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Poly(ethylene oxide) Adsorption on Polystyrene Latex Particles in the Presence of Poly(styrenesulfonate sodium)

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ABSTRACT: The effect of a polyelectrolyte, poly(styrenesulfonate sodium) (PSS), on poly(ethylene oxide) (PEO) adsorption on the polystyrene latex (PSL) particle/water interface at different sodium chloride (NaCl) concentrations has been investigated by small-angle neutron scattering (SANS). Our study shows that in the absence of NaCl or with a low NaCl concentration, PSS forms a complex with PEO in the bulk solution and therefore strips PEO off from the latex particle surface because of the electrostatic repulsion between the latex particles and the PEO/PSS complexes. With increasing NaCl concentration, the electrostatic repulsions between the PEO/PSS complexes and PSL particles are reduced, and at the same time, PEO/PSS complexes break down and PEO adsorption is enhanced. With a further increase in NaCl concentration, PSS itself starts to adsorb on the PSL particles and competes with the PEO adsorption, which is then reduced.

Introduction

Polymer adsorption onto the colloidal interface has been extensively studied.[1] When two polymers that form complexes are present and one of them is adsorbing and the other is nonadsorbing, polymer adsorption will be affected, and a variety of situations can occur. The situation will become more complicated when the nonadsorbing polymer becomes adsorbing through changing other physiochemical parameters, such as the ionic strength. A complete understanding of this system is not straightforward, but the structure of the adsorbed polymer layer can provide much useful information.

In this study, polystyrene latex (PSL) particles dispersed in water with negative surface charges were used as the substrate. Poly(ethylene oxide) (PEO) has long been known to adsorb at this interface.[2−5] Poly(styrenesulfonate sodium) (PSS) is nonadsorbing when the ionic strength is low because of the electrostatic repulsion between the surface and the negatively charged polymer chains; however, with increasing ionic strength, this repulsion can be screened, and PSS becomes adsorbing.[6,7] It has also been shown that PSS and PEO can form complexes in solution.[8] Therefore, one can expect that in the systems studied here, in the absence of salt, PEO chains will adsorb on the colloidal particles surface, and the PSS chains in solution may either strip the PEO chains off or be physically connected to the surface by the PEO chains by the formation of an interpolymer complex. This will depend on the relative strength of the repulsion between the colloidal particle and the PSS chains and the interactions between PEO and PSS. In the presence of salt, PSS chains may also compete with PEO for adsorption and therefore change the PEO adsorption.

Among the many available techniques, a very useful and straightforward method for studying polymer adsorption at the colloid surface is small-angle neutron scattering (SANS), which can selectively focus on either the adsorbed polymer layers or the substrate colloidal particles by using the so-called contrast-matching strategy.[2,9−17] When the neutron scattering length density (SLD) of the substrate colloidal particles is matched to that of the solvent, denoted as core contrast matching, only scattering from the adsorbed polymer is visible. (The scattering from the free polymer in the solution is negligible compared with that from the adsorbed layer.) Under this contrast condition, the scattering from the adsorbed polymer layer as a function of the momentum transfer (Q), $I_{ll}(Q)$, can be described as[13,15]

$$I_{ll}(Q) = \bar{I}_{ll}(Q) + \tilde{I}_{ll}(Q) \tag{1}$$

where $\bar{I}_{ll}(Q)$ is the scattering from the average adsorbed polymer layer and $\tilde{I}_{ll}(Q)$ is the scattering from the concentration fluctuations in the adsorbed polymer. $\tilde{I}_{ll}(Q)$ can be directly related to the volume fraction profile of the adsorbed polymer, $\phi(z)$. Taking into account the finite resolution in the Q space and the size distribution of the substrate colloidal particles,[9,13] we obtained the following form for the scattering

$$\bar{I}_{ll}(Q) = \frac{6\pi\rho_{ls}^2\varphi_p}{Q^2 r_0}\left|\int_0^t \varphi(z)\exp(iQz)\,\mathrm{d}z\right|^2 \tag{2}$$

where ρ_{ls} is the difference between the SLDs of the adsorbed polymer layer and the solvent, which is normally referred to as the contrast, ϕ_p is the volume fraction, and r_0 is the mean radius of the substrate colloidal particles. Previous studies have indicated that a $\tilde{Q}^{-4/3}$ term is adequate for describing the fluctuation term, $\tilde{I}_{ll}(Q)$.[18]

As a useful approximation, an exponentially decaying volume fraction profile can describe a physically adsorbed homopolymer at the colloidal interface reasonably well;[15−17] the function we have used is given by

$$\varphi(z) = \varphi_S \exp(-z/z_0) \tag{3}$$

where ϕ_S is the volume fraction of adsorbed polymer in direct contact with the surface (the train layer) and z_0 controls the span of the profile. Once a volume fraction profile has been obtained for an adsorbed polymer layer, it is possible to obtain a number of derived parameters;[19] these include the adsorbed polymer amount (Γ) as mass per unit surface area

$$\Gamma = \rho_m \int_0^t \varphi(z)\,\mathrm{d}z \tag{4}$$

where ρ_m is the physical mass density of the adsorbed polymer and t is the maximum extent of the adsorbed layer. Another

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important parameter is the root-mean-square layer thickness, defined as[19]

$$\delta_{\mathrm{rms}} = \sqrt{\frac{\int_0^t \varphi(z) z^2 \, \mathrm{d}z}{\int_0^t \varphi(z) \, \mathrm{d}z}} \tag{5}$$

Experimental Section

Materials. PSL with negative surface charge was prepared by the modified surfactant-free emulsion polymerization of freshly distilled styrene with 5 wt % sodium styrenesulfonate as comonomer and potassium persulfate as initiator.[20-25] These latex particles were partially deuterated with 2.8 vol % D-styrene, giving a calculated neutron SLD of 1.56×10^{-6} Å^{-2}. The PSL was extensively dialyzed against MilliQ water to remove any salt or remaining monomers and was further concentrated by rotary evaporation. This latex was then dialyzed against a mixture of H_2O and D_2O to give a final solvent composition of 67.0 wt % H_2O, matched to the SLD of the latex; this will be referred to as the stock PSL dispersion. Deuterated poly(ethylene oxide) (D-PEO) was purchased from Polymer Source (no. P2632-dEO) with a quoted molecular weight of $M_w = 132\,000$ g·mol^{-1} and $M_w/M_n = 1.07$. D-PEO had an SLD of 7.05×10^{-6} Å^{-2}, which yielded a good contrast between the adsorbed polymer layer and the substrate PSL particles. Sodium polystyrene sulfonate (PSS) was purchased from Aldrich with an average molecular weight of $M_w = 200\,000$ g·mol^{-1} and was polydisperse. These polymers were used as received. Sodium chloride (NaCl) was purchased from Fluka and was used as received.

Sample Preparation. NaCl, D-PEO, and PSS were both dissolved in the mixture of 67.0 wt % H_2O and 33.0 wt % D_2O (hereafter referred to as the contrast-matching solvent) to make the stock NaCl, D-PEO, and PSS solutions. A D-PEO solution was then added to the stock PSL dispersion dropwise with stirring and was left for at least 48 h to reach adsorption equilibrium. The contrast-matching solvent, PSS solution, and sodium chloride solution were added dropwise also with stirring. The samples were left for at least 24 h before the measurement. In the final dispersions, the PSL particle volume fraction was fixed at 0.011, D-PEO concentration was kept at 0.7 mg·mL^{-1}, PSS concentration was kept at 3 mg·mL^{-1}, and the sodium chloride concentration varied from 0 to 90 mM. This composition was chosen to cover the latex particle surface fully with PEO. In the final dispersions, the specific surface area was ~1.3 m^2·mL^{-1}, and the nominal adsorbed PEO amount was 0.53 mg·mL^{-1}, assuming a complete adsorption. PSL particles dispersed in different ratios of D_2O to H_2O were used to measure the bare latex SLD. To observe the effect of NaCl on the interaction between D-PEO and PSS, solutions containing 0.7 mg·mL^{-1} D-PEO and 3 mg·mL^{-1} PSS with various amount of NaCl were also prepared using the contrast-matching solvent.

Small-Angle Neutron Scattering Measurements. The SANS measurements were performed on both NG7 at NCNR (NIST) and LOQ at ISIS (U.K.). The setup used for NG7 used a neutron beam wavelength (λ) of 5 Å ($\Delta\lambda/\lambda = 10\%$) and a sample–detector distance of 13.16 m. This covers a Q range from 0.0045 to 0.049 Å^{-1}. The measurements on LOQ used the full Q range available ($\Delta\lambda/\lambda$ is wavelength dependent and ranges from 2.9% to 3.8%). Hellma quartz rectangle cells with 2 mm pass length were used for all samples. All measurements were carried out at ambient temperature. A typical measurement took ~1.5 h on NG7 and 2 h on LOQ. The raw data were reduced following the standard procedures provided by NG7 and LOQ, and an empty cell was used for background subtraction. All data were fit to eq 1 using an exponential volume fraction profile for the adsorbed polymer layer (eqs 2 and 3) and a $\tilde{Q}^{-4/3}$ term for the layer fluctuation scattering. Additional terms describing the smearing effect of the particle polydispersity and instrument resolution are also included.[26] The volume fraction of substrate latex particles, the difference in the SLD, and the latex particle size were fixed during the fitting process. The fit was carried out using the PLAYTIME program, which is a nonlinear least-squares fitting procedure using the Levenberg–Marquardt algorithm. The adsorbed polymer volume fraction profiles were generated from the fit, and the adsorbed amount (Γ) and the root-mean-square layer thickness (δ_{rms}) were obtained according to eqs 4 and 5. The sets of parameters giving the best agreement to the experimental data were accepted (lowest χ^2 value).

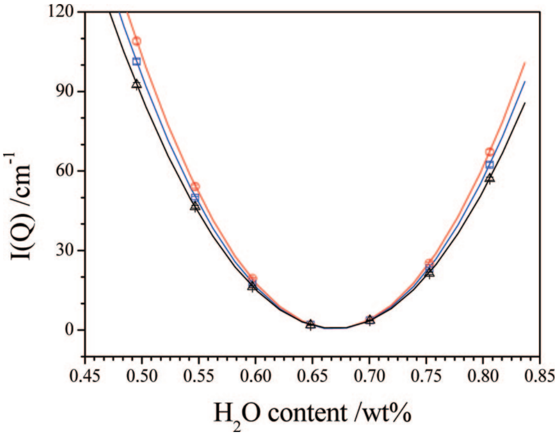

Figure 1. Contrast-match plot of the PSL particles.

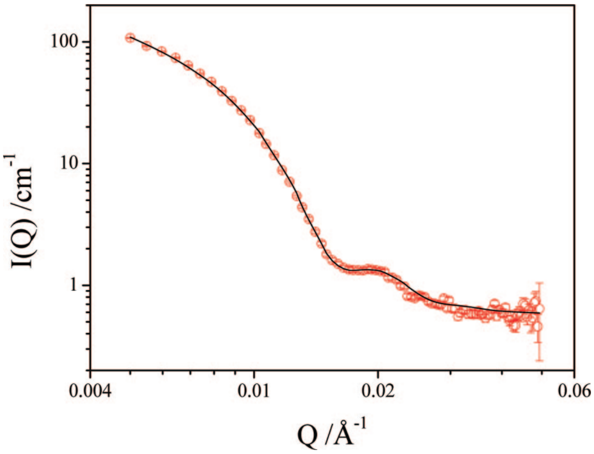

Figure 2. Scattering from the substrate latex particles of the mixture of H_2O/D_2O at a volume fraction of 0.011 and H_2O content of 49.6 wt %. The solid line is the fit to a hard sphere model (eq 6).

Results

Latex Particles. In this study, the latex particles were very critical. They needed to be at the appropriate composition to be effectively contrast matched to the PSS and the solvent. From the composition, the SLD of the latex was calculated to be 1.56×10^{-6} Å^{-2}, and it was also measured by the contrast-matching method. This was done by measuring the scattering from a series of bare latex at a fixed particle volume fraction but varying the H_2O/D_2O ratio in the solvent and then plotting the first three points in the scattering intensity against the water content, where the minimum position is the contrast-matching point (Figure 1). The SLD of these substrate latex particles was then calculated according to the water content at the contrast-matching point to be $(1.57 \pm 0.02) \times 10^{-6}$ Å^{-2}, which is very close to the theoretical value and is effectively contrast-matched to PSS.

Another important aspect is the polydispersity of the latex particles because narrowly distributed particles will give oscillations in the scattering data, making the interpretation less ambiguous. The size of the particle is also an important factor because this determines the required Q range and affects the adsorbed amount. The size and size distribution of the particles can also be readily measured by SANS. Figure 2 shows the

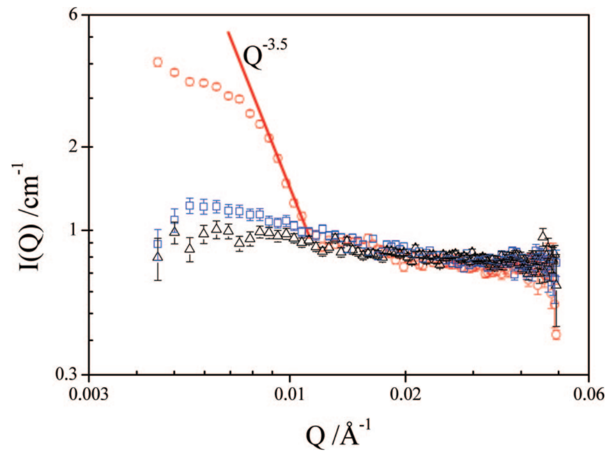

Figure 3. SANS spectra from D-PEO/PSS (0.7:3 mg·mL^{-1}) solution at NaCl concentrations of (○) 0, (□) 45, and (△) 90 mM. PSS is contrast matched.

scattering from the bare latex particles and the fit to a simple hard sphere model[26]

$$I(Q) = \Delta\rho^2 \varphi_P V_P \left[\frac{3(\sin(Qr_0) - Qr_0\cos(Qr_0))}{(Qr_0)^3}\right]^2 \qquad (6)$$

where $\Delta\rho$ is the difference in SLDs between the scattering units and their surrounding media. The particle size distribution was described by a log-normal distribution function.[25] The particle radius was measured to be 260 ± 2 Å, and the log-normal size distribution index was 0.08, which makes them ideal model particles in this study. These two parameters were fixed when fitting the scattering data from adsorbed polymer layers alone.

Scattering from D-PEO Solution in the Presence of PSS. The D-PEO used in this study has a radius of gyration (R_g) of ~20 nm in water,[27] and the overlap concentration was calculated to be ~6 mg·mL^{-1}; 0.7 mg·mL^{-1} is then well below the overlap concentration, where a power law Q dependency of its scattering around −1.66 is expected.[28] The scattering spectra from the D-PEO/PSS solution at various NaCl concentrations are presented in Figure 3. In these systems, PSS has been contrast matched to the solvent; therefore, only the scattering from D-PEO is visible. As expected, it is evident that complexes have been formed between D-PEO and PSS chains in the absence of NaCl where a high Q dependency of ~3.5 rather than ~1.66 (characteristic of polymer chains in good solvent) is observed.[28] Although it is hard to determine the Q dependency at high NaCl concentrations accurately because of the high incoherent background and relatively weak scattering, it is clear that with increasing NaCl concentration, the scattering at low and intermediate Q dramatically decreases, indicating that the complexes break down.

Scattering from the Adsorbed D-PEO Layer. In these dispersions, latex particles were effectively contrast matched to the solvent and PSS. Therefore, only the scattering from D-PEO is visible. Compared with the adsorbed D-PEO, scattering from free D-PEO in the solution is negligible at these equilibrium concentrations, as suggested by many previous studies.[13−17] D-PEO adsorption in the absence of PSS under the same contrast condition was studied by SANS as a control (Figure 4), demonstrating the effect of the PSL surface at various electrolyte concentrations. For clarity, the error bars for only the first three data points of each scattering spectrum are shown. These data can be fit to the model on the basis of an exponential volume fraction profile plus a $Q^{-4/3}$ fluctuation term (eq 1). Only the parameters controlling the adsorbed layer structure were left to vary: ϕ_S and z_0 in eq 3. It is worth noting that because of the limited Q range available, the data obtained from LOQ had a larger uncertainty than those from NG7. However, these two data sets are highly compatible with each other, and the position of the primary minimum in the scattering spectra is clearly evidenced. Similarly, the scattering data from adsorbed D-PEO in the presence of 3 mg·L^{-1} PSS were fitted (Figure 5), and the key parameters were obtained. The adsorbed polymer amount (Γ) and the root-mean-square layer thickness (δ_{rms}) were calculated according eqs 4 and 5. These parameters are plotted in Figures 6, 7, and 8.

It can be seen that the PEO adsorption changes with NaCl concentration and the presence of PSS makes a significant difference. In the absence of PSS, the adsorbed D-PEO amount first decreases with NaCl concentration and then increases, reaching a minimum of ~45 mM NaCl (Figure 6). The root-mean-square layer thickness first increases with the NaCl concentration and then decreases. Salt generally decreases the solvency of PEO in water;[29−31] one would expect that the PEO adsorbed amount would monotonically increase with increasing NaCl concentration. The different behavior observed in this study might be explained by considering the influence of NaCl on the latex particle surface. (Note that there is 5 wt % sodium styrenesulfonate in these latex particles and they tend to accumulate at the surface because of their hydrophilic nature.)

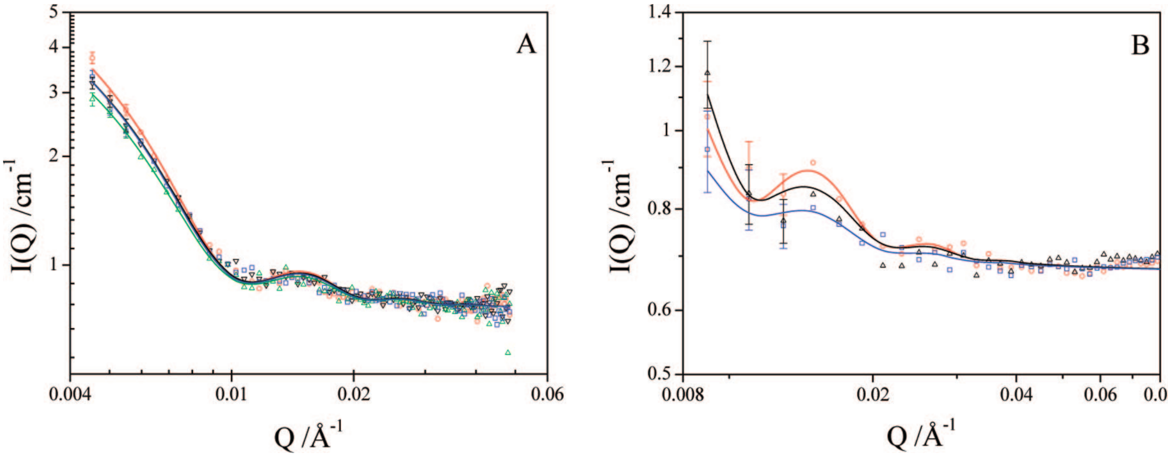

Figure 4. SANS spectra from adsorbed PEO layers at the PSL/water interface at different NaCl concentrations in the absence of PSS. (A) Data obtained from NG7 in the presence of (○) 0, (□) 30, (△) 60, and (▽) 90 mM NaCl. (B) Data obtained from LOQ in presence of (○) 15, (□) 45, and (△) 75 mM NaCl.

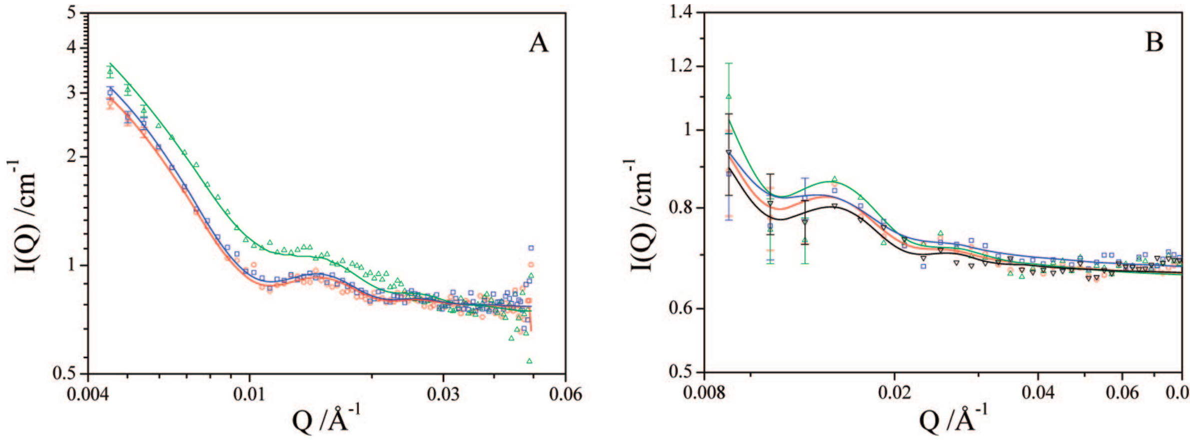

Figure 5. SANS data from adsorbed PEO layers at the PSL/water interface at different NaCl concentrations in the presence of 3 mg·L^{-1} PSS. (A) Data obtained from NG7 in the presence of (○) 0, (□) 30, and (△) 60 mM NaCl. (B) Data obtained from LOQ in the presence of (○) 15, (□) 45, (△) 75, and (▽) 90 mM NaCl.

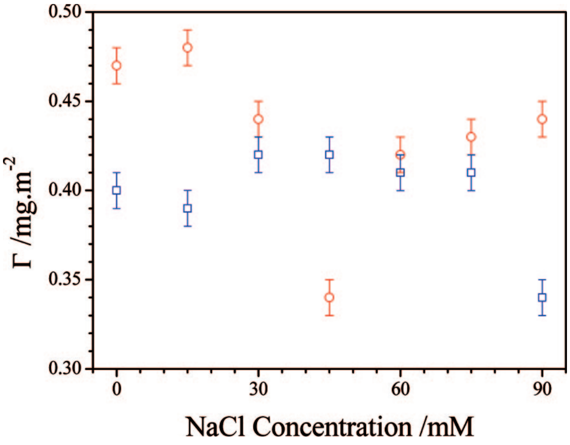

Figure 6. Adsorbed amount of PEO on the PSL latex (Γ) as a function of NaCl concentration. ○, without PSS; □, with 3 mg·mL^{-1} PSS.

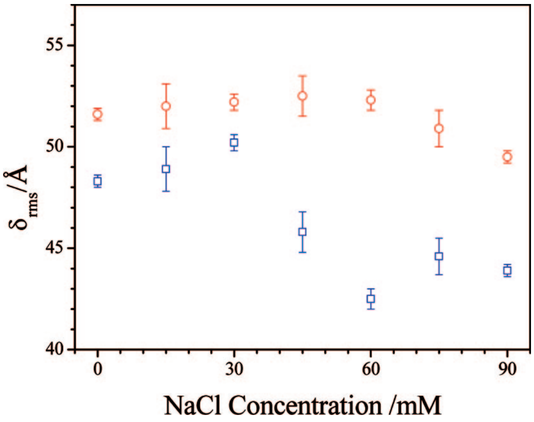

Figure 7. Root-mean-square layer thickness of adsorbed PEO on the PSL latex (δ_{rms}) as a function of NaCl concentration. ○, without PSS; □, with 3 mg·mL^{-1} PSS.

The root-mean-square layer thickness first gradually increases and then decreases with NaCl concentration, which also seems to be counterintuitive but might be explained by considering the changes in the adsorbed amount as well as the layer structure (Figure 7). The adsorbed PEO volume fraction at the latex particle surface changes in a manner similar to that of the adsorbed amount (Figure 8), which is also supposed to be related to the changes in the latex surface property.

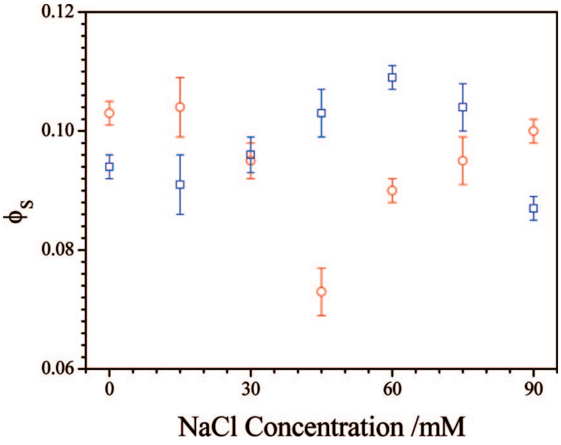

Figure 8. Volume fraction of the adsorbed PEO in direct contact with PSL surface (ϕ_S) as a function of NaCl concentration. ○, no PSS; □, in the presence of 3 mg·mL^{-1} PSS.

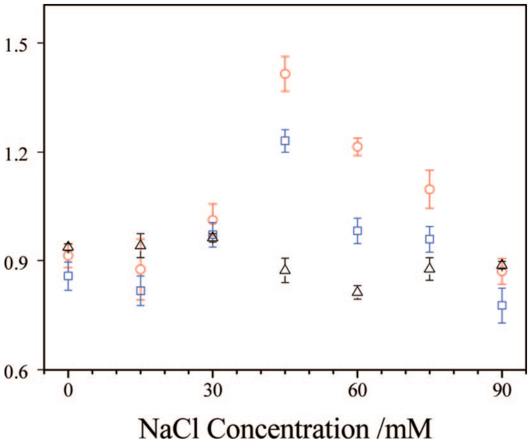

Figure 9. Normalized characteristics of the adsorbed PEO on the PSL surface in the presence of 3 mg·L^{-1} PSS. ○, ϕ_S; □, Γ; △, δ_{rms}.

In the presence of PSS, very different behaviors were observed (Figures 6−8). Compared with those in the absence of PSS, the differences should be brought about by the PSS because PSS can interact with both the latex particle and PEO, and this interaction is influenced by NaCl concentration;[6−8] this is also confirmed by the study of the solutions of D-PEO/PSS with salt (Figure 3). A detailed discussion is given in the next section.

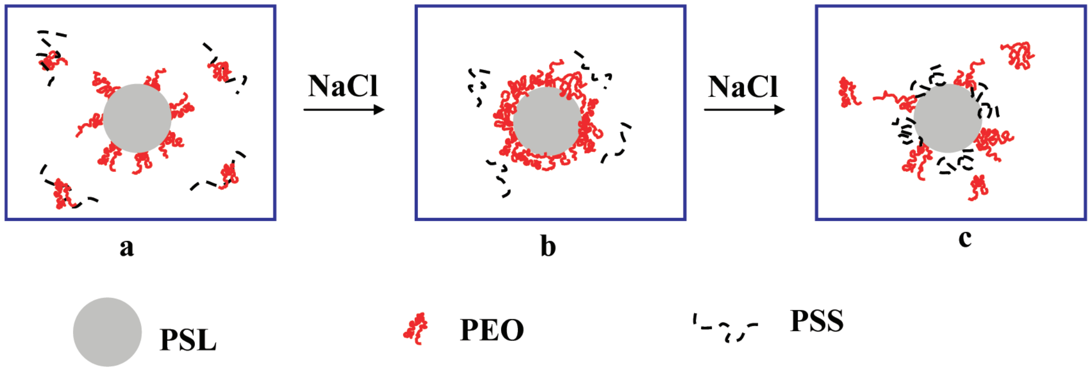

Figure 10. Illustration of the effect of PSS on the adsorption of PEO at the PSL/water interface at different NaCl concentrations. (The drawings are not to scale.)

Discussion

Adsorption of PEO in the Absence of PSS. In this situation, it is the salt that actually affects the PEO adsorption. In a previous study, it was found that PEO adsorption on colloidal silica surface increases with NaCl concentration.[32] Therefore, to understand the different result in this study, the surface property of the substrate particles needs to be considered. The adsorption of PEO on silica surface is assisted by the hydrogen bond with silanol groups at the interface;[33] whereas on the PSL, it is not. The PSL used in this study has styrenesulfonate moieties brought from the synthesis process that were partially from the initiator and partially from the comonomer. Owing to their hydrophilic nature, sulfonate moieties tend to appear preferentially on the particle surface.[25] It is reasonable to assume that the interaction between PEO and SS will contribute to the surface adsorption because they form complexes. On one hand, with increasing NaCl concentration, the decreasing solvency drives more PEO chains to the surface, which increases the PEO adsorbed amount; on the other hand, it breaks down the interaction between PEO and SS and thus reduces the PEO adsorbed amount. As shown in Figure 3, from 0 to 45 mM NaCl, the change is enormous, but little happens above 45 mM NaCl; this agrees very well with the observation that a minimum in the PEO adsorption amount is found to be ~45 mM (Figure 6). Similarly, the volume fraction of the adsorbed PEO in direct contact with the PSL surface decreases from 0 to 45 mM NaCl because of the breaking down of the PEO/SS interaction and then increases as a result of the worsening solvency (Figure 8). While the interaction between PEO and SS is reduced, the adsorbed PEO layer becomes more diffuse, which might be responsible for the gradual increase in the root-mean-square layer thickness from 0 to 45 mM NaCl, and after that, the continuing worsening of solvency drives the adsorbed layer to collapse partially (Figure 7).

PEO Adsorption in the Presence of PSS. It can be seen from Figures 6−8 that the presence of PSS brings about significant changes in the PEO adsorption compared with those without PSS. Because the PEO adsorption is affected by both the surface property of the particles and the presence of PSS, it is necessary to separate these two contributions. The effect of particle surface on the PEO adsorption has been demonstrated in the PSS-free systems, as discussed above. One can highlight the changes brought about by PSS by dividing structural parameters with those of the corresponding PSS-free systems (Figure 9), and any changes in the PEO adsorption will mainly be a result of the added PSS.

It can be seen that in the presence of PSS, with increasing NaCl concentration, the volume fraction of adsorbed PEO at the interface (ϕS) and the adsorbed PEO amount (Γ) reach a maximum around 45 mM NaCl; the root-mean-square adsorbed layer thickness (δ_{rms}) has a minimum around 60 mM NaCl, but its variation is less pronounced. This suggests that PSS in solution can drag PEO off from the particle surface by forming PEO/PSS complexes (Figure 10a) because both the particles and the complexes are negatively charged. With increasing NaCl concentration, the repulsion between the substrate particle and PSS is partially screened, and the PEO/PSS complexes can be readsorbed through PEO segments; at the same time, the PEO/PSS complexes break down (Figure 3), which releases more PEO for adsorption. Therefore ϕ_S and Γ both increase (Figure 10b). With a further increase in NaCl concentration, PSS becomes adsorbing[6,7] and competes with PEO; therefore, ϕ_S and Γdecrease (Figure 10c). The changes in the root-mean-square layer thickness (δ_{rms}) are more complicated because it depends on both the adsorbed amount and the layer structure. The initial increase in δ_{rms} might be a result of the increase in the adsorbed amount; the worsening of the solvency by increasing NaCl concentration, however, drives the adsorbed layer to collapse and therefore reduces δ_{rms}. When NaCl concentration is further increased, more space on the surface is taken by adsorbed PSS, which may force adsorbed PEO to take a more extended conformation and thus δ_{rms} increases again. However, the changes in δ_{rms} are less pronounced than those in ϕ_S and Γ.

Conclusions

The effect of polyelectrolyte PSS on PEO adsorption at the PSL/water interface at different NaCl levels was investigated by SANS. It was found that at zero or low NaCl concentration, because of the electrostatic repulsion between the PSL particles and the negatively charged PSS, PSS can strip PEO off from the interface by forming PEO/PSS complexes. With increasing NaCl concentration, the repulsion between PSL particles and PSS was reduced and the PEO/PSS complexes broke down; PEO adsorption was enhanced. With a further increase in the NaCl concentration, PSS itself became adsorbing on PSL particles and competed with PEO adsorption, which reduced the PEO adsorption.

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