurements. Measurements were carried out on a modified and automated Rudolph Research thin–film null ellipsometer, model 43603–200E. The light source was a Xenon arc lamp. An interference filter was used to operate with a wavelength of 401.5 nm. The angle of incidence Φ was set at 68°. The instrument is equipped with five-phase stepper motors from Berger-Lahr, type VRDM 566. The main optical components are polarizer, compensator and analyzer. A photomultiplier is used to measure the intensity of the light passing through the analyzer. All experiments were performed at 25 °C using a 5 mL trapezoidal cuvette of optical glass. Prior to the adsorption studies the bare silica surfaces were characterized in both air and salt solution. Polymer stock solutions of 3000 ppm were freshly prepared by dissolving 75VP/25QVI, 50VP/50QVI, and 25VP/75QVI

in 10 and 100 mM NaCl, respectively. In a typical experiment using protocol 1, the premixed polymer/surfactant complex was injected into the trapezoidal cuvette, which originally contained 4.8 mL of salt solution. To ensure proper mixing of the polymer and polymer/surfactant solution, we stirred the solution by a magnetic stirrer at 300 rpm. Ellipsometric angles Ψ and Δ were recorded continuously as a function of time until plateau values were reached. The polymer/surfactant solution was then diluted (rinsing) by a continuous flow of 7 mL/min of neat salt solution, by means of a two channel peristaltic pump (Ole Dich model 110 AC 20 G75) where the inlet of the salt solution is placed in the bottom of the cuvette and the drainage in the top of the cuvette so that the volume is maintained at 5 mL. For protocol 2, measurements, the polymer was first injected while the adsorption was recorded until steady state is reached. Once steady state is reached, an aliquot of surfactant is sequentially added to the polymer solution; once steady-state adsorption is obtained, the surfactant concentration was once again sequentially increased. This process was repeated until the desired maximum surfactant concentration was obtained. The protein/surfactant solution was then diluted (rinsing) as described above. Methods and experimental setup are described in detail by Landgren and Jönsson.³⁶

3. RESULTS

3.1. Adsorption of Cationic Copolymers Increases with Decreasing Charge Density and with Added Salt.

The purpose of this study was to serve as a reference to study of adsorption from the mixed polymer/surfactant solutions. Although the main observations are according to what is expected from theory⁴⁴ and our previous experimental studies,⁴⁵ the adsorption from this particular system has not been investigated in detail before. The adsorption behavior of the cationic copolymers 75VP/25QVI, 50VP/50QVI, and 25VP/75QVI was studied in distilled water as well as in 10 mM and 100 mM NaCl. These measurements were performed for both hydrophilic silica and hydrophobized silica. For all copolymers, the adsorption kinetics was fast under the experimental conditions studied as the adsorbed amount increased sharply with time within the first few minutes (data not shown). The polyion concentration was increased sequentially, and the adsorbed amount eventually approached a plateau value (Table 2). Maps of the adsorption versus polymer concentration on silica and hydrophobized silica are shown in Figure 2.

The observed plateau values of the adsorbed amounts varied in the range 0.4–0.7 mg/m² for hydrophilic silica, and in the range 0.3–1.1 mg/m² for hydrophobized silica. On both surfaces, the adsorbed amount increased with a decreasing fraction of charged residues on the polyion, and with an increasing ionic strength in the bulk. Notably, both the charge density effect and the salt effect were much more pronounced on the hydrophobized silica, in particularly for the most highly charged polymer.

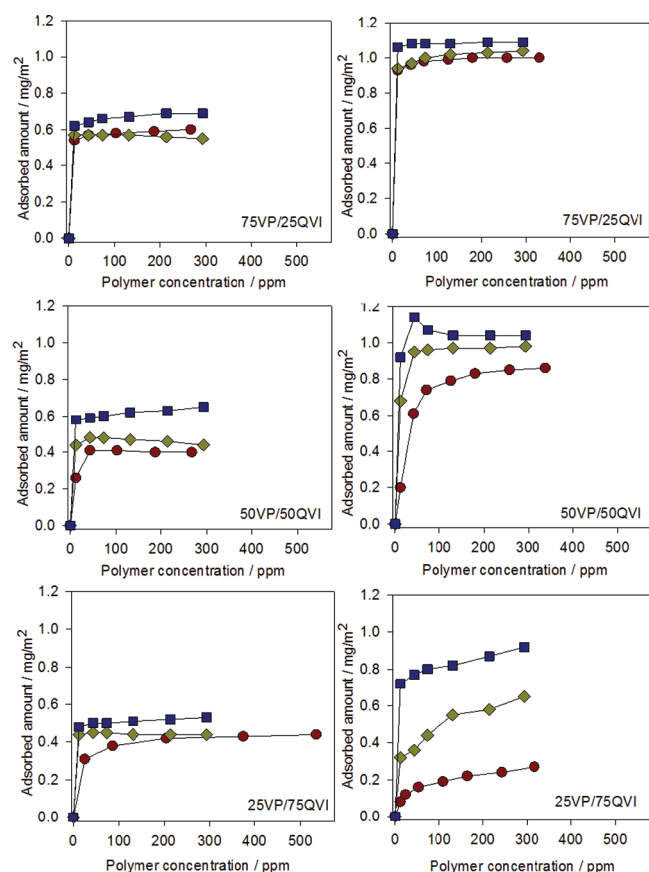


Figure 2. Adsorbed amount on silica (left) and hydrophobized silica (right) for 75VP/25QVI, 50VP/50QVI, and 25VP/75QVI as a function of polymer concentration in neat water (circles), in water with 10 mM (diamonds) and 100 mM NaCl (squares), respectively.

No desorption of either of the cationic copolymers from silica was observed when the bulk polymer solution was replaced with pure salt solution (data not shown). This suggests that all polymers were, in practice, irreversibly adsorbed onto the negatively charged surface. A similar behavior was observed for the polymers adsorbed on hydrophobized silica although, a slight desorption of 25VP/75QVI was observed at high salt concentration (100 mM NaCl).

3.2. Adsorption from Mixtures with SDS on Silica. The adsorption of premixed copolymer/SDS solutions on silica was studied. Complexes were prepared by mixing an appropriate amount of freshly prepared polymer stock solution with aliquots of SDS solution in 10 and 100 mM NaCl, respectively. After the adsorption of the polymer/surfactant complex solution reached a plateau value, the bulk polymer solution was diluted with NaCl solution (“rinsing”). Figures 3 and 4 show the results from the initial adsorption experiments and key results are summarized in Table 3 together with the estimated error in the measurements, whereas Figures 6 and 7 illustrate the effect of subsequent dilution. The results show that the adsorbed amount is strongly dependent on the anionic surfactant concentration, in agreement with previous results for other cationic polymers.^{33,46 17–19,32}

Low SDS Concentration Does Not Affect Adsorption. Panels a and b in Figure 3 show that the amount adsorbed between 0.001 mM and 0.02 mM SDS was practically independent of the surfactant concentration (Table 3). Very thin (≤ 5 Å) adsorbed layers were found for 75VP/25QVI at a low concentration of salt of 10 mM NaCl, whereas at high ionic strength the layer thickness increased sufficiently, which made it possible to determine it (~ 50 Å). Also, for 50VP/50QVI and 25VP/75QVI mixtures with SDS, only minor adsorption to the silica surface was observed in this low SDS concentration region. When the cuvette was flushed with salt solution no desorption was observed (see results for 0.2 mM SDS in Figure 5), suggesting an irreversible adsorption process.

Intermediate SDS Concentration Gives a Maximum in Adsorption. As the concentration of SDS was increased from 0.02 mM, a significant increase in the adsorbed amount was found for all three types of polymer, indicating that binding of SDS is highly cooperative. For example, the low charge density polymer 75VP/25QVI in 10 mM NaCl yielded maximum in adsorption of 4.0 mg/m^2 at 0.20 mM SDS. At a high salt concentration, 100 mM NaCl, the peak in adsorbed amount decreased to 2.7 mg/m^2 at 0.20 mM SDS (Figure 3a, b). As observed for the adsorbed amount, the layer thickness increased with the surfactant concentration. However, the thickness was rather similar in both 10 mM and 100 mM NaCl. Typical peak values obtained are 130 Å at low ionic strength in the presence of 0.06 mM and 0.20 mM SDS, respectively (Figure 4a,b). The adsorption from 50VP/50QVI and 25VP/75QVI/SDS yielded significantly higher values of the amount

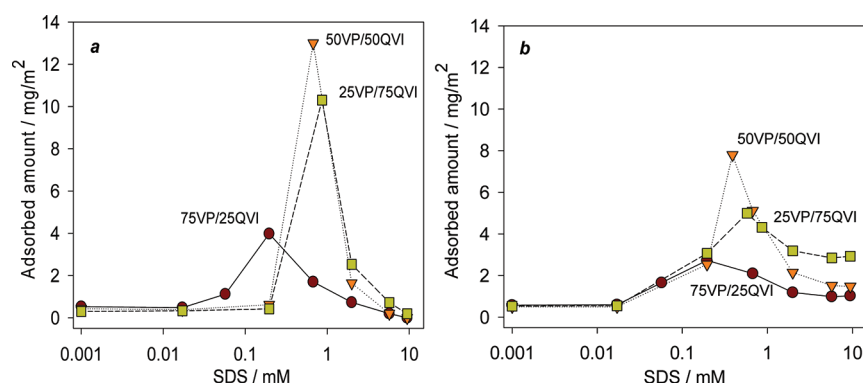


Figure 3. Amount of the complex adsorbed from premixed 75VP/25QVI/SDS (circles), 50VP/50QVI/SDS (triangles), and 25VP/75QVI/SDS solutions (squares) on silica. The polymer concentration was fixed at 100 ppm, corresponding to a concentration of polymer charges of 0.12, 0.33, and 0.42 mM for 75VP/25QVI/SDS, 50VP/50QVI/SDS, and 25VP/75QVI/SDS, respectively. The NaCl concentration was (a) 10 and (b) 100 mM, respectively. The cmc of SDS is 5.7 and 1.5 mM, respectively.⁴⁷

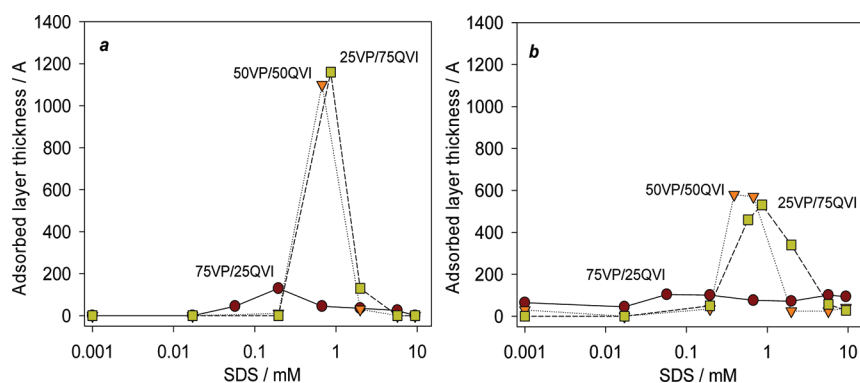


Figure 4. Layer thickness of the complex adsorbed from premixed 75VP/25QVI/SDS (circles), 50VP/50QVI/SDS (triangles), and 25VP/75QVI/SDS solutions (squares) on silica. The polymer concentration was fixed at 100 ppm, and the NaCl concentration was (a) 10 and (b) 100 mM, respectively.

Table 3. Values of the Adsorbed Amount, Γ , and Thickness, d , at Steady-State from Mixtures of 75VP/25QVI, 50VP/50QVI, and 25VP/75QVI with SDS onto Silica^a

polymer	10 mM NaCl ^b		100 mM NaCl ^c	
	Γ (mg/m ²)	d (Å) ^d	Γ (mg/m ²)	d (Å) ^d
low SDS concentration 0.001–0.02 mM SDS				
75VP/25QVI	0.50 ± 0.04	≤5	0.60 ± 0.04	60–45 ± 5
50VP/50QVI	0.50 ± 0.04	≤5	0.50 ± 0.04	≤5
25VP/75QVI	0.50 ± 0.04	≤5	0.50 ± 0.04	≤5
intermediate SDS concentration ~0.02–1 mM SDS ^e				
75VP/25QVI	4.0 ± 0.1	130 ± 8	2.73 ± 0.08	130 ± 8
50VP/50QVI	13.0 ± 0.2	1160 ± 50	7.8 ± 0.2	580 ± 10
25VP/75QVI	10.3 ± 0.2	1100 ± 50	5.0 ± 0.1	530 ± 10
high SDS concentration ≥1 mM SDS ^f				
75VP/25QVI	0.00		1.00 ± 0.05	60 ± 5
50VP/50QVI	0.00		1.50 ± 0.06	30 ± 5
25VP/75QVI	0.00		3.00 ± 0.1	20 ± 5

^a[polymer] = 100 ppm. ^bAdsorption from 10 mM NaCl aqueous solution. ^cAdsorption from 100 mM NaCl aqueous solution. ^dWhen it is not possible to resolve the layer thickness (thin adsorbed layer), the thickness is given as ≤5 Å. ^eValue refers to the peak value, which occurs at different SDS concentrations for the different polymers. ^fValues given for highest SDS concentration of 9.4 mM SDS.

adsorbed than from the corresponding SDS mixtures with 75VP/25QVI. As the concentration of surfactant was further increased from 0.02 mM to 0.68 mM SDS, the adsorption of 50VP/50QVI/SDS and 25VP/75QVI/SDS showed sharp increases in the adsorbed amount to 13.0 and 10.3 mg/m², respectively. The corresponding maxima in layer thickness were about 1100 Å, indicating that large amounts of complexes adsorbed at the hydrophilic surface. The maximum amounts adsorbed at 100 mM NaCl were about 40% lower for 50VP/50QVI/SDS and 50% lower for 25VP/75QVI/SDS, compared to the values at 10 mM.

The adsorbed amount decreased in all cases to significantly lower values of ≤1.00 ± 0.06 mg/m², independently of the ionic strength, when the polyelectrolyte/SDS solutions were replaced with neat salt solution, see Figure 7a. At same time, the layer thickness of 75VP/25QVI/SDS in 0.06 and 0.20 mM SDS, respectively, significantly increased from 45 ± 5 and 130 ± 8 Å to 80 ± 6 and 680 ± 20 Å when the polymer/surfactant mixture is diluted with 10 mM NaCl. The corresponding increase in the adsorbed layer thicknesses at high ionic strength was approximately 100 Å in presence of 0.06 mM and 0.20 mM

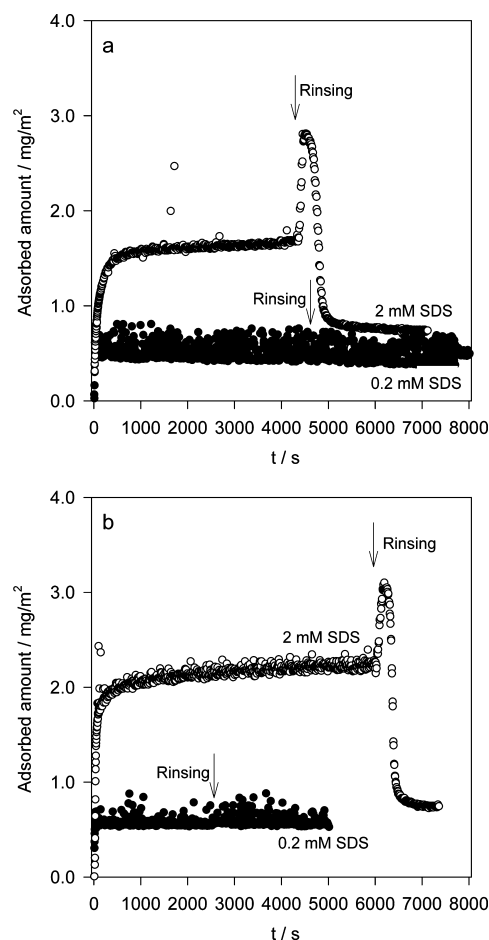


Figure 5. Effect on the 50VP/50QVI/SDS layer on silica, adsorbed from (a) 10 and (b) 100 mM NaCl solution, when the solution was diluted with the corresponding neat salt solution. The polymer concentration was fixed at 100 ppm and the SDS concentration was as indicated in the figure. Dilution of the polymer surfactant solution was started as indicated by arrows, after the adsorption of complexes from premixed solutions had reached a plateau.

SDS, respectively, to 190 ± 10 Å and 280 ± 10 Å (compare Figures 4a and 7a). Finally, the dilution of mixtures of 50VP/50QVI or 25VP/75QVI with SDS yielded in all cases significant lower thicknesses of ≤250 Å and 150 ± 8 Å in 10 mM and 100 mM NaCl, respectively (compare Figures 4b and 7b).

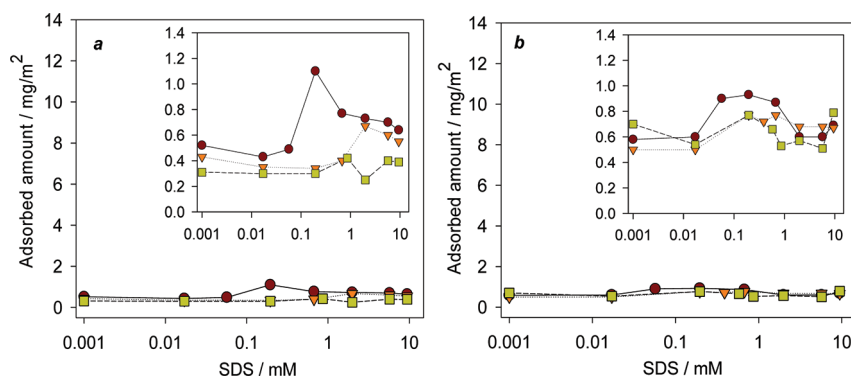


Figure 6. Effect of replacing (“rinsing”) the polymer/surfactant solution with (a) 10 and (b) 100 mM NaCl solution on the adsorbed amount of 75VP/25QVI/SDS (circles), 50VP/50QVI/SDS (triangles), and 25VP/75QVI/SDS (squares) on silica. The dilution with salt solution (rinsing) was started after the adsorption of complexes from premixed solutions had reached a plateau value. The polymer concentration was fixed at 100 ppm. The inset gives a magnification of the y-axis to illustrate that there is still an adsorption maxima, although very small.

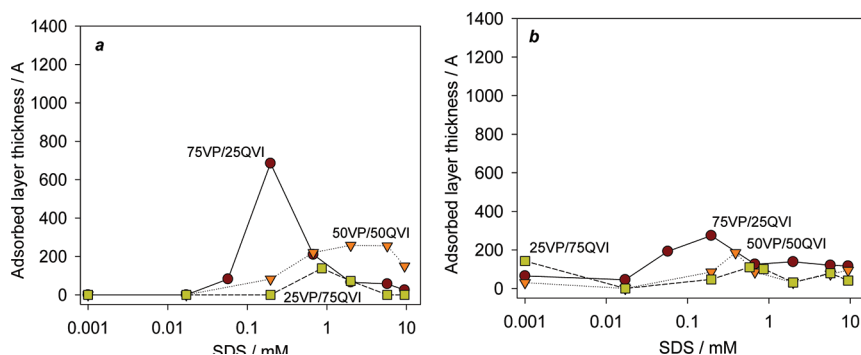


Figure 7. Effect of replacing (“rinsing”) the polymer/surfactant solution with (a) 10 and (b) 100 mM NaCl solution on the layer thickness of 75VP/25QVI/SDS (circles), 50VP/50QVI/SDS (triangles) and 25VP/75QVI/SDS (squares) on silica. The dilution with salt solution (rinsing) was started after the adsorption of complexes from premixed solutions had reached a plateau. The polymer concentration was fixed at 100 ppm.

High SDS Concentration Reduces Adsorbed Amount. With further increase in surfactant concentration, the amount adsorbed from a mixed solution decreased steeply with increasing SDS concentrations and reached values until no adsorption of copolymer/surfactant was observed in the presence of high concentrations of SDS (9.4 mM). By contrast, at high concentration of salt (100 mM) the amount adsorbed was significantly higher also at 9.4 mM SDS (Figures 3a and 3b, Table 3), and the amount adsorbed increased with the charge density of the polymer. As apparent from Figure 4, the layer thickness was slightly higher than at very low SDS concentration. When the cuvette was flushed with salt solution, in both 10 mM and 100 mM NaCl at ≥ 2 mM SDS, we observed a rapid increase in the adsorbed amount within the first few minutes after rinsing (data for the 50VP/50QVI/SDS system is shown in Figure 5.) This phenomenon, which has also been observed for the other polymer surfactant mixtures,³³ can be directly related to a passing through the adsorption maximum during the dilution process. Once the solution has been sufficiently diluted to reach the low SDS concentration region, the adsorbed amount decreased to reach a steady state value around or below 1 mg/m^2 (compare Figures 3 and 6) accompanied by an increase in the layer thickness (Figures 4 and 7), in particular at low ionic strength (Figures 4a and 7a). It is clear that this is linked to the lowering of the surfactant concentration.

3.3. SDS Addition to a Preadsorbed Layer of 50VP/50QVI on Silica. Adsorption of 50VP/50QVI/SDS complexes was studied on silica in the presence of 100 mM NaCl. SDS was

added to the preadsorbed polymer layer without removing the polymer (100 ppm) from bulk solution. The change in adsorbed amount and thickness versus time were measured while the SDS concentration was sequentially increased, and the data are shown in Figures 8 and 9, respectively. After each addition of SDS, the adsorbed amount was allowed to reach

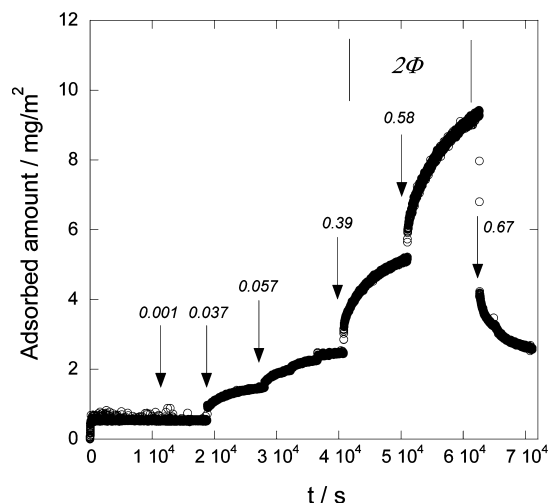


Figure 8. Adsorption on silica as a function of time in presence of 50VP/50QVI (100 ppm) in 100 mM NaCl with sequentially increasing the SDS concentration (in mM). The shaded area indicates the two-phase region.

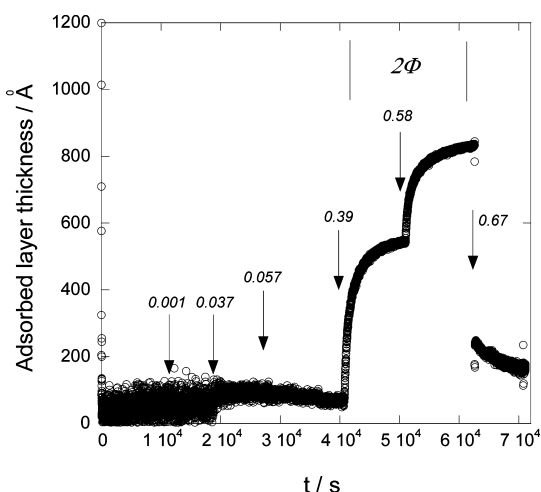


Figure 9. Adsorbed layer thickness on silica as a function of time in presence of 50VP/50QVI (100 ppm) and 100 mM NaCl, when sequentially increasing the SDS concentration (in mM). The data are recorded at the same time as the data presented in Figure 8a.

steady state before the next SDS addition was made. Figure 8 shows that no effect on the adsorbed amount was observed at low levels of added surfactant. As the concentration of SDS was increased to 0.04 mM, again a sharp increase in the adsorbed was observed. With further increase in surfactant concentration, the adsorbed amount gradually increases over a broad range of SDS concentration, until macroscopic phase separation occurred at 0.4 mM SDS. In the phase separation region the adsorbed amount increased steeply with SDS concentration, indicating that the binding of SDS was highly cooperative. Finally, at high surfactant concentration beyond the phase separation region, the adsorbed amount decreased significantly, showing that the polymer/surfactant complex formed under this high surfactant concentration has markedly less affinity to the surface.

The effect on the layer thickness of SDS addition to preadsorbed polymer is shown in Figure 9. No influence on the layer thickness by changing the SDS concentration was observed below 0.04 mM SDS. As discussed above, desorption of 50VP/50QVI on silica yielded in a very thin film, giving average layer thickness below 5 Å, which is below the limit where the thickness can be determined independently with ellipsometry as it is coupled with the refractive index value at low adsorbed amount (see Experimental Section). With further increase in SDS concentration, the adsorbed layer expanded to approximately 60 Å, until a macroscopic phase separation occurred at 0.4 mM SDS. As observed for the adsorbed amount, the layer thickness steeply increases with the surfactant concentration in the phase separation region. Above the phase separation region and at high SDS concentration the layer thickness was significantly decreased in parallel to the adsorbed amount.

The results show that maximum adsorption was obtained at a surfactant concentration close to the phase separation region. At higher SDS concentration, the complex partly desorbed from the surface. It is interesting to note that below 0.4 mM SDS the thickness of the layer is constant, while the adsorbed amount increases between about 0.04 mM SDS. This suggests that the layer has the same dimensions, while more material is accumulated at the interface. The likely explanation is that more SDS is accumulated in the polyion layer with increasing

SDS concentration in this range. This is a further evidence that the polyion adsorption leads to a charged reversal of the negatively charged silica surface.

4. DISCUSSION

4.1. Adsorption of Copolymers onto Solid Surfaces.

As mentioned in the Experimental Section, 75VP/25QVI, 50VP/50QVI, and 25VP/75QVI contain 25, 50, and 75 wt % quaternized vinylimidazol monomers, respectively. In this study, we used both silica and hydrophobized silica surfaces and the experiments were carried out in neat water and in the presence of various concentrations of salt, see Figure 2 and Table 2.

The results for the polymer adsorption on the oppositely charged silica surface are according to what is expected from theory⁴⁴ and our previous experimental studies of other polyelectrolytes.⁴⁵ Lower adsorbed amounts were observed for 25VP/75QVI on silica compared to those for the copolymers 75VP/25QVI and 50VP/50QVI. This is most likely due to the high cationic charge, since a lower amount of high cationic charge density polymer is required to compensate for the negative charges of the surface. Because of the electrostatic attraction between the negatively charged surface and the cationic polymers, the positively charged monomer subunits will attempt to neutralize any opposite charge present on the surface. Thus, the polymer will generally remain very close to the surface. Depending on the charge density of the polymers, adsorption commonly results in an overcompensation of the surface charge. In such a case, the adsorption of polymer onto the surface is limited by the electrostatic repulsion between segments within the adsorption layer. Thus, one would expect that increase in ionic strength would lead to an increase in adsorbed amount as observed by Samoshina et al.⁴⁵ Indeed, we observed that the adsorbed amount slightly increases with an increase in the ionic strength at low ionic strength, and a more significant increase in adsorbed amount plateau values was observed for 100 mM NaCl.

Adsorption of cationic copolymers onto the oppositely charged silica surface is driven by the electrostatic attraction and in this respect it is basically different from the polymer adsorption onto a noncharged hydrophobic surface. Polyelectrolyte adsorption on hydrophobic surfaces is also less studied, both experimentally and in terms of modeling. We will therefore discuss this in more detail. The first important issue is the way the hydrophobic surface is prepared and the resulting surface properties. Chemical modification of silica by reactions with, e.g., octyldimethylchlorosilane, yields hydrophobized silica surface.⁴⁸ The main reactions in forming the hydrophobized surface is the self-assembly by means of horizontal polymerization of the alkylchlorosilane on the surface, covalent attachment to the silanol groups of the silica surface, but also vertical polymerization might occur. For a more complete discussion of the silanization, the paper by Feedeov is strongly recommended.⁴⁸ They also showed that octyldimethylchlorosilane in gas phase as used in this study gives a high water contact angle ($\sim 100^\circ$) with very low hysteresis, suggesting a smooth and homogeneous surface. For this type of very hydrophobic surface, hydrophobic interactions are expected to be the main driving force for polymer adsorption. In fact, strong hydrophobic interactions may overcome the loss of entropy and therefore contribute to considerably adsorption of cationic polymers onto a hydrophobized silica surface.²⁰ For instance,

the two cationic cellulose derivatives, LM-200 and JR-400, showed higher adsorbed amounts and thicker adsorbed layers on hydrophobized silica than on silica.¹⁷ In addition, Poncet et al. have reported that the adsorbed amount of hydrophobically modified poly (sodium acrylates) on hydrophobized silica significantly increased with an increase in the hydrophobicity of the polymer.⁴⁹ In a recent study, the adsorption of a series of cationic copolymers of varying hydrophobicity on hydrophobized silica was investigated by in situ ellipsometry by Santos et al.³³ They concluded that the plateau value of the adsorbed amount increased with increasing hydrophobicity as inferred from the chemical structures of the neutral comonomers. All the latter polymers formed rather thin layers, which is in line with the strong hydrophobic interaction with the surface.

Our results, summarized in Table 2, are in good agreement with these observations. All cationic copolymers, i.e., 75VP/25QVI, 50VP/50QVI, and 25VP/75QVI, adsorbed at the hydrophobic surface and we expect that hydrophobic interactions also play a role for the polymer adsorption studied here. The isotherms in Figure 2 show that 75VP/25QVI and 50VP/50QVI give higher adsorbed amounts on hydrophobized silica, than on silica. 75VP/25QVI has more hydrophobic character than 50VP/50QVI and is therefore less sensitive to changes of the ionic strength. In fact, 75VP/25QVI adsorption in the presence and absence of salt yielded almost same plateau values of ~ 1.0 mg/m². A similar trend is also observed for 50VP/50QVI, for which the adsorption isotherm (Figure 2) is not markedly affected by increasing the salt concentration from 10 mM to 100 mM NaCl. Only in water, a slightly lower plateau adsorption value of ~ 0.8 mg/m² was found.

Because of the high 25VP/75QVI polymer charge density, the adsorption on hydrophobized silica is quite sensitive to changes in the ionic strength. As evident from the adsorption isotherms, increasing the concentration of salt results in a significant increase in the adsorbed amount (Figure 2). Again, salt screens the electrostatic repulsive interactions between the cationic polymer charges. It is of interest to note that on hydrophobized silica the 25VP/75QVI isotherms do not show any leveling off to a true plateau within the concentration range studied. Moreover, as the concentration of salt was increased from 10 mM to 100 mM NaCl, a dramatic increase in the layer thickness from 45 Å to 150 Å (Table 2) was observed. Despite the higher adsorbed amounts on hydrophobized silica, in neat water the adsorbed layers of 75VP/25QVI and 50VP/50QVI were significantly thinner and close to the layer thickness on silica (≤ 5 Å), which implies that the polymer layers were much denser on hydrophobized silica than on silica. However, also for 75VP/25QVI and 50VP/50QVI, the mean layer thicknesses significantly increased with salt concentration (to about 100 Å, see Table 2). This change was accompanied by a significant increase also in adsorbed amount. Finally, when comparing the isotherms at high ionic strength, 100 mM NaCl, the layer thicknesses strongly increases with the fraction of cationic groups. An increase in the layer thickness as an effect of increasing the ionic strength was also observed under certain conditions by An et al., who studied the adsorption of an amphiphilic and weakly charged block copolymer poly(2-(dimethylamino)ethyl methacrylate-block-methyl methacrylate) (poly-(DMAEMA-*b*-MMA)) containing 70% DMAEMA on hydrophobized silica with neutron reflectometry.⁵⁰ They discussed the reason for their findings in relation to the study of polymer brushes by Pincus.⁵¹ He presented a simple scaling

theory to describe the thickness of a polymer layer as a consequence of counterion distribution, which was used to calculate the disjoining pressure between opposing polymer layers. He found that if the electrolyte concentration is such that the Debye length is shorter than the thickness of the brush (or in our case the polymer layer), which is the situation at the highest ionic strength used in the present study, then the counterions are located within the layer and their gain in entropy will cause the polymer to swell (osmotic swelling). The presence of large number of (hydrated) ions may thus cause a swelling of the surface polymer layer (Figure 10).

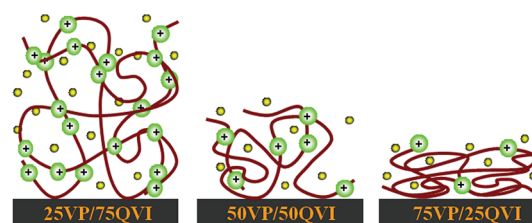


Figure 10. Schematic representation of the copolymers adsorbed at high ionic strength (100 mM NaCl) at hydrophobized silica surface. The higher the fraction of cationic groups, the longer the loops and tails. Counterions (spheres) with hydration shell (not indicated) are accumulated close to the positively charged groups.

4.2. Adsorption/Formation of Copolymer/SDS Complexes on Silica. In mixed solutions of oppositely charged polymers and surfactants, associative phase separation is a well-known phenomenon and we will start our discussion by highlighting some of the main features.⁵² The main driving force for the formation of the complexes is the release of counterions from the polyelectrolyte and the ionic surfactant upon association, which leads to a significant entropy gain. The polymer–surfactant association can therefore be modulated by the presence of electrolytes. In fact, the addition of salt can lead to dissolution of the concentrated phase, if the polyion–surfactant ion association is purely electrostatic. The interaction between surfactant and the polymer are often cooperative, i.e., the polymer interaction promotes surfactant micellization, as a consequence of the reduced water–hydrocarbon contact, and/or by decreasing the headgroup repulsion between surfactants in the micelle. Phase separation and redissolution of oppositely charged complexes can generally be explained as function of surfactant concentration as follows: In the presence of a low concentration of surfactant, the molecules bind noncooperatively to the polymer chain. As the surfactant concentration is increased, surfactant aggregates are formed on the polymer chain at a critical aggregation concentration (*cac*). Eventually, the increase of surfactant concentration leads to charge neutralization of the polyelectrolyte and the solubility of the formed complexes decreases. Thus, the solution becomes turbid and the aggregates precipitate. It should be noted that this process is generally kinetically controlled and consequently the adsorption in this regime occurs under nonequilibrium conditions.^{53,54} When the surfactant concentration is further increased, a second cooperative surfactant binding step to the polyion may occur (*cac2*).^{33,55,56} This step requires an additional hydrophobic interaction between the polymer and the surfactant, giving rise to a reversal of the charge and, finally, a redissolution of the complexes. As a result, the solution becomes clear again. Various aspects of bulk properties in

polymer/surfactant solutions have been discussed in a number of reviews.^{7,52,57–59}

Decrease in Solubility Drives the Deposition/Formation of Polymer/SDS Complexes. We have previously discussed that the polymer itself adsorb to the silica surface because of the attractive interaction with the oppositely charged surface. However, SDS does not adsorb on silica itself,¹⁷ and due to the electrostatic repulsion between the ionized silanol groups on the silica surface and the negatively charged dodecylsulfate ions, one would expect that anionic surfactant molecules are depleted from the interfacial region unless they are in a complex with the polymer.

At low surfactant concentration, the adsorption is controlled by the polymer adsorption, likely to be driven by electrostatic attractive interaction. The cooperative binding of SDS to the oppositely charged polymer at the cac occurs well below the critical micelle concentration (cmc). As a consequence, significant changes in the adsorption from copolymer/surfactant mixtures are expected to occur at a surfactant concentration below the cmc. Indeed, we observed that a marked increase in adsorbed amount is observed far below the surfactant cmc (cf. Figure 3). Since the polymer surfactant complex is now less cationic this cannot be explained by electrostatic attractive interaction between the surface and the polymer complex. In fact the adsorbed amount peaks at a SDS concentration that corresponds closely to the concentration of cationic charges of the different polymers as indicated in the figure. The fact that peak in adsorbed amount scales so well with the charge density of the polyelectrolytes suggests that the cac and hence the concentration of noncomplexed surfactant are low. The adsorption behavior is governed by the net charge of the polymer–surfactant complex as the surfactant binding to the oppositely charged copolymers results in a significant decrease in the solubility of the complexes, which leads to very high adsorbed amounts (Table 3), up to 20 times the amount adsorbed for the neat polymer (Table 2), as seen in Figure 3a,b. This mechanism of adsorption, being driven by a decrease in solubility is expected to give a maximum in adsorption when stoichiometric polymer/surfactant complexes are formed as observed in this study. Previous work revealed the effect of SDS on the adsorption behavior of three different cationic hydroxyethyl celluloses (JR-125, JR-400, and JR-30M) at silica surface.¹⁷ Adsorption from these systems was observed to increase dramatically at surfactant concentration slightly below the bulk phase separation region, which suggested that the decrease in solubility of the complex causes the large increase in deposition on the surface.

The importance of electrostatic interactions between the polyion and the surfactant was verified by the fact that 50VP/50QVI/SDS and 25VP/75QVI/SDS solutions were found to give significantly higher adsorbed amounts and layer thicknesses than 75VP/25QVI/SDS at low ionic strength of the bulk solution. This is most likely due to the high cationic charge density of these polymers (3.32 and 4.18 mequiv/g, respectively), which require higher amounts of oppositely charged surfactant to compensate for the positive charges than for 75VP/25QVI (1.20 mequiv/g).

An increase in salt concentration from 10 to 100 mM NaCl decreases the electrostatic attraction between the polyion and the oppositely charged surfactant, but also decreases the repulsion between and within the complex particles. It is interesting to note that for the 50VP/50QVI and 25VP/75QVI complexes with SDS, the maxima in adsorbed amount occur at

0.63 and 0.97 mM SDS, respectively, at 10 mM NaCl, whereas in 100 mM NaCl, they occur at 0.4 and 0.63 mM SDS, respectively. These values should be compared with the amount needed for charge equivalence, which at a polymer concentration of 100 ppm is expected to occur at 0.33 and 0.42 mM SDS for the 50VP/50QVI and 25VP/75QVI, respectively. It should also be noted that the cmc of SDS is 5.7 and 1.5 mM in 10 and 100 mM NaCl, respectively.⁴⁷ The maxima in adsorption at low ionic strength (10 mM NaCl) occur above the calculated point of charge neutralization. This can be an affect of that not all surfactant molecules bind to the polymer. In fact, increasing the ionic strength move the maxima in adsorption to lower concentration of SDS, as also observed for cmc of the neat SDS solution. This may be an effect of a decrease in cac with increasing salt promotes of the surfactant to the polymer. The 75VP/25QVI/SDS adsorption peaks 0.2 mM SDS at both 10 and 100 mM NaCl, which is higher than the expected point of charge neutralization at 0.12 mM. It is noteworthy, that unlike for the more charged polymers, the position of the maxima in adsorption from the surfactant polymer mixture is not affected by the ionic strength. It should also be noted that for the neat polymer adsorption lowest effect of ionic strength on adsorption, in particular on the hydrophobic surface, is observed for the polyelectrolyte with the lowest charge density, 75VP/25QVI. As discussed in a number of studies, the effect of added salt on the associative phase separation for mixtures of polyelectrolyte and oppositely charged surfactants is complex and strongly dependent on the system.^{60,61} In fact, both increase and decrease in the phase separation region has been reported. For instance, poly{[2-(propionyloxy) ethyl]trimethylammonium chloride} (PCMA)/SDS mixed systems showed that the phase separation occurs over a wider SDS concentration range at higher ionic strength to 100 mM NaCl.⁶² On the other hand, studies of anionic polysaccharide sodium hyaluronate (NaHy) and the cationic surfactant tetradecyltrimethylammonium bromide (C14TABr), show that low concentrations of NaBr reduces the two-phase region, which disappears at 250 mM NaBr, whereas high NaBr concentrations (≥ 500 mM) leads to segregative phase separation.⁶³ The present study confirms that the effect of ionic strength depends on the polymer/surfactant system as increasing ionic strength only influences the adsorption of SDS mixtures with highly charged polymers 50VP/50QVI and 25VP/75QVI. For these polymers, we observed both a decrease in adsorbed amount of material and a shift in adsorption maxima to lower SDS concentrations. The reason for this can be that less surfactant is needed to neutralize the complex, hence the shift of the adsorption maxima to lower SDS concentration. The decrease in the adsorbed amount with increasing ionic strength can possibly be explained as either the effect of the difference in aggregate composition or as a consequence of the shift in balance from surface deposition to bulk aggregation. The reduction in repulsion between complexes in solution as a consequence of electrostatic screening can promote aggregation rather than deposition.

High Surfactant Concentration Can Solubilize Polymer/SDS Complexes and Decrease Adsorption. Polyelectrolytes and oppositely charged surfactants form precipitates, which in many cases can be resolubilized by addition of excess surfactant.⁶⁴ The interaction is more favorable the longer the surfactant hydrocarbon chain and the presence of hydrophobic functionalities on the polymer also favors resolubilisation.⁷

The amount and thickness of the layer adsorbed from polymer/surfactant mixtures were found to decrease significantly with increasing surfactant concentration well above the neutralization point as seen in Figures 3 and 4. It is clear that this decrease can be attributed to a recharging of the polymer/surfactant complexes because of additional association of surfactant to the polymer. The sharp decrease is a manifestation of the cooperativity of this process, that is the second cooperative surfactant binding step to the polymer (cac2).^{55,56} However, it is noteworthy that in contrast to our previous studies, we do not observe an increase in thickness of the layer at high surfactant concentration, which was explained as a swelling of the aggregates at the surface due to internal electrostatic repulsion.¹⁷ In this early study, we used a low concentration of added electrolyte (max 10 mM), whereas in the present study, the concentration added up to 100 mM. This clearly demonstrates the effect of added salt and the internal electrostatic repulsion for the polymer/surfactant layer properties. As mentioned above, the adsorption of 75VP/25QVI/SDS is qualitatively similar to that obtained for 50VP/50QVI and 25VP/75QVI/SDS, but both the amounts adsorbed and the corresponding layer thicknesses are significantly smaller. This can be attributed to the lower cationic charge density of 75VP/25QVI as discussed above.

Finally, at low ionic strength and high surfactant level, 10 mM SDS, we do not observe any adsorption from premixed solutions. This implies that complexes under these conditions are negatively charged with no affinity to the negatively charged surface. However, in the presence of 100 mM NaCl considerable adsorption of the copolymer/surfactant complexes was observed even at high concentration of SDS (Figure 3b). This implies an effect of charge screening, which allows considerable amounts of complex to adsorb onto the negatively charged surface. As would be expected, the amount of complexes adsorbed at high surfactant concentration was found to increase with increasing cationic charge density of the polymer, with decreasing excess of SDS, and with increasing ionic strength (Figure 3). Thus, at high ionic strength, 1.05, 1.50, and 2.90 mg/m² for 75VP/25QVI, 50VP/50QVI, and 25VP/75QVI/SDS, respectively, were found. Despite the higher adsorbed amount of the 25VP/75QVI/SDS complex, the layer thickness is similar to the values observed for 50VP/50QVI and 75VP/25QVI/SDS. This implies less dense layers on silica of the two latter complexes at high ionic strength.

It is interesting that many of the above trends regarding the adsorbed amount vanish after dilution with salt solutions. The difference between the various copolymer-SDS complexes in the adsorbed amount that remains after dilution is rather small (Figure 6), but the weak trend observed is more in line with the adsorption of the neat polymer in Figure 2, that is, an increase in adsorption with a decrease in charge density. This implies that little excess surfactant remains on the surface after dilution. Comparing panels a and b in Figure 6, we also see that the adsorption generally increases with increasing ionic strength of the salt solution used for dilution, again in accordance with the ionic strength trend in Figure 2. However, the initial conditions of deposition nevertheless seems to affect the layer properties after dilution, because for each polymer, a weak maximum in adsorbed amount is still observed, after dilution, around the SDS concentration giving the maximum initial adsorbed amount.

Adsorption from Polyelectrolyte and Oppositely Charged Surfactant Mixtures Is Path Dependent. Previous work has

shown that the formation of the adsorbed layer is dependent on the path of by which the layer is obtained.^{16,17,53} This can be used to obtain a polymer-surfactant surface layer trapped in a nonequilibrium state, which is frequently used in many applications.^{19,20,33} For this purpose, we investigated to what extent the studied system is determined by the mode of adding the surfactant and polymer is affecting the adsorption behavior. This was done by comparing the adsorption from premixed polymer/surfactant solution and by sequential increase of surfactant concentration in the polymer solution. Figure 11

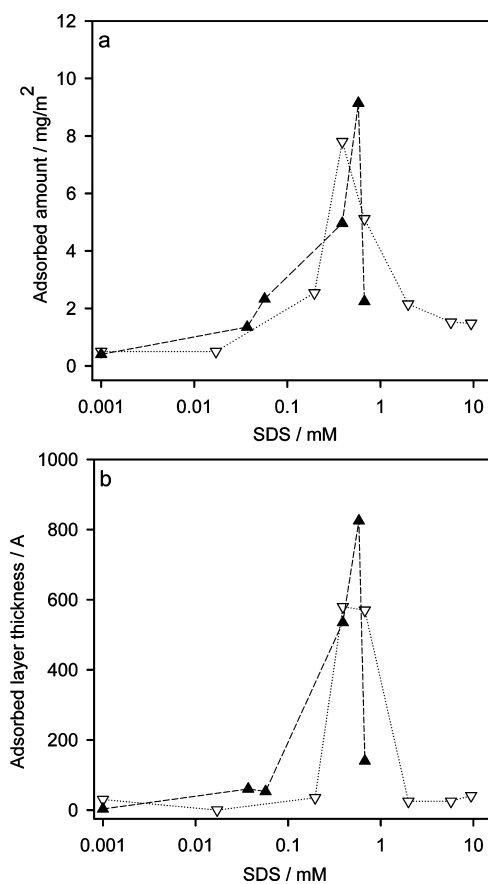


Figure 11. (a) Amount of the complex adsorbed from premixed 50VP/50QVI/SDS solutions on silica (open triangles) and the effect of SDS addition on the adsorbed amount to preadsorbed 50VP/50QVI layers on silica (filled triangles). (b) Adsorbed layer thickness formed from premixed 50VP/50QVI/SDS solutions on silica (open triangles) and the effect of sequential increase of SDS concentration on the preadsorbed 50VP/50QVI layers on silica (filled triangles). The polymer concentration was fixed at 100 ppm. The NaCl concentration was 100 mM.

compares the data from Figures 8 and 9 with those from Figures 3 and 4. Figure 11a shows the amount of the complexes adsorbed from premixed 50VP/50QVI/SDS solutions compared to the effect of SDS addition on the adsorbed amount to a preadsorbed 50VP/50QVI layer on silica. The corresponding effect on the adsorbed layer thickness is shown in Figure 11b. When the bare surface was exposed to premixed 50VP/50QVI and SDS solutions, changes in the adsorbed amount were qualitatively similar to the results obtained when the SDS concentration was sequentially increased in the polymer solution. However, we note two marked differences between the two sets of data, namely that the adsorbed amount at SDS

concentration slightly below the peak in adsorption is higher and that the peak in adsorption is shifted toward higher SDS concentration for the sequential addition of the surfactant relative to the premixed solution. It is clear that this is a kinetic effect, that is a balance between the rate of adsorption and the rate of formation of the polymer/surfactant complexes. From Figure 8, we note that the kinetics of adsorption is particularly slow in the two-phase region. This implies that the complexes are formed as the surfactant concentration is increased. Thus, additional surfactant is needed and the maximum is shifted toward higher surfactant concentration for the case where the surfactant is sequentially added.

Another manifestation of the importance of the kinetics of the process is the effect of dilution of the bulk solution illustrated in Figure 5. The maxima in the adsorbed amount, observed when diluting a polymer surfactant solution at surfactant concentrations beyond the 2-phase region within the first few minutes is likely to be related to the decreased solubility of the copolymer/surfactant complex as we pass the two-phase region. The decreased solvency upon dilution is a very important factor in controlling the adsorption in mixed polymer/surfactant solutions, and explains why additional adsorption can be induced by the dilution of a mixed solution. We have previously observed the same phenomena for a range of polymer surfactant systems.^{17,19,33,65,66} The deposition upon dilution is highly relevant for a range of applications such as hair shampoo. Such formulation usually contains large excess of surfactant and during dilution the system phase separation and an increased deposition (of a particular active component) is obtained. Recently, we have shown that the system can be tuned in such a way that the deposition can be made selective for a certain type of surface.⁶⁵

5. CONCLUSIONS

The adsorption of the cationic VP/QVI copolymers onto charged or hydrophobized silica surfaces is influenced by the polymer charge density. The adsorbed amount decreases with increasing polymer charge density and, consequently, an increase in ionic strength leads to an increase in adsorbed amount. These effects of polymer charge density and ionic strength were, in fact, even more pronounced on the hydrophobic surface.

The maxima in adsorption/deposition of polymer–SDS complexes occur close to the point of phase separation slightly above the SDS concentration corresponding to charge equivalence in the phase separation region. This suggests that the cac is low and that the adsorption behavior is governed by the net charge of the polymer–surfactant complexes. The amount and thickness of the layer adsorbed from polymer/surfactant mixtures were found to decrease significantly with increasing surfactant concentration well above charge equivalence. This decrease can be attributed to a recharging of the polymer/surfactant complexes because of the additional association of surfactant to the polymer, where the association between SDS and uncharged VP units presumably plays an important role.

Above the adsorption maxima, the adsorption of polymer–surfactant complexes increased with increasing polyion charge density, with decreasing excess surfactant concentration, and with increasing ionic strength. These observations imply that the complexes in this region are net negatively charged, but that the total charge on the complex is less for a more highly charged cationic copolymer.

After dilution with salt solution, the variation in adsorbed amount was less, and the trends with polyion charge density and ionic strength of the solution were now the same as for the adsorption of the polyion alone. This suggests that little surfactant may remain after dilution.

The adsorption from polyelectrolyte and oppositely charged surfactant mixtures is path dependent as the sequential addition of surfactant to the polymer gives a different adsorption behavior compared to a premixed solution, namely adsorption peaks at a higher surfactant concentration compared to that of the premixed solution.

The decreased solvency upon dilution is a very important factor in controlling the adsorption from mixed polymer/surfactant solutions, and explains why additional adsorption can be induced by the dilution of a mixed solution. These effects can be utilized in a range of applications and tuned by the polymer charge density, hydrophobic modification of the polymer, and the surfactant system.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Hunting, A. L. L. *Cosmet. Toiletries* **1984**, *99* (6), 57–60.
- (2) Lochhead, R. Y. *Soap Cosmet., Chem. Spec.* **1992**, *68* (10), 42.
- (3) Reich, C. In *Surfactants in Cosmetics*, 2nd ed.; Rieger, M. M., Rhein, L. D., Eds.; Marcel Dekker: New York, 1997; Vol. 68.
- (4) Goddard, E. D. *Colloids Surf.* **1986**, *19* (2–3), 255–300.
- (5) Goddard, E. D. *Colloids Surf.* **1986**, *19* (2–3), 321–309.
- (6) Brackmann, J. C.; Engberts, J. B. F. N. *Chem. Soc. Rev.* **1993**, *22* (2), 85–92.
- (7) Lindmann, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993; pp 203–276.
- (8) Kwak, J. C. T. *Polymer–Surfactant Systems*; Marcel Dekker: New York, 1998.
- (9) Holmberg, K.; Jönsson, B.; Kronberg, B.; Lindman, B. *Surfactants and Polymers in Aqueous Solution*, 2nd ed.; John Wiley & Sons: Chichester, U. K., 2002.
- (10) Ananthapadmanabhan, K. P.; Mao, G. Z.; Goddard, E. D.; Tirell, M. *Colloids Surf.* **1991**, *61*, 167–174.
- (11) Shubin, V. *Langmuir* **1994**, *10* (4), 1093–1100.
- (12) Shubin, V.; Petrov, P.; Lindman, B. *Colloid Polym. Sci.* **1994**, *272* (12), 1590–1601.
- (13) Claesson, P. M.; Fielden, M. L.; Dedinaite, A.; Brown, W.; Fundin, J. J. *Phys. Chem. B.* **1998**, *102* (7), 1270–1278.
- (14) Fielden, M. L.; Claesson, P. M.; Schillen, K. *Langmuir* **1998**, *14* (19), 5366–5375.

- (15) Dedinaite, A.; Claesson, P. M. *Langmuir* **2000**, *16* (4), 1951–1959.
- (16) Dedinaite, A.; Claesson, P. M.; Bergstrom, M. *Langmuir* **2000**, *16* (12), 5257–5266.
- (17) Terada, E.; Samoshina, Y.; Nylander, T.; Lindman, B. *Langmuir* **2004**, *20*, 1753–1762.
- (18) Terada, E.; Samoshina, Y.; Nylander, T.; Lindman, B. *Langmuir* **2004**, *20*, 6692–6701.
- (19) Samoshina, Y.; Nylander, T.; Lindman, B. *Langmuir* **2005**, *21* (10), 4490–4502.
- (20) Nylander, T.; Samoshina, Y.; Lindman, B. *Adv. Colloid Interface Sci.* **2006**, *123–126*, 105–123.
- (21) *Handbook of Polyelectrolytes and Their Applications*, Tripathy, S. K.; Nalwa, H. S., Eds.; American Science Publisher: Stevenson Ranch, CA, 2002.
- (22) Goddard, E. D. *J. Colloid Interface Sci.* **2002**, *256* (1), 228–235.
- (23) Mears, S. J.; Cosgrove, T.; Obey, T.; Thompson, L.; Howell, I. *Langmuir* **1998**, *14*, 4997.
- (24) Cosgrove, T.; Mears, S. J.; Obey, T.; Thompson, L.; Wesley, R. D. *Colloids Surf.* **1999**, *149* (1–3), 329–338.
- (25) Imae, T. *Advanced Chemistry of Monolayers at Interfaces: Trends in Methodology and Technology*; Academic Press: New York, 2007; Vol. 14.
- (26) Lu, J. R.; Su, T. J.; Thomas, R. K.; Penfold, J. *Langmuir* **1998**, *14*, 6261.
- (27) Manne, S.; Gaub, H. E. *Science* **1995**, *270* (no. 5241), 1480–1482.
- (28) Flemming, B. D.; Wanless, E. J.; Biggs, S. *Langmuir* **1999**, *15*, 8719.
- (29) Claesson, P. M. e. a. In *Physical Chemistry of Polyelectrolytes*; Radeva, T., Ed.; Marcel Dekker: New York, 2001; pp 447–507.
- (30) Somasundaran, P.; Krishnakumar, S. *Colloids Surf.* **1994**, *93*, 79–95.
- (31) Duffy, D. C.; Davies, P. B.; Creeth, A. M. *Langmuir* **1995**, *11*, 2931.
- (32) Svensson, A. V.; Huang, L.; Johnson, E. S.; Nylander, T.; Piculell, L. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2431–2442.
- (33) Santos, O.; Johnson, E. S.; Nylander, T.; Panandiker, R. K.; Sivik, M. R.; Piculell, L. *Langmuir* **2010**, *26*, 9357–9367.
- (34) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North Holland: Amsterdam, 1989.
- (35) Tiberg, F.; Landgren, M. *Langmuir* **1993**, *9* (4), 927–932.
- (36) Landgren, M.; Jonsson, B. *J. Phys. Chem.* **1993**, *97*, 1656–1660.
- (37) McCrackin, F. L.; Passaglia, E.; Stromberg, R. R.; Steinberg, H. L. *J. Res. Natl. Bur. Stand., Sect. A* **1963**, *67A* (4), 363–377.
- (38) de Feijter, J. A.; Benjamins, J.; Veer, F. A. *Biopolymers* **1978**, *17* (7), 1759–1772.
- (39) Nylander, T.; Tiberg, F.; Su, T. S.; Lu, J. R.; Thomas, R. K. *Biomacromolecules* **2001**, *2*, 278–287.
- (40) Vandoolaeghe, P.; Campbell, R. A.; Rennie, A. R.; Nylander, T. *J. Phys. Chem. C* **2009**, *113*, 4483–4494.
- (41) Benjamins, J. W.; Thuresson, K.; Nylander, T. *Langmuir* **2005**, *21*, 149–159.
- (42) Antippa, A. F.; Leblanc, R. M.; Ducharme, D. J. *Opt. Soc. Am. A* **1986**, *3*, 1794–1802.
- (43) Cuypers, P. A.; Corsel, J. W.; Janssen, M. P.; Kop, J. M. M.; Hermens, W. T.; Hemke, H. C. *J. Biol. Chem.* **1983**, *258*, 2426–2431.
- (44) Fleer, J. I.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, 1993.
- (45) Samoshina, Y.; Nylander, T.; Shubin, V.; Bauer, R.; Eskilsson, K. *Langmuir* **2005**, *21* (13), 5872–5881.
- (46) Angelescu, D. G.; Nylander, T.; Piculell, L.; Linse, P.; Lindman, B.; Tropsch, J.; Detering, J. *Langmuir* **2011**, *27*, 9961–9971.
- (47) Evans, D. F.; Mitchell, D. J.; Ninham, B. W. *J. Phys. Chem.* **1984**, *88*, 6344–6348.
- (48) Fadeev, A. Y.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7268–7274.
- (49) Poncet, C.; Tiberg, F.; Audebert, R. *Langmuir* **1998**, *14*, 1697–1704.
- (50) An, S. W.; Thirtle, P. N.; Thomas, R. K.; Baines, F. L.; Billingham, N. C.; Armes, S. P.; Penfold, J. *Macromolecules* **1999**, *32*, 2731–2738.
- (51) Pincus, P. *Macromolecules* **1991**, *24*, 2912–2919.
- (52) Piculell, L.; Lindman, B.; Karlström, G. In *Polymer–Surfactant Systems*; Kwak, J. C. T., Ed.; Marcel Dekker: New York, 1998; Vol. 77, pp 65–141.
- (53) Campbell, R. A.; Angus-Smyth, A.; Yanez Arteta, M.; Tonigold, K.; Nylander, T.; Varga, I. *J. Phys. Chem. Lett.* **2010**, *1*, 3021–3026.
- (54) Campbell, R. A.; Yanez Arteta, M.; Angus-Smyth, A.; Nylander, T.; Varga, I. *J. Phys. Chem. B* **2011**, *115*, 15202–15213.
- (55) Lynch, I.; Sjöström, J.; Piculell, L. *J. Phys. Chem. B* **2005**, *109*, 4258–4262.
- (56) Sjöström, J.; Piculell, L. *Colloids Surf., A* **2001**, *183–185*, 429–448.
- (57) Goddard, E. D.; Hannan, R. B. *J. Am. Oil chem. Soc.* **1977**, *54* (12), 561–566.
- (58) Kogej, K. *Adv. Colloid Interface Sci.* **2010**, *158*, 68–83.
- (59) Bain, C. D.; Claesson, P. M.; Langevin, D.; Meszaros, R.; Nylander, T.; Stubenrauch, C.; Titmuss, S.; von Klitzing, R. *Adv. Colloid Interface Sci.* **2010**, *155*, 32–49.
- (60) Mezei, A.; Ábrahám, A.; Pojják, K.; Mészáros, R. *Langmuir* **2009**, *25*, 7304–7312.
- (61) Wang, Y.; Kimura, K.; Huang, Q.; Dubin, P. L.; Jaeger, W. *Macromolecules* **1999**, *32*, 7128–7134.
- (62) Naderia, A.; Claesson, P. M.; Bergström, M.; Dédinaite, A. *Colloids Surf., A* **2005**, *253*, 83–93.
- (63) Thalberg, K.; Lindman, B.; Karlstrom, G. *J. Phys. Chem.* **1991**, *95*, 6004–6011.
- (64) dos Santos, S.; Gustavsson, C.; Gudmundsson, C.; Linse, P.; Piculell, L. *Langmuir* **2011**, *27*, 592–603.
- (65) Clauzel, M.; Johnson, E. S.; Nylander, T.; Panandiker, R. K.; Sivik, M. R.; Piculell, L. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2451–2462.
- (66) Svensson, A. V.; Johnson, E. S.; Nylander, T.; Piculell, L. *ACS Appl. Mater. Interfaces* **2010**, *2*, 143–156.