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ORIGINAL CONTRIBUTION

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Competitive adsorption of an anionic and a nonionic surfactant on polystyrene latex particles as monitored by small x-ray scattering

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Abstract Adsorption of the anionic surfactant sodium dodecylsulfate (SDS) as well as competitive adsorption of SDS with the nonionic surfactant Triton X-405 on a polystyrene latex has been examined by the use of small-angle x-ray scattering (SAXS). Since the latex particles only have a low contrast towards water whereas the electron densities of the added surfactants are rather high, their gradual adsorption can be monitored with good sensitivity. The particles covered with SDS have been investigated by the contrast variation method. A distinct core-shell structure has been observed. After maximum coverage of the surface is reached, the additional surfactant forms free micelles. The analysis presented here allows the simultaneous investigation of the covered particles and the free micelles. This is due to their respective characteristic scattering contributions in different angular ranges. Information on the competitive adsorption could be obtained by analyzing the structure of the coated particles and the composition of the free mixed micelles. The adsorption is shown to be an equilibrium process where adsorption of the nonionic component is found to be much stronger than of the SDS molecules.

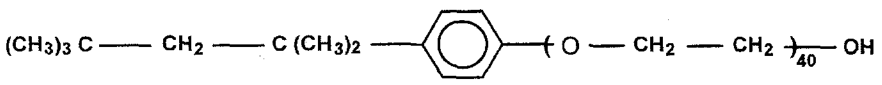
Key words Small-angle x-ray scattering – latex – surfactant – competitive adsorption

Introduction

The adsorption of surface active agents on latex particles in most cases leads to an increase in colloid stability. The effectiveness of stabilization is dependent on the surface structure of the particles [1]. In particular, binary surfactant systems often show superior properties for practical applications. This field has been a topic of major research recently [1–6].

Dynamic light scattering [2, 3], electrophoretic [2, 3, 7, 8] and surface tension [9, 10] measurements have been applied by several authors to study the adsorption of anionic, nonionic and cationic surfactants on latex particles. Using NMR-spectroscopy [11] and ESR-spectroscopy [12] the simultaneous detection of saturated latex particles coexisting with free surfactant micelles in solution has been reported. Competitive adsorption on latex surfaces has been studied by Kayes [8] and by Kronberg et al. [4, 5]. Small-angle neutron scattering (SANS) [13, 14] has been applied by Ottewill and co-workers [15–17] to study a broad variety of systems. SANS measurements allow to discriminate between the core particle and the adsorbed layer by the contrast variation method. The contrast can easily be changed by using different mixtures of H_2O and D_2O due to the marked difference between the scattering cross-sections of hydrogen and deuterium [13, 14].

In a previous paper we have shown [18] that small-angle x-ray scattering (SAXS) [13, 14] is suitable to monitor the adsorption of the nonionic surfactant Triton X-405 [(1,1,3,3-tetramethyl-butyl) phenoxy polyoxyethylene glycol] on the surface of a polystyrene latex with high sensitivity.


$(CH_3)_3C-CH_2-C(CH_3)_2-C_6H_4-(O-CH_2-CH_2)_{40}-OH$

The contrast can easily be changed by adding sucrose or glycerol to the dispersion medium [13, 14, 18–21]. Since there is no incoherent contribution to the background scattering, the SAXS-analysis can also be performed at higher scattering angles with sufficient accuracy. It could be shown that in a system of saturated latex particles coexisting with free surfactant micelles each component gives a characteristic scattering contribution in different angular ranges.

In the present paper this investigation is extended to the study on the adsorption of the anionic surfactant sodium dodecylsulfate (SDS) on the surface of the same polystyrene latex particles. The scattering can be expected to be strongly dependent on the surface coverage because the polystyrene core has only a low excess electron density towards water (6/nm^3; [22]), whereas the contrast of the SDS molecules is rather high due to the high electron density of their polar headgroups [23]. Thus, the observed scattering will be dominated by the adsorbed surface layer.

Further insight in the particle surface structure can be gained with the contrast variation technique [24–28]. The average particle contrast may be varied from positive to strongly negative by adding glycerol to the dispersion medium. Having investigated the adsorption in single surfactant systems in great detail it is interesting to turn to the competitive adsorption of a mixture of the anionic and nonionic surfactants. By this the relative strength of adsorption of both components can be compared qualitatively.

This paper is organized as follows: At first, SAXS-measurements monitoring the gradual adsorption of SDS on the latex particles are presented. Then, the scattering intensities measured at varying contrast at different coverage of the surface are compared. In the second part the competitive adsorption of SDS and Triton X-405 on the polystyrene latex is analyzed. For this purpose the effects of adding increasing amounts of Triton to the particles fully covered with SDS and vice versa have been investigated.

Materials and methods

Materials

Styrene (Fluka, p.a.) was first destabilized with a 10 wt.% sodium hydroxide solution, washed with water and subsequently dried over calcium chloride. Then it was distilled for further purification. Sodium dodecylsulfate (SDS, $M = 288.4$ g/mol; Lancaster) was used as received. The initiator potassium peroxodisulfate (Fluka) was recrystallized twice from bidistilled water. The polystyrene latex was prepared by a conventional batch emulsion polymerization of 50 g styrene in 525 ml bidistilled water using 1.4965 g SDS and 0.3120 g $K_2S_2O_8$. The polymerization temperature was 80 °C. The latex was purified by dialysis against a large volume of 0.0025M KCl solution for 3 weeks.

Triton X-405 ($M = 1968$ g/mol; Fluka) and glycerol (BASF, DAB7) were used without further purification. A given amount of the respective surfactant was added to the latex and subsequently shaken thoroughly for at least 24 hours. SAXS-measurements started at various times after the addition of the surfactants showed that the adsorption equilibrium was reached in all cases within less than 24 hours.

Methods

The densities of the aqueous solutions as well as of the latex were determined using a DMA-60 apparatus (Paar, Graz, Austria). The electron densities (number of electrons per nm^3) of glycerol solutions are calculated from these data according to the following equation: $\rho_m = 332.8 + 0.749 \cdot (\text{wt.\% glycerol})$ [18]. The density of the polystyrene particles is 1.049 g/cm^3. The number-average core radius R_n of the particles as determined by SAXS was 30.4 nm and the polydispersity expressed by $R_W/R_n = 1.052$ [18]. The solid content of the stock latex (8.2 wt.%) was measured gravimetrically.

SAXS-analysis

Small-angle x-ray scattering (SAXS) measurements were performed at room temperature using a Kratky–Kompakt–Kamera (Parr, Graz, Austria) with a block collimation system [19, 22]. The scattering intensities were registered with a position-sensitive detector (Braun, Germany) in the q-range of $0.08\ \text{nm}^{-1} < q < 5\ \text{nm}^{-1}$ (scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$; θ: scattering angle; λ: wavelength of the Cu-Kα radiation used in the experiment). Absolute scattering intensities were obtained by the moving-slit method [29]. The principal steps of data treatment are as follows:

First the scattering contributions by the empty capillary and by the respective dispersion medium were subtracted. For the discussion of the curves in the region of lowest scattering angles ($q < 0.5\ \mathrm{nm}^{-1}$) the data were desmeared taking into account the smearing effects of the finite height and width of the slit in the collimation system. The scattering curves in the range of high q-values were not desmeared because in this region only a qualitative comparison of the respective intensities is given. Finally, all curves displayed here were normalized to the volume concentration of the polystyrene core particles. Further details concerning the measurements as well as the subsequent data treatment including the desmearing procedures have been described elsewhere [19, 22].

The analysis of the scattering curves is based on the following equations: For a dilute system of polydisperse particles the intensity per volume normalized to the scattering intensity of a single electron (e.u./nm^3) follows as (cf. refs. [19, 30])

$$I(q) = \sum_i N_i B_i^2(q) \tag{1}$$

where N_i is the number of particles of radius R_i per unit volume and $B_i(q)$ is the scattering amplitude. For spherical symmetric particles of radius R and with the radial electron density distribution $\rho(r)$ dispersed in a medium of electron density ρ_m, $B(q)$ is given by:

$$B(q) = 4\pi \int_0^R [\rho(r) - \rho_m] r^2 \frac{\sin(qr)}{qr} dr \,. \tag{2}$$

Details concerning the evaluation of the curves measured at various contrasts have been described previously [19, 21].

Measurements could be done at rather high concentrations (6–7 vol.%) of the latex to obtain good counting statistics. This is due to the fact that in the q-range under consideration here the influence of the interaction between the latex particles, i.e., of the structure factor is practically negligible [22].

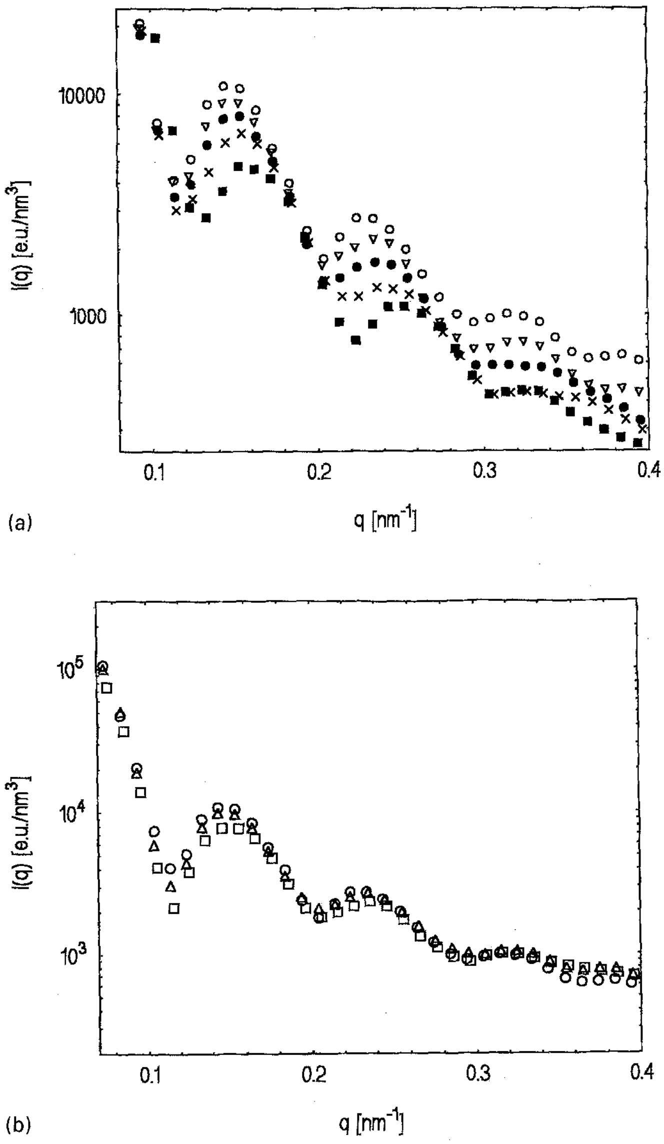


Fig. 1 Scattering curves at low q-values measured from the PS-latex after addition of different amounts of SDS. The curves refer to the following SDS concentrations (expressed in mg SDS per g PS): A) ■: 0 mg/g; X: 21 mg/g; ●: 37 mg/g; ∇: 65 mg/g (saturation); ○: 121 mg/g. B) ○: 121 mg/g; △: 202 mg/g; □: 342 mg/g

Results and discussion

Adsorption of SDS on the latex surface

To assess the adsorption of SDS in detail, several mixtures of the latex with increasing amounts of this surfactant were prepared. Figure 1a, b display the resulting SAXS-intensities.

Even small amounts of added SDS cause an increase in scattering intensity and a marked shift of the side maxima towards smaller scattering angles. The shift continues up to an amount of about 65 mg SDS per g polystyrene (see Fig. 1a). At higher surfactant concentrations (see Fig. 1b) the measured intensities are rather insensitive to additional amounts of SDS in the region of small scattering vectors ($q < 0.4\ \mathrm{nm}^{-1}$).

The polystyrene core has only a low contrast towards water (6 excess electrons per nm^3), whereas the scattering of the adsorbed SDS molecules is dominated by their polar headgroups of rather high electron density. In consequence, the shifts in the observed scattering curves reflect the formation of particles with a more and more pronounced core-shell structure. Figure 1a, b therefore suggests the saturation of the particle surfaces at an SDS concentration of ca. 65 mg per g PS.

This assumption is corroborated by the observations of the same scattering curves at higher q-values displayed in Fig. 2a.

Additional amounts of SDS beyond 65 mg/g show up at high scattering angles in a broad, very characteristic maximum. The obvious explanation for this new feature is given by the formation of free micelles from the excess of surfactant which are not bound to the surface of the latex particles.

If in first approximation negligible interactions between the covered polystyrene particles and the SDS micelles are assumed, the scattering intensities of both species simply add up throughout the entire range of scattering angles. For the further evaluations the concentration of 65 mg SDS per g PS is referred to be the point at which the latex particles are fully covered with SDS but where no free surfactant micelles are present yet. If additional surfactant will not adsorb but solely form free micelles, then the scattering of the micelles alone should be obtained by subtraction of the scattering curve at saturation from the ones with higher SDS concentrations. The scattering intensity of the free single SDS-molecules can be disregarded since it will be negligibly small. The curves resulting by this subtraction can be compared with the curves measured separately from the SDS micelles at the same ionic strength for a number of concentrations. The results of this analysis are displayed in Fig. 2b for the two scattering curves measured at highest surfactant concentrations.

Good agreement between the difference curves and the curves measured separately from the micelles at a proper concentration was found in both cases. Thus the concentration of free micelles can be determined and be compared to the respective concentrations deriving from the overall mass balance: If the amount of free SDS is subtracted from the total amount added, one should obtain the amount of SDS being adsorbed on the latex particles. The calculated adsorbed amounts from the two curves are 46 and 51 mg SDS per g PS, respectively. Given the various uncertainties, the agreement between these figures and the value of 65 mg per g obtained from Fig. 1 in combination with Fig. 2a is satisfactory. Thus, the consistency in the interpretation of the data obtained in two different q-ranges can be observed.

In SAXS the form factors of the SDS micelles show a prominent peak around $q = 1.6\ \text{nm}^{-1}$ (cf. Fig. 2b) while the intensity at smallest angles is comparably low. The explanation for this has been given by Zemb and Charpin [23]: The mean electron density of the whole micelle is very close to that of the solvent water. The electron density of the hydrocarbon moieties in the micellar core is below that of water but the polar shell with the associated counter-ions has a very high positive contrast.

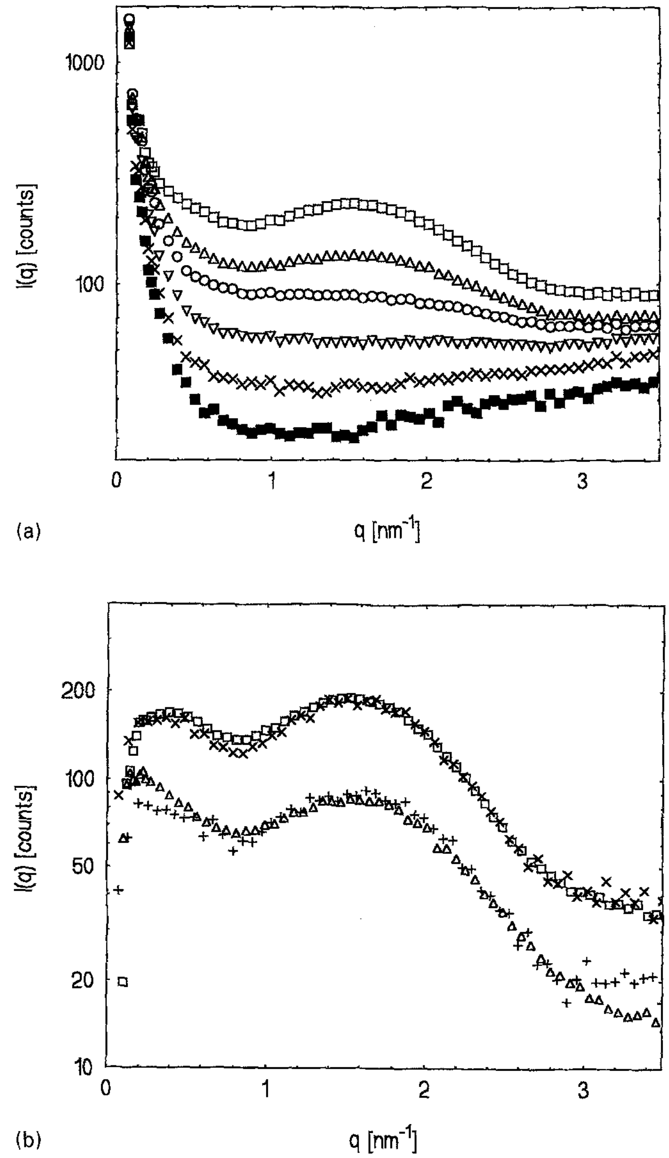


Fig. 2 Analysis of the smeared scattering curves at higher q-values measured from the PS-latex after addition of different amounts of SDS. A) The curves refer to the following SDS concentrations (expressed in mg SDS per g PS): ■: 0 mg/g; X: 21 mg/g; ▽: 65 mg/g (saturation); ○: 121 mg/g; △: 202 mg/g; □: 342 mg/g. B) Scattering contribution of free SDS micelles: Comparison of the scattering curves measured separately from SDS solutions with those obtained from the subtraction as described in the text. The curves refer to the following concentrations by weight of SDS: +: 1.20%; X: 2.35%. The curves obtained from the subtraction refer to the following SDS concentrations (expressed in mg SDS per g PS): △: 202 mg/g; □: 342 mg/g

Contrast variation

For a more detailed analysis of the adsorbed surfactant layer we measured the scattering of the polystyrene particles at varying contrast using glycerol as contrast agent. The characterization of the uncoated PS core particles by the contrast variation method has already been reported in a previous publication [18]. For further comparison these scattering curves are displayed again in Fig. 3a. Reference [18] gives also a comprehensive discussion of influences of the added glycerol on the structure of the particles. By comparison of scattering curves obtained at same contrast but using different agents (glycerol or sucrose) it could be shown that the radial structure is independent of the nature of the added agent.

It was found that the characteristic shift of the extrema with contrast clearly points to particles with a core-shell structure and the curves could be fitted assuming the radial electron density profile displayed in the inset. The thin shell of about 1 nm thickness with increased electron density observed there is probably due to the SDS molecules used for the preparation of the latex. From mass balance of the latex preparation we conclude that 30% at most of the particle surface is already covered with SDS. It is known that a part of the surfactant is removed from the particle surface by dialysis. Thus, for all the following mass balances presented, an initial surface coverage of 15% was assumed. The uncertainty of this value, however, does not seriously affect the results presented in the following sections.

Figure 3b displays the scattering curves obtained from the nearly fully covered particles (50 mg additional SDS per g PS) measured at the same glycerol contents in the dispersion medium as above. In this case there is a stronger shift of the extrema with contrast and the curves at low contrast have moved closer together. As expected, these features point to a more pronounced core-shell structure of the particles than in the case discussed above. Trying to fit these curves under the assumption of various radial electron density distributions [21] it became obvious, that the thickness of the shell did not change very much and is

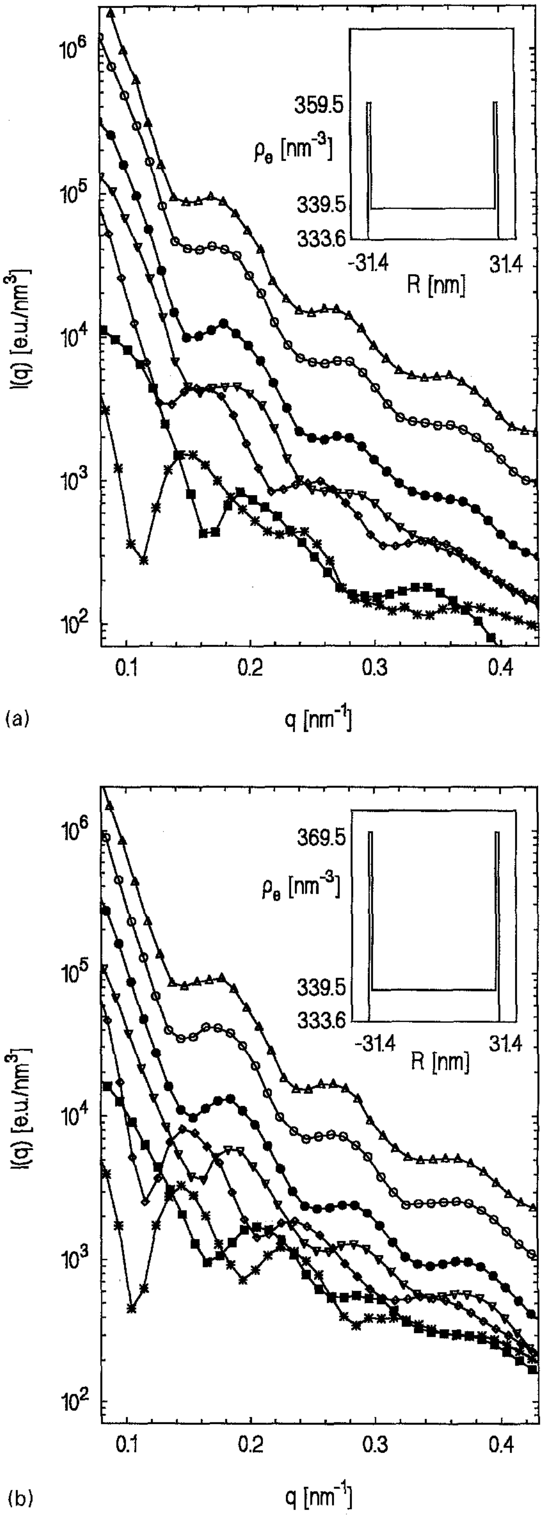


Fig. 3 Scattering curves measured at different contrast using glycerol as contrast agent. For clarity the points were connected by lines. The curves refer to the following concentrations by weight of glycerol whereas the numbers in parentheses indicate the average contrast (in nm^{-3}) A) uncoated PS-latex (reproduced from ref. 18): ◇: 0% (7.8); *: 6.3% (3.9); ■: 13.5% (− 1.5); ▿: 20.5% (− 6.8); ●: 27.4% (− 11.9); ○: 41.4% (− 22.5); ▵: 55.4% (− 32.9). The curves can be fitted with an electron density profile shown in the inset. (Core radius 30.4 nm, shell thickness 1 nm, $\bar{\rho} = 341.4$ nm^{-3}; the electron density of water was taken as reference in the profile). B) PS-latex after addition of 50 mg SDS per PS: ◇: 0% (8.7); *: 6.4% (4.7); ■: 13.4% (− 0.6); ▿: 20.6% (− 6.0); ●: 27.4% (− 11.0); ○: 41.4% (− 21.6); ▵: 55.4% (− 32.0). The curves can be fitted with an electron density profile shown in the inset. (Core radius 30.4 nm, shell thickness 1 nm, $\bar{\rho} = 342.3$ nm^{-3}; the electron density of water was taken as reference in the profile)

below 2 nm. Assuming a shell thickness of 1 nm as in the discussion of Fig. 3a, the fit gives an electron density in the shell clearly higher than for the particles without additional SDS (cf. electron density profile in the inset of Fig. 3b).

Comparing the shell thickness with the dimensions of the SDS molecules, these findings are in accordance to what is expected if one assumes a dense monomolecular layer of SDS molecules when the polystyrene surface is saturated and the molecules being adsorbed with their hydrophobic moiety. Furthermore, from the SDS concentration of 65 mg per g PS at saturation as determined in the previous section, the average area occupied by one SDS molecule is calculated to $0.59 \pm 0.06\,\mathrm{nm}^2$. This value compares favorably with the figures supplied by literature [9, 10]. Thus it is safe to conclude that adsorption of secondary micelles on the particle surfaces has not taken place in the range of concentrations studied here. This finding is in contradiction to what has been reported by Zhao and Brown [3]. At present we have no explanation for this discrepancy.

Competitive adsorption of Triton X-405 and SDS on the polystyrene latex

In a previous publication [18] we reported SAXS-measurements concerning the adsorption of the nonionic surfactant Triton X-405 on the surface of the same polystyrene latex. For the analysis of these data we proceeded along the same lines as described above for the case of SDS. The amount of Triton necessary for the saturation of the particles was determined to be 115 mg or 5.8×10^{-5} mol per g PS (SDS: 65 mg or 22.5×10^{-5} mol per g PS, cf. above). From this the average area occupied per Triton molecule at saturation is calculated to be $2.6\,\mathrm{nm}^2$ (SDS: $0.59\,\mathrm{nm}^2$; cf. above). Furthermore it could be shown that the shell thickness of the adsorbed molecules is below 3 nm. Thus, we came to the conclusion that the Triton molecules strongly adsorb, forming a dense monolayer.

Having studied the adsorption of both single surfactant systems in great detail we now turn to the investigation of the competitive adsorption process of the anionic and the nonionic surfactants. In a first series the latex particles were fully covered with SDS and subsequently increasing amounts of Triton were added to the system. Next, the inverse case, i.e., the effect of adding various amounts of SDS to the particles fully covered with Triton was examined.

Effect of adding Triton X-405 to the latex fully covered with SDS

In Fig. 4a the effect of adding increasing amounts of Triton to the PS latex fully covered with Triton is shown in the region of low q-values. The addition of an amount of Triton equal to the concentration which would be necessary to saturate the uncovered particles (114 mg/g) results in a pronounced increase in scattering intensity. Higher Triton concentrations affect the scattering pattern only for $q > 0.2\,\mathrm{nm}^{-1}$. By comparison with separate measurements [18] from the Triton micelles it is clear that the strong increase of the scattering intensity upon addition of the surfactant cannot be explained by an additional scattering originating from free Triton micelles. Thus we conclude that some kind of reorganization must have taken place in the adsorbed surfactant layer. It is very instructive to compare these curves obtained from the mixed systems with the scattering from the particles fully covered with Triton but without previous addition of SDS.

As shown in Fig. 4b the coincidence with the curve measured after addition of 209 mg Triton per g PS (equivalent to an overall molar ratio Triton to SDS of 0.41/1) is quite good up to $q \approx 0.3\,\mathrm{nm}^{-1}$. For the concentration of 114 mg (molar ratio Triton to SDS of 0.22/1) Triton per g PS there are still some minor discrepancies. From this observation one might conclude that the Triton molecules replace the SDS molecules quantitatively from the particle surface if only a small excess amount of Triton is added to the system. Then the discrepancies observed at $q > 0.3\,\mathrm{nm}^{-1}$ in Fig. 4b should be due to the additional scattering from free mixed micelles formed from the desorbed SDS and from the excess amount of added Triton molecules.

To prove this, the analysis of the scattering intensities at higher q-values can be done in the same way as introduced in the single surfactant systems. Thus, the scattering from the single surfactant micelles and from their mixtures in 0.003M KCl solution has been measured separately at various compositions first.

The results displayed in Fig. 5 show that the scattering intensity from the Triton micelles is most significant for $q \leq 1\,\mathrm{nm}^{-1}$. On the other hand, the micelles formed from SDS have a comparatively low intensity in this q-range, but show a prominent peak around $q = 1.6\,\mathrm{nm}^{-1}$ as discussed in the first section of this paper. For the mixtures of both surfactants the peak position and the relative scattering intensities in the different q-ranges varies in a very characteristic way with the composition of the micelles. An investigation on the aggregation behavior of micelles formed from SDS and Triton X-100 (a nonionic surfactant of the same family as Triton X-405 but with only 10 EO-units) has been reported [31].

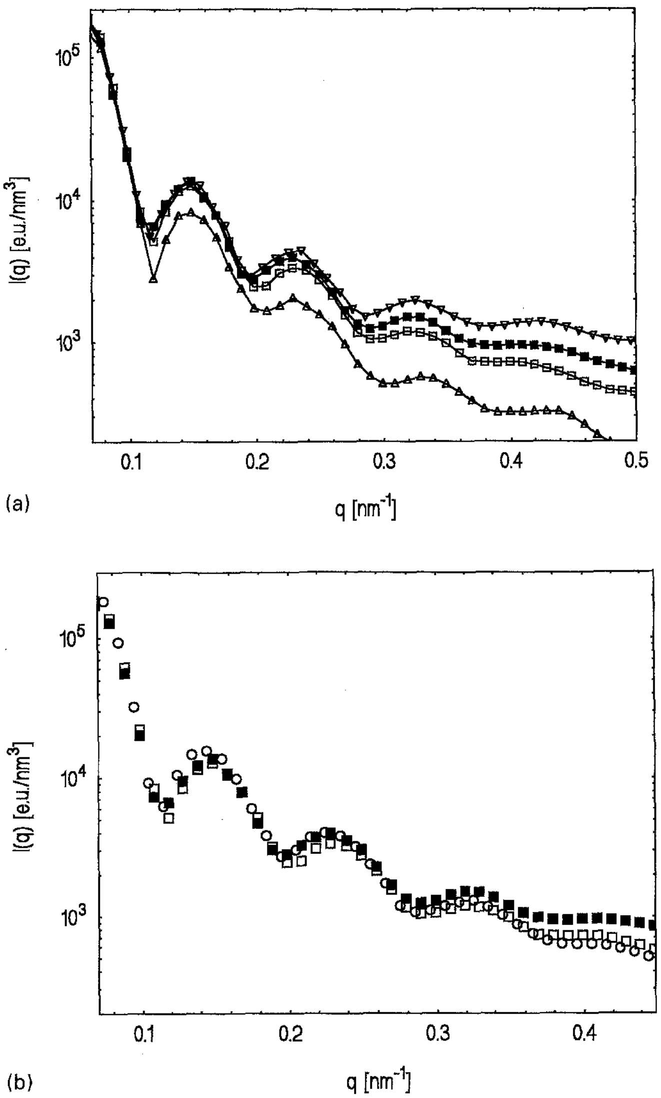


Fig. 4 Analysis of the competitive adsorption at low q-values: A) Scattering curves showing the effect of adding different amounts of the nonionic surfactant Triton X-405 to the PS-latex which has been fully covered with SDS. For clarity the points were connected by lines. The concentrations of added Triton [SDS] (expressed by mg surfactant per g PS respectively) are as follows: △: 0 mg/g [64 mg/g]; □: 114 mg/g [64 mg/g]; ■: 209 mg/g [64 mg/g]; ▽: 357 mg/g [64 mg/g]. B) Comparison of the scattering curves measured from the PS-latex fully covered with SDS after addition of different amounts of Triton X-405 (from Fig. 4a) with the curves measured from the PS-latex fully covered with Triton (without addition of SDS). The concentrations of added Triton [SDS] (expressed by mg surfactant per g PS respectively) are as follows: □: 114 mg/g [64 mg/g]; ■: 209 mg/g [64 mg/g]; ○: 116 mg/g (saturated) [0 mg/g]

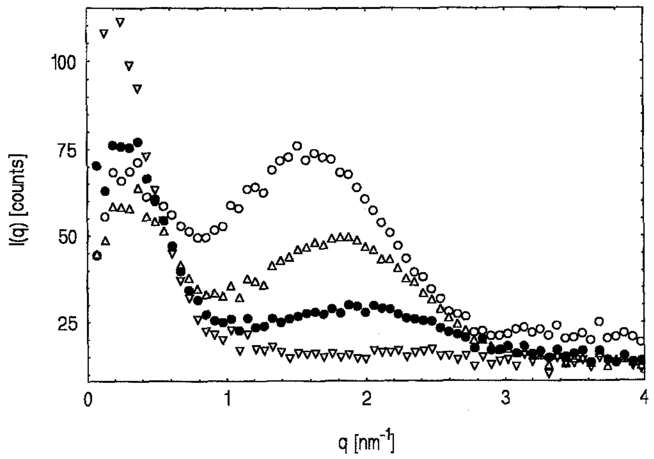


Fig. 5 Smeared scattering curves measured from micelles of SDS, Triton X-405 and their mixtures at a concentration of 1 vol%. The weight fractions of Triton in the micelles are as follows: ○: 0.0; △: 0.32; ●: 0.71; ▽: 1.0

In Fig. 6a the scattering curve at high q-values measured from the particles saturated with Triton (without previous addition of SDS) is compared with the ones obtained from the systems after addition of an excess amount of Triton to the particles saturated with SDS.

The observed discrepancies show that free surfactant micelles are present in the systems represented by the two upper curves. Again, the scattering originating from the free micelles should be obtained by the subtraction of the lowest curve in Fig. 6a from the upper ones. The curves resulting from this subtraction and the comparison with the scattering measured from the mixed micelles separately at a proper concentration and composition are shown in Fig. 6b. Good agreement within given limits of experimental uncertainty was found in both cases. For calculating the concentrations as well as the compositions of the free mixed micelles from mass balance it has been assumed that all SDS was replaced by Triton. The results for the two systems under consideration are a weight concentration for the micelles of 1.13% and 2.12% with the composition of 55 wt.% Triton/45 wt.% SDS and 76 wt.% Triton/24 wt.% SDS respectively. From the analysis of Fig. 6b we obtained weight concentrations of 1.22% and 2.04% with the composition of 71 wt.% Triton/29 wt.% SDS and 83 wt.% Triton/17 wt.% SDS respectively. Thus, the assumption of the replacement of the SDS by Triton resulting from the discussions in the region of low q-values in Fig. 4a,b is consistent with the analysis of the free micelles which has been performed at higher q-values.

These results corroborate our findings from the previous paper [18] that the adsorption of the Triton molecules on a polystyrene surface is rather strong: A small amount of excess Triton is sufficient to replace the previously adsorbed SDS molecules quantitatively.

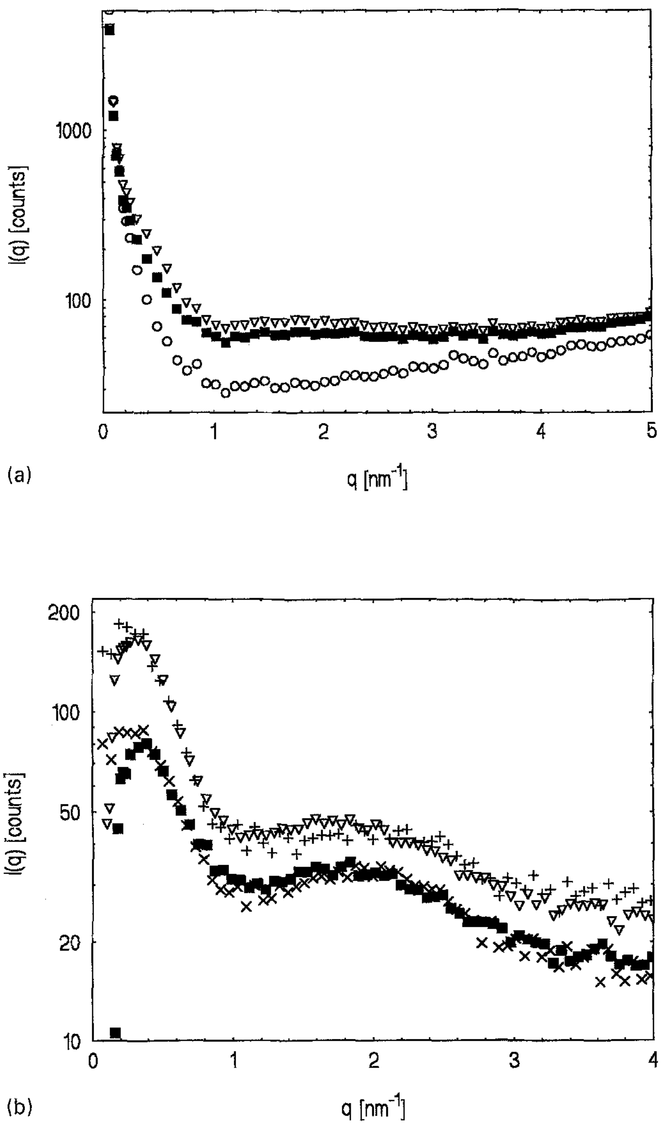


Fig. 6 Analysis of the competitive adsorption from the smeared scattering curves at higher q-values: A) Scattering curves measured from the PS-latex fully covered with SDS after addition of different amounts of Triton X-405 and from the PS-latex fully covered with Triton (without addition of SDS). The concentrations of added Triton [SDS] (expressed by mg surfactant per g PS respectively) are as follows: ■: 209 mg/g [64 mg/g]; ▽: 357 mg/g [64 mg/g]; ○: 116 mg/g (saturated) [0 mg/g]. B) Scattering contribution of free mixed micelles consisting of SDS and Triton X-405: Comparison of the scattering curves measured separately from solutions of the mixed micelles with those obtained from the subtraction as described in the text. The curves refer to the following concentrations by weight of the micelles whereas the numbers in parentheses indicate the weight fraction of Triton in the micelles: X: 1.22% (0.71); +: 2.04% (0.83). The curves obtained from the subtraction refer to the following concentrations of added Triton [SDS] (expressed by mg surfactant per g PS respectively) are as follows: ■: 209 mg/g [64 mg/g]; ▽: 357 mg/g [64 mg/g]

Effect of adding SDS to the latex fully covered with Triton X-405

In Fig. 7 the effect of adding increasing amounts of SDS to the PS latex fully covered with Triton is shown in the region of low q-values.

In the range of $q < 0.4\ \mathrm{nm}^{-1}$ a gradual decrease in the scattering intensities is observed when adding rather high amounts of SDS. Comparing these curves with the one obtained from the latex fully covered with SDS (but without previous addition of Triton) coincidence in the region of the first side maximum can be seen for the highest SDS concentration of 242 mg per g PS (equivalent to an overall molar ratio SDS to Triton of 14.2/1). From this we conclude that a gradual replacement of Triton by SDS has taken place. Thus, a rather large excess amount of SDS replace the preadsorbed Triton molecules quantitatively. The discrepancy at higher q-values as well as the crossing of the curves around $q = 0.4\ \mathrm{nm}^{-1}$ in Fig. 7 must in consequence be caused by the additional scattering of free mixed micelles.

The analysis of the free micelles is again done at high scattering vectors: Fig. 8a shows the comparison of the curves measured at saturation with SDS (without Triton) and of the mixed system measured at highest amount of additional SDS. A distinct scattering contribution of the free micelles is obvious in the upper curve. In Fig. 8b the

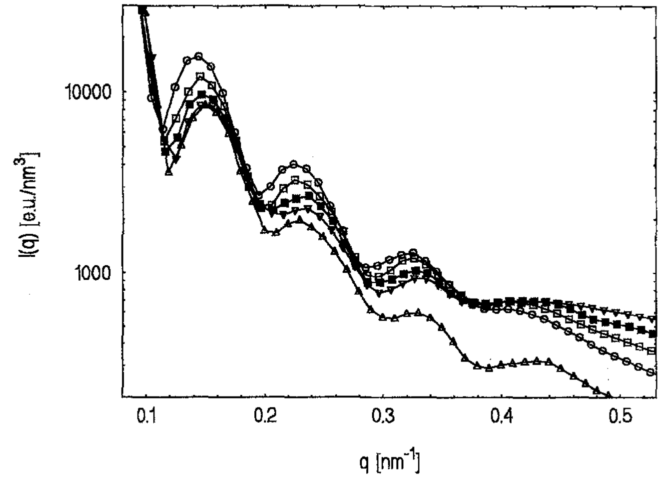


Fig. 7 Scattering curves at low q-values showing the effect of adding different amounts of the ionic surfactant SDS to the PS-latex which has been fully covered with Triton X-405. For clarity the points were connected by lines. The concentrations of added SDS [Triton] (expressed by mg surfactant per g PS respectively) are as follows: ○: 0 mg/g [116 mg/g]; □: 70 mg/g [116 mg/g]; ■: 150 mg/g [116 mg/g]; ▽: 242 mg/g [116 mg/g]. The curves are compared with the scattering of the PS-latex fully covered with SDS (without addition of Triton): △: 64 mg/g (saturated) [0 mg/g]

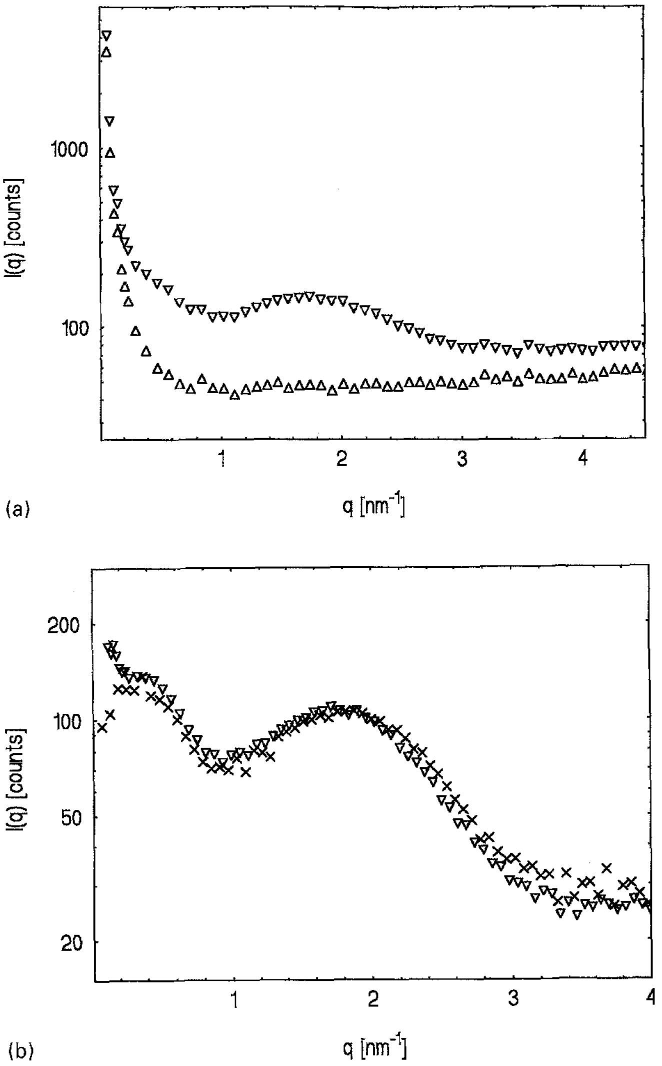


Fig. 8 Analysis of the competitive adsorption from the smeared scattering curves at higher q-values: A) Scattering curves measured from the PS-latex fully covered with Triton X-405 after addition of an excess amount of SDS and from the PS-latex fully covered with SDS (without addition of Triton). The concentrations of added SDS [Triton] (expressed by mg surfactant per g PS respectively) are as follows: ▽: 242 mg/g [116 mg/g]; △: 64 mg/g (saturated) [0 mg/g]. B) Scattering contribution of free mixed micelles consisting of SDS and Triton X-405: Comparison of a scattering curve measured separately from a solution of the mixed micelles with the one obtained from the subtraction as described in the text. The curve refers to the following concentration by weight of the micelles whereas the number in parentheses indicates the weight fraction of Triton in the micelles: X: 2.15% (0.32). The curve obtained from the subtraction refers to the following concentration of added SDS [Triton] (expressed by mg surfactant per g PS respectively): ▽: 242 mg/g [116 mg/g]

calculated difference curve obtained from Fig. 8a is compared with a separate measurement from the mixed micelles of proper concentration and composition.

Assuming complete replacement of Triton by SDS the weight concentration of the free mixed micelles is calculated from mass balance to 1.97% with the composition of 60 wt.% SDS/40 wt.% Triton. We find from Fig. 8b a weight concentration of 2.15% and a composition of 68 wt.% SDS/32 wt.% Triton. These figures compare favorably and it seems to be certain to conclude that Triton has been replaced by the excess of SDS quantitatively.

Effect of sample preparation

The previous sections demonstrated that the mutual replacement of the surfactants from the latex particle surfaces was observed. This points to the fact that the adsorption is a reversible process. We have also investigated the effect of sample preparation on the measured scattering curves by comparing two systems with the same composition but prepared in different ways: In the first case the PS latex was fully covered with SDS and subsequently a given amount of Triton was added. In the other case the Triton was added to the latex first and SDS subsequently.

The good superposition of both curves displayed in Fig. 9 shows that the mode of sample preparation is inconsequential for the observed scattering intensities as expected for an equilibrium process. The reorganization in the surfactant layer is complete within less than 24 h when the samples are shaken thoroughly. In consequence, adding the surfactants separately, one after the other, at a given molar ratio to the latex particles as done here should result in the same partition of the surfactants as in the case when both surfactants were mixed at the respective composition first and added subsequently.

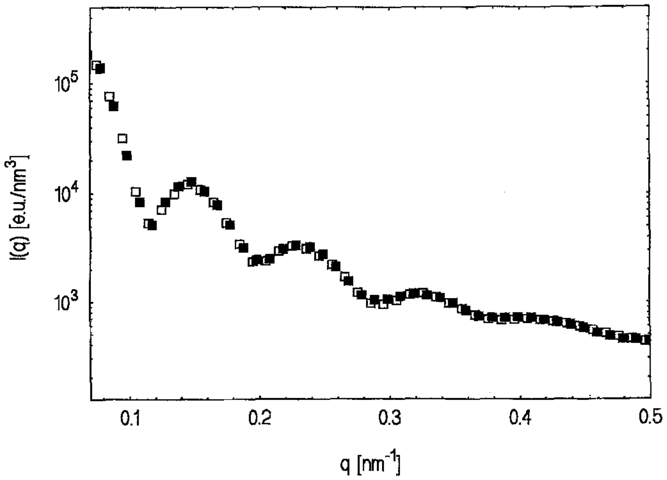


Fig. 9 Scattering curves of mixed systems with approximately the same composition but prepared in different ways. The concentrations of added SDS [Triton] (expressed by mg surfactant per g PS respectively) are as follows: □: 70 mg/g [116 mg/g], Triton added first; ■: 64 mg/g [114 mg/g], SDS added first

Conclusion

The present study has shown that SAXS is a highly useful method to monitor the adsorption process of single and mixed surfactant systems on latex particles. The method of contrast variation provides information concerning the structure and dimensions of the adsorbed layer. Detection of free micelles beside the covered particles is possible because of their characteristic scattering contributions in different q-ranges. The conclusions drawn from the analysis of the scattering curves in the low angle region are consistent with the concentrations and compositions of the free micelles determined at higher scattering angles. In the systems studied here the surfactant layers are rather compact and no adsorption of secondary surfactant micelles could be observed.

The competitive adsorption of SDS and Triton X-405 on the surface of the polystyrene latex is an equilibrium process: The nonionic surfactant replaces the anionic surfactant from the surface quantitatively when only a small excess amount of Triton is added. This process, however, is reversed upon addition of a rather high amount of SDS. In the present system there is a preferential adsorption of the nonionic surfactant. This is in accordance with the results of Kronberg et al. [5] who investigated a similar system experimentally as well as by application of thermodynamic models.

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