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# Adsorption of Sodium Dodecyl Sulfate on Polystyrene Latex Particles Using Dynamic Light Scattering and Zeta Potential Measurements

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ABSTRACT: The adsorption of sodium dodecyl sulfate (SDS) to polystyrene latex particles of low negative charge has been examined as a function of surfactant concentration by estimation of the hydrodynamic radius and also the zeta potential ($\zeta$) by electrophoretic measurements. Adsorption isotherms were also determined by a surface tension method. Adsorption at zero and low ionic strength ($10^{-3}$ M) is two-stepped: an initial hydrophobically-driven adsorption of single surfactant molecules followed at increased SDS concentrations by a cooperative adsorption at SDS concentration close to the critical micelle concentration (cmc). At higher ionic strength (0.032 M), the initial adsorption is succeeded by two maxima in $R_H$ and $\zeta$, where the second step may be related to further growth of the primarily adsorbed SDS micelles. The influence of temperature on the adsorption is small but significant.

## Introduction

The adsorption of surfactants at solid/liquid interfaces is a widely studied phenomenon because of its direct bearing on colloid stability. Adsorption phenomena are therefore relevant to industrial processes, such as emulsion polymerization. Some background literature is given in refs 1-10.

Monodisperse, spherical latex particles are frequently used as model substrates in investigations of colloid stability where different methods have been employed: e.g., surface tension,[1,4,5] electrophoresis,[2,8] spectroscopy,[9,10] and conductance.[5] In the present paper we study adsorption to well-defined latex particles of uniform size and charge. The main technique used is dynamic light scattering. This technique has been surprisingly little employed in investigations of adsorption phenomena. As currently practiced, the hydrodynamic radius, and therefore the effective thickness of an adsorbed surfactant layer at the particle/solvent interface, can be determined with high accuracy by measurement of the latex diffusion coefficient at high dilution in the presence and, respectively, the absence of surfactant. Illustrations of the usefulness of this approach are provided by recent papers dealing with the adsorption of polymers to latex particles.[11] A more comprehensive interpretation of the data, however, also requires information on the total amount of adsorbed material. For this reason complementary measurements have been made here of the adsorption isotherms using a surface tension method to determine the equilibrium level of free surfactant. Zeta potential measurements, which quantify the changes in surface charge, have also been made. The effects of changing the parameters (SDS concentration, simple electrolyte (NaBr) concentration, and the temperature) have been investigated.

## Experimental Section

**Materials.** SDS was obtained ("special purity" grade) from BDH. The SDS purity was checked by surface tension measurements to determine the cmc. The latter gave a cmc value in good agreement with literature values (≈8 mM). There was no characteristic dip prior to the cmc "knee point" (Figure 1) which would have indicated the presence of impurities. The SDS was used without further purification. Water was deionized and distilled. Latex samples were purchased from Serva AG, Heidelberg, Germany. Latex 12 had a nominal diameter of 202 μm. The latex was further purified by exhaustive dialysis against a large volume of distilled water in well-washed bags to remove possible traces of polysaccharides and for the removal of surfactants and traces of salts. The pH was adjusted to 7 using NaOH. Conductometric titration was performed on the dialyzed latex preparations. The content of sulfate groups was estimated as ≈9.7 mmol/kg latex. The zeta potential was −27 mV for the salt-free suspension. Conductometric titration was employed to determine the total concentration of bound surface charge groups. Experiments were in general made using a constant concentration of latex = $5 \times 10^{-5}$%. All solutions were filtered through 0.45-μm Millipore filters.

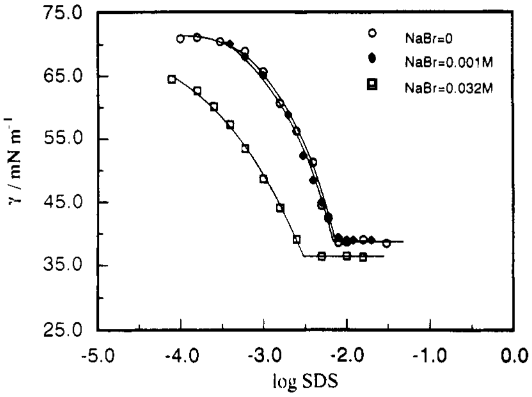

**Figure 1.** Semilogarithmic plot of surface tension ($\gamma$) versus SDS concentration at three ionic strengths. The "knee" corresponds to the critical micelle concentration (cmc) of SDS at that salt concentration. These plots are used as calibration curves for the estimation of adsorption isotherms by measurement of surface tension by the drop-volume method.

**Dynamic light scattering** measurements were made in the homodyne mode using a 50-mW 633-nm He-Ne laser as the light source. The scattering cells (10-mL cylindrical ampules) were immersed in a large-diameter (10 cm) thermostated bath of index-matching liquid (*trans*-decalin) of $n$ = 1.479 at 25 °C. The detector system comprised an ITT FW130 photomultiplier, the output of which was digitized by an ALV amplifier-discriminator. The signal analyzer was an ALV multibit, multi-sample time autocorrelator (ALV3000) with 191 channels covering approximately 8 decades in delay time. Analyses were made using both the method of cumulants and inverse Laplace transformation using the algorithm REPES. The autocorrelation functions were close to single exponential, with low values of the second cumulant (<0.05).

**Electrophoretic light scattering** (zeta potential) determinations were made using a Malvern Zetasizer-II instrument for

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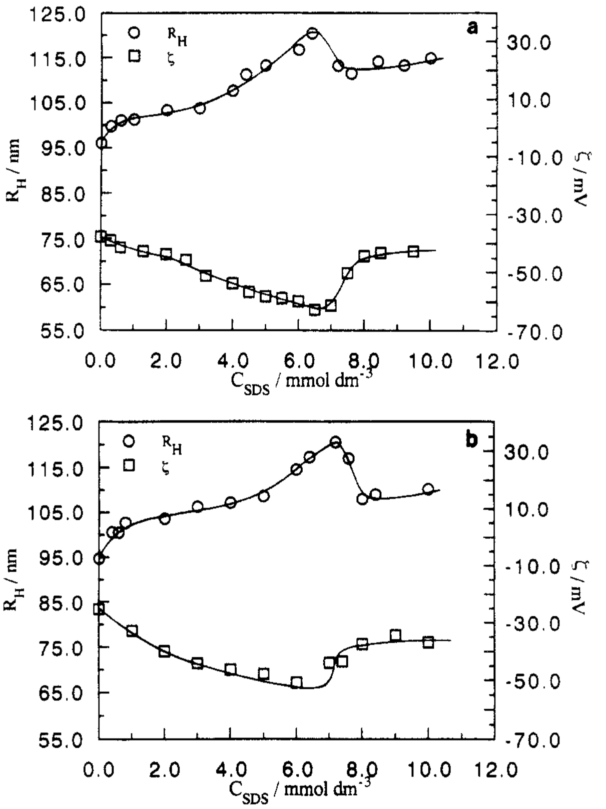

**Figure 2.** Hydrodynamic radius ($R_H$) (left) and zeta potential (ζ) (right) as a function of SDS concentration for a latex suspension (a) in the salt-free system and (b) at ionic strength 0.001 M NaBr.

electrophoretic mobility measurements. The zeta potential (ζ)—i.e., the potential at the particle/electrolyte interface—is calculated from the measured mobility ($u$) using the expression $u = E\zeta/4\pi\eta_0$, where $E$ is the dielectric constant of the medium and $\eta_0$ its viscosity. The instrument required a sample volume of 0.5 mL, and measurements were made at an angle of 90° and at pH 7.

**Adsorption isotherms** were measured by determining the concentration of free SDS by surface tension measurements using the drop-volume method. Latex particles were suspended in a SDS solution of known concentration for 48 h, after which the latex was removed by centrifugation (20 000 rpm for 30 min). Typical calibration curves for SDS at various ionic strengths are shown in Figure 1, where the cmc is given by the "knee point". The steeply rising initial part of the curves was used for determining the SDS concentration in the supernatant liquid by measurement of the surface tension.

## Results and Discussion

**Hydrodynamic Radii and Zeta Potential Data.** Figure 2a shows the variation in the hydrodynamic radius, $R_H$, of the latex particle in the salt-free system and the corresponding change in the zeta potential, ζ. Figure 2b, which corresponds to a low ionic strength of 0.001 M, is virtually identical. The variation in ζ, showing an increasing negative charge as SDS is adsorbed at the latex interface, almost precisely mirrors that in $R_H$. In the electrophoretic experiment, the latex particle has a speed which depends on both the charge and the effective hydrodynamic radius, since the mobility is given by the ratio of the particle charge to the friction coefficient. Because a change in the electrophoretic mobility may reflect a change in the charge and/or a change in the particle radius, the apparent changes in the electrokinetic surface charge might be interpreted as substantiating the data on the hydrodynamic radius. The changes in $R_H$ with surfactant concentration are large (with an estimated uncertainty in the radius of ±0.3 nm) and are also pronounced when the ionic strength or temperature is altered. These observations suggest that the pendant polystyrene chains at the latex surface may be a key feature in determining the adsorption of surfactants. The magnitude of the changes, however, implies that the effect is not simply confined to the surface layer but that the swelling of the latex occurs within the latex particle through diffusion of the surfactant molecules to sites in the particle interior.

The data show two main features: (1) an initial increase in $R_H$ at low SDS concentrations ($C < 4$ mmol/L); (2) a strong increase at $C > 5$ mmol/L SDS, before decreasing to an approximately constant level above $C = 8$ mmol/L SDS. Complementary data provided by the adsorption isotherms (below) show that the peaks in Figure 2a,b reflect real increases in the adsorbed amount of SDS, and thus both surface charge and $R_H$ change on adsorption of SDS molecules.

We place the following tentative interpretation on the data summarized in Figure 2a,b.

(i) At low SDS concentration, single SDS molecules adsorb by hydrophobic interaction at the latex surface (made up of anchored PS chains terminated in $SO_4^-$ groups), giving an increase in the zeta potential. The primary driving force must be hydrophobic since the SDS charge and the charge on the latex surface have the same sign. The alkyl chains will most likely lie flat on the surface. Since a pronounced increase in $R_H$ of the latex (≈10 nm) is observed, it is possible that the alkyl chains of the surfactant also associate with the polystyrene chains. Changes in the conformation of polymer chains at the interface may then be involved: steric interaction and repulsive forces would lead to extension of the polymer chains and the initial increase which is observed in $R_H$.

(ii) With further increase in SDS concentration with greater surface coverage, SDS molecules adsorb cooperatively. There is a strong but gradual increase both in $R_H$ and in the electrophoretic mobility. The magnitude of the increase could suggest that more than a single layer is involved. It is important that the DLS correlation functions are always strictly monoexponential, showing that there are no association effects between latex spheres. The orientation of the surfactant molecules is primarily determined by the charge interactions between the head groups of the surfactants and hydrophobic interactions between the surfactant tails with each other and with the polymeric surface. With increasing SDS concentration at the interface, the surfactant molecules should thus move into a more vertical position so that the head groups become orientated toward the solution. The alkyl chains can then interact more effectively, favoring the formation of micelles or hemimicelles as the cmc for the surfactant in solution is approached. Above 7–8 mmol/L SDS, the latex radius becomes abruptly smaller and there is a corresponding reduction in the mobility. This concentration is very close to the cmc of free SDS micelles in aqueous, salt-free solution where free micelles are formed. Any further addition of SDS, and thus excess $Na^+$ counterions, functions to screen the interactions between the anchored SDS micelles and leads to a reduction in the surface potential and produces a more compact form. In this way it is possible to understand the observed maxima in $R_H$ and the zeta potential.

Two main steps—an initial, noncooperative process, followed by a cooperative one—are thus visualized in the adsorption, as will substantiated by the adsorption isotherms; see, for example, Figures 4 and 5. Earlier interpretations of data on the adsorption of surfactants implicitly assumed that at saturation the surfactant forms a monolayer at the latex interface with solvent.

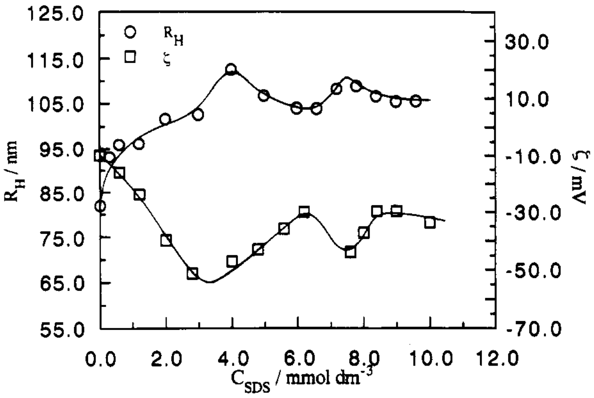

**Figure 3.** Analogous plots to those in Figure 2 for the same latex suspension at ionic strength 0.032 M NaBr.

There are close similarities here with the adsorption of ions at the latex surface as discussed in detail by Voegtli and Zukoski.[12] According to classical electrokinetic theory, the electrophoretic mobility should increase monotonically with decreasing ionic strength due to expansion of the double layer and an increase in the particle surface potential. However, the mobility is observed to pass through a maximum as the ionic strength is reduced, a phenomenon which has been variously explained by the adsorption of ions, morphological changes at the surface, and changes in the conformation of the pendant polymer chains at the interface. Ma et al.[13] used measurement of the electrophoretic mobility to study the adsorption of salts into hydrolyzed latex particles. Their results and those of Voegtli and Zukoski[12] suggest that the origin of the electrokinetic charge is the adsorption of anions onto the hydrophobic portions of the latex surface.

The fact that SDS does not adsorb significantly to silica gel having a similar charge density[14] suggests that hydrophobic forces are primarily involved. We have recently studied the binding of SDS micelles to poly(ethylene oxide) (PEO) chains. The latter system has been extensively examined using a variety of experimental methods, such as neutron scattering, fluorescence decay, conductance, viscosimetry, and light scattering. In this case, the accumulated evidence is persuasive that the PEO chain wraps around the small SDS micelles and the polymer segments are associated with the micellar head group region. A succession of such micelles is present along the PEO backbone up to a saturation level with the formation of a charged complex and associated expansion of the chain due to repulsive interactions. Beyond the saturation point, screening effects from excess $Na^+$ counterions lead to diminished chain expansion. Other types of polymer chain having less polar moieties, e.g., poly(vinylpyrrolidone) and ethyl (hydroxyethyl)cellulose, also interact with SDS, and it is probable that a similar mechanism is involved.

**Influence of Ionic Strength.** While at low ionic strength (0.001 M NaBr) the adsorption levels are similar to those in the salt-free system, raising the ionic strength to $3.2 \times 10^{-2}$ M leads to qualitatively different behavior. Figure 3 shows that the initial increase in $R_H$ is now greater than for the low- or zero-salt case but is now succeeded by two maxima. These changes are mirrored by the strong corresponding changes in the zeta potential with two well-separated peaks.

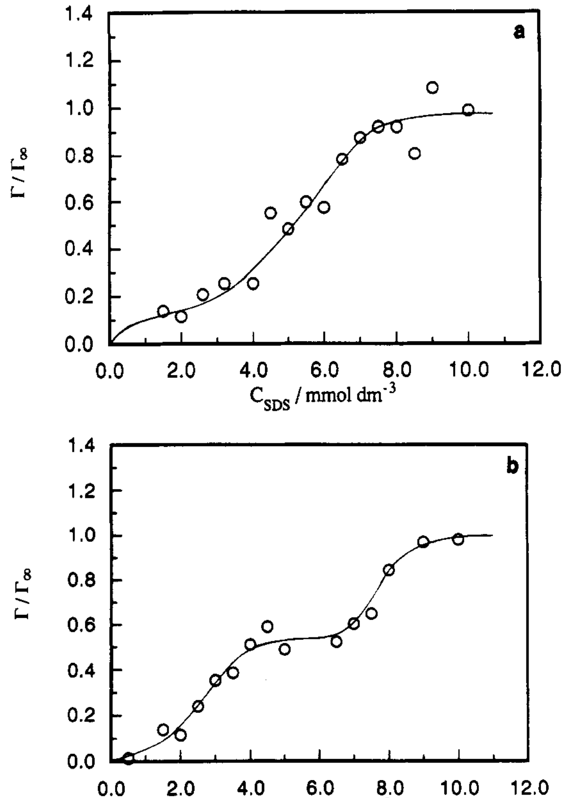

**Figure 4.** Relative adsorption isotherms for a latex suspension obtained through surface tension measurements ($\Gamma/\Gamma_\infty$) versus SDS concentration (a) for the salt-free system and (b) in 0.001 M NaBr.

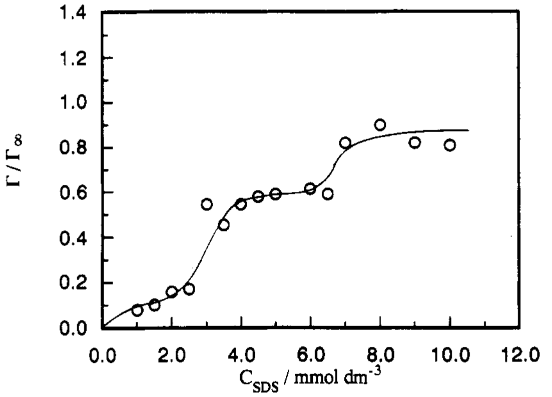

**Figure 5.** Relative adsorption isotherm analogous to Figure 4 at ionic strength 0.032 M NaBr.

It is relevant to note that, at this high ionic strength, the hydrodynamic radius of the latex itself is substantially smaller (about 12 nm smaller in radius) than that in the salt-free system or at very low ionic strength. This effect was noted earlier in latex–salt solutions.[11] One thus concludes that the ionic atmosphere is less extensive and the surface hydration is smaller in the system at high ionic strength. The magnitude of the effect suggests that it is not restricted to the surface layer and that the interior swelling of the latex sphere changes with ionic strength.

The first peak in $R_H$ (Figure 3) at a concentration of about 3–4 mmol/L is close to the cmc for SDS in an aqueous solution of the same ionic strength (≈4 mmol/L), the cmc being lower in the presence of salt than in the salt-free system. Thus, as above, we associate the first peak with the formation of micelles in the system by a cooperative process and the subsequent reduction in $R_H$ with an increasing concentration of free $Na^+$ counterions.

The second, less well-pronounced, peak at $C_{SDS} \approx 8$ mmol/L may be associated with further growth of the primary micelles, possibly with formation of a secondary layer. The change in $R_H$ is then smaller as would be expected. Micellar growth with increasing ionic strength has been noted using fluorescence decay measurements in, for example, the PEO/SDS system. A stronger adsorption of surfactants in the presence of simple salts is anticipated since the repulsive forces between the polar

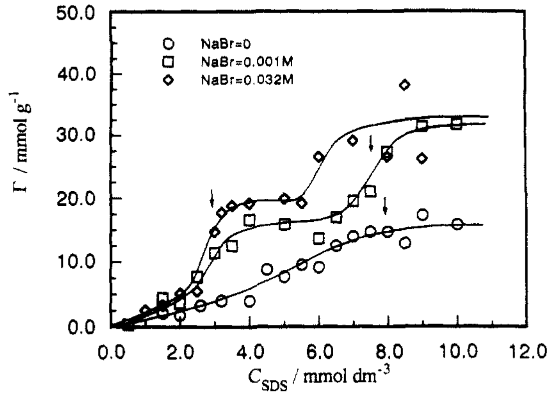

**Figure 6.** Absolute adsorption isotherms at three ionic strengths and 25 °C. The vertical arrows indicate the cmc at each ionic strength.

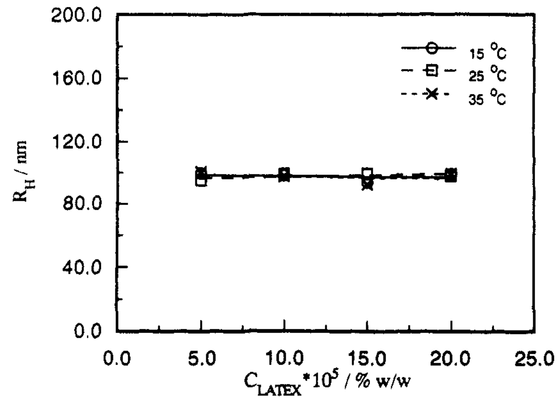

**Figure 7.** Hydrodynamic radius (nm) from dynamic light scattering measurements at different temperatures for the latex concentration range shown.

head groups of the surfactant will be reduced by (i) screening effects, (ii) the lower degree of ionization of the surfactant molecules, and (iii) a reduction in hydration shells: thus more SDS molecules can adsorb and pack more compactly at the interface with less energy. The above results are also in accord with the data in refs 1, 2, 15, and 16 for the increase of surfactant adsorption at a solid surface when simple electrolyte is added. For the same reasons, the cmc of the solution decreases as the ionic strength is increased.

**Adsorption isotherms** have been obtained as described in the Experimental Section. Relative adsorption data for the salt-free system and in 0.001 M NaBr are shown in Figure 4a,b. The curves are two-stepped, as was suggested by the curves in Figure 2a,b. Figure 5 shows similar behavior for the data in the high ionic strength, which displays the three steps as seen in Figure 4.

Figure 6 shows that the adsorption is initiated at a lower SDS concentration in the presence of salt and that the absolute quantity of SDS bound increases with increasing ionic strength as expected at a given SDS concentration.

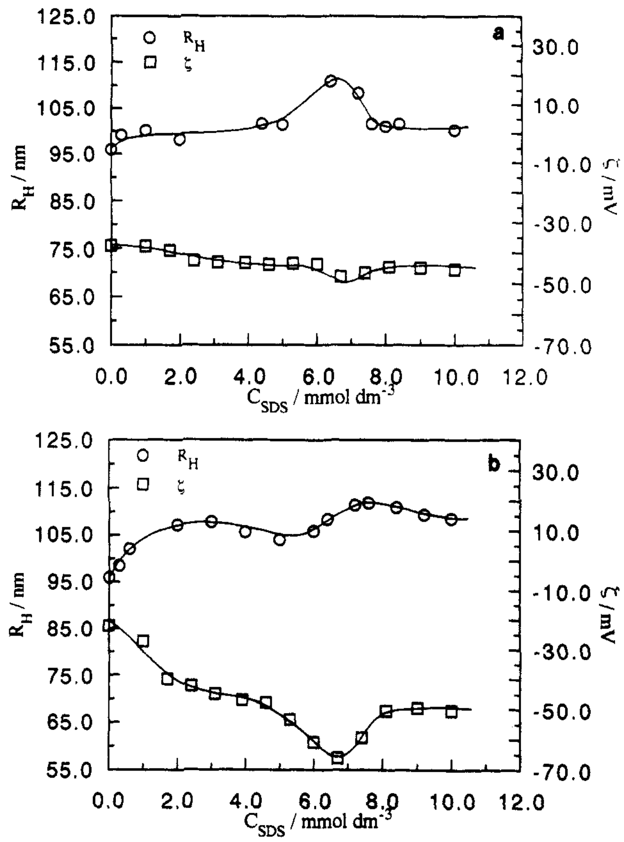

**Figure 8.** Hydrodynamic radius ($R_H$) from dynamic light scattering and zeta potential ($\zeta$) from mobility measurements as a function of SDS concentration at (a) 15 °C and (b) 35 °C.

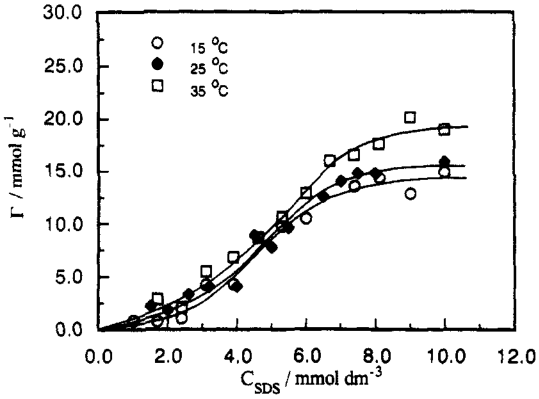

**Figure 9.** Absolute adsorption isotherms for a latex suspension in the salt-free system at the three temperatures indicated.

Zhu and co-workers[20-23] have used a two-step adsorption model and derived a general isotherm equation to describe the adsorption mechanism. Adapted to the present framework, in a first noncooperative step single surfactant molecules are adsorbed by hydrophobic interactions with the solid surface. In the second cooperative step at higher surface coverage, surfactant molecules reorientate to expose the head groups to the solution and to optimize interactions between the alkyl chains with the formation of micelles or hemimicelles. By mass action reasoning, such a model gives

$$\Gamma = \frac{\Gamma_\infty k_1 C(1/n + k_2 C^{n-1})}{1 + k_1 C(1 + k_2 C^{n-1})} \qquad (1)$$

where $n$ is the aggregation number of the micelle and $k_1$ and $k_2$ are the equilibrium constants for the first and second steps. There are, of course, substantial differences between the latex particles used here and the planar inorganic substrates considered by the authors, since the former are characterized by an uneven surface covered by polymer chains. Nevertheless, fitting to the data gives physically reasonable parameters: $n \approx 5$, $k_1 = 1.0 \times 10^3$, and $k_2 = 2.0 \times 10^9$ for the system with zero salt.

**Influence of Temperature.** Measurements of the hydrodynamic radius at different temperatures have been made by dynamic light scattering and also using electrophoretic light scattering. The hydrodynamic radius of the latex itself is insensitive to temperature change in the range 15–35 °C as seen in Figure 7. Data are shown in

Figure 8a,b for the salt-free system at various concentrations of SDS at the same temperatures. There is a small but clear increase in adsorption with increasing temperature. Such an effect of temperature change on the adsorption of SDS is anticipated when the surface hydration is diminished. We note that Piirma and Chen[4] find a small influence of temperature on the adsorption of SDS to PS latex particles by determining the molecular area of the surfactant on the particle surface at different temperatures. Corresponding adsorption isotherms are shown in Figure 9 and, in spite of the data scatter, it is seen that the plateau level increases with increasing temperature.

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