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***In Situ*, Nonlinear Optical Probe of Surfactant Adsorption on the Surface of Microparticles in Colloids**

Hongfei Wang,^{†,‡,§} Thomas Troxler,^{†,‡} An-Gong Yeh,[‡] and Hai-Lung Dai^{*,†}

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323,
and DuPont Marshall Laboratory, 3401 Grays Ferry Avenue, Philadelphia, Pennsylvania
19146

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The demonstration of a nonlinear optical technique for directly monitoring adsorption of surfactants on the surface of microparticles in colloids is reported. In this approach, dye molecules with strong hyperpolarizability are first adsorbed on the particle surface to give detectable second-harmonic generation. The surfactant is then added to the colloidal solution in competition with dye for adsorption on the surface. The displacement of the dye molecules on the surface results in a decrease of the second-harmonic signal, indicating the adsorption of the surfactant molecules. A continuous flow/titration system in combination with a high-repetition-rate femtosecond laser allows the adsorption to be monitored in real time. This approach was first demonstrated on a methacrylate polymeric surfactant on latex and talc particles in an aqueous solution. The adsorption free energy and surface density of this surfactant on these particles have been determined.

I. Introduction

Colloidal systems are of great importance to many aspects of life, ranging from environmental and health issues to applications in chemical, energy, agricultural, and pharmaceutical industries. A key to further the understanding of colloidal properties and to affect their use in technology is our understanding of and ability to control the interactions at the liquid/solid interfaces in colloids. A conventional way of influencing liquid/solid interactions is to modify particle surface properties by adsorption of surfactant molecules.¹ Adding surfactant has become a common practice in changing the dispersion and emulsion properties of colloids that are important to industrial applications.

To characterize the interaction between the microparticles and the molecules in the colloidal solution, it is desirable that the adsorption of surfactant molecules onto the solid particle surfaces be directly monitored. Traditional methods for monitoring adsorption, that is, establishing the adsorption isotherm, have involved spectroscopic analyses of the aliquot solutions before and after establishing the adsorption equilibrium following the addition of a known quantity of the surfactant. Such *indirect* methods can be time-consuming, tedious, and prone to errors induced by contamination, as pointed out by a recent review.²

Ideally, surfactant adsorption should be probed with real time resolution to reflect the instantaneous condition of the colloidal solution. The probe should not interfere

with the adsorption process itself. Most importantly, such a probe should have sensitivity for *buried* surfaces; that is, the molecules adsorbed on the surfaces can be differentiated from the ones dissolved in the liquid, which exist with an orders of magnitude larger quantity. Linear optical probes, such as absorption spectroscopy, light scattering, ellipsometry, and fluorescence spectroscopy, have the advantages of real time resolution and nonintrusiveness. These methods, however, require a separation step for detecting only the molecules adsorbed on the surface.

Second-order nonlinear optical processes, such as second-harmonic generation (SHG) and the more general sum frequency generation, have been shown to be a surface-specific probe for interfacial structure and processes in various environments.³ In SHG an optical signal is detected at twice the frequency but along the same propagation direction of the incident light. As an optical technique, SHG has real time, spatial, and frequency resolutions and is nonintrusive and suitable for all pressure ranges. The surface sensitivity arises from the lack of inversion symmetry at the surface of a centrosymmetric medium. In such materials with a center of inversion symmetry, the dipole contribution to SHG is symmetry forbidden. Only at the surface, due to the breakdown of the inversion symmetry, is the dipole-allowed SHG restored. Adsorption on surfaces results in surface–adsorbate bonding, which often reduces the substrate electron polarizability and causes a decrease in SHG. For substrates with strong polarizability, such as metals or semiconductors, submonolayer adsorption sensitivity at the interface can be easily achieved.⁴

Most SHG studies so far were successfully performed on planar surfaces. Adopting this technique for probing the surfaces of the microparticles in a colloidal solution faces additional challenges. The particles are often not in

[†] University of Pennsylvania.

[‡] DuPont Marshall Laboratory.

[§] Present address: Institute of Chemistry, Chinese Academy of Sciences, Beijing, People's Republic of China 100080.

(1) (a) *Adsorption from Solution at the Interface*, Parfitt, G. D., Rochester, C. H., Eds.; Academic Press: London, 1983. (b) Adamson, A. W.; Gast, A. *Physical Chemistry of Surfaces*, 6th ed.; John Wiley & Sons: New York, 1997. (c) Chatteraj, D. K.; Birdi, K. S. *Adsorption and the Gibbs Surface Excess*; Plenum Press: 1984. (d) *Powder Technology Handbook*; Gotoh, K., Masuda, H., Higashitani, K., Eds.; Marcel Dekker: New York, 1997.

(2) Parfitt, G. D.; Rochester, C. H. In *Adsorption from Solution at the Interface*; Parfitt, G. D., Rochester, C. H., Academic Press: London, 1983; Chapter 1, p 13.

(3) (a) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984; *Annu. Rev. Phys. Chem.* **1989**, *40*, 327. (b) Richmond, G. L.; Robinson, J. M.; Shannon, V. L. *Prog. Surf. Sci.* **1988**, *28*, 1. (c) Eiseenthal, K. B. *Annu. Rev. Phys. Chem.* **1992**, *43*, 627; *Chem. Rev.* **1996**, *96*, 1343–60. (d) Corn, R. M.; Higgins, D. A. *Chem. Rev.* **1994**, *94*, 107–25. (e) Dai, H. L. *J. Chin. Chem. Soc. (Taipei)* **1995**, *42*, 461.

a crystalline form with an inversion symmetry, so their surfaces present no unique source for the SHG. In fact, the bulk portion of the particles may contribute substantially to the SHG, making the differentiation of the surface contribution difficult.

An alternative approach using SHG to acquire surface adsorption sensitivity in colloids has been recently demonstrated for a special class of molecules that has large dipole polarizability by Eisenthal and co-workers.⁵ A significant SHG signal can be detected from the surface of micron-sized polystyrene sulfate latex particles upon adsorption of the dye molecule malachite green (MG), due to the resonantly enhanced, strong hyperpolarizability of the MG molecule.

When the MG molecules are adsorbed onto the particle surfaces, two qualitatively different situations, depending on the size of the particles, may result. The nonlinear optical response of the system, which includes the adsorbed molecules and the particles, is a linear vector sum of all the individual molecular polarizabilities within the coherent length, often on the order of the wavelength, of the incident light. If the microparticles are smaller than the coherent length, the linear sum of the dipolar hyperpolarizabilities of all the adsorbed molecules on the spherical particle, pointing to all 360° around this sphere, will be zero. However, for cases where the particle diameter is *larger than or comparable to* the coherent length, the linear sum is now *nonzero* and gives SHG.^{5a} The dye molecules dissolved in the liquid are oriented isotropically, so their hyperpolarizability adds up to zero. Only the molecules on the surface may acquire the same orientation relative to the particle surface normal and provide a nonzero addition of the hyperpolarizability for SHG.

From detecting the SHG from colloidal solutions prepared with known MG concentrations using infrared fundamental light, Eisenthal and co-workers have shown that the isotherm can be established for the adsorption of the MG dye onto micron-sized latex particles, and the adsorption free energy and the maximum surface density of the dye molecules can in principle be determined.^{5b}

This approach, however, is hard pressed to be used directly for detecting the adsorption of surfactant molecules. Unfortunately, most polymeric surfactant molecules, for lack of a highly polarizable chromophore, normally do not have a sufficiently large hyperpolarizability to be detected just like the dye molecules. As a result, we propose an alternative approach, based on the competition of adsorption onto the particle surface between the SHG-detectable dye molecules and the surfactant molecules, to directly detect the adsorption of surfactant molecules.

The procedure is as follows: An appropriate dye is first selected so that a saturation coverage on the particle surface can be reached at a modest dye concentration in the liquid solution where the colloidal solution properties are not much disturbed by the presence of the dye molecules. This saturation coverage of dye molecules on the surface will give a constant SHG signal. When the surfactant molecules are added to the solution, their adsorption will displace the dye from the surface, resulting in a decrease of the SHG signal. The adsorption free energy

and surface density of the dye molecule can be deduced first from the SHG-measured adsorption isotherm. With these quantities known, the same parameters for the surfactant molecule can then be obtained from the surfactant adsorption isotherm manifested through the displacement of the dye molecules.

We have devised a flow system interfaced with a continuous titration apparatus so we can measure the instantaneous SHG response to any change in the particle surface coverage. With this apparatus we now have the ability to directly observe the adsorption isotherm of any molecules that are SHG detectable within the time scale required to achieve equilibrium, whether it be a fraction of a second or minutes. In fact this time required for reaching equilibrium can be directly observed in the time-resolved SHG response. Here we report direct observation of adsorption of molecules with low hyperpolarizabilities, like the polymeric surfactant, through competition with the SHG-detectable molecules on the surface of microparticles.

II. Experimental Section

For nonlinear optical experiments, a high peak power from the light source is preferred. On the other hand, absorption of the light energy by the colloid should be kept at the minimum to avoid heating and photochemistry. For these reasons, a Ti-sapphire femtosecond laser with oscillator only (Coherent Mira Seed pumped by a Coherent Innova 300 Ar ion laser) is used. This laser generates nominally 50 fs laser pulses at a 76 MHz repetition rate tunable from 760 to 870 nm. The femtosecond laser is used essentially as a continuous bright light source for second-harmonic generation while its low pulse energy (below 1 nJ) ensures no heating effect from absorption of the light. For the experiments here, the wavelength is set at 846 nm and the 0.5 W output in the 1 mm diameter beam is focused with a 2 in. f1 lens into the sample, a liquid jet described below. A filter (Schott RG695) is placed before the lens to cut off any possible SHG from elements in the optical path up to this point (Figure 1).

The sample is prepared in a flow/titration system (see Figure 2). At the center of this flow system is a reservoir containing a solution with a total volume of 500 mL. The solution is circulated through a liquid pump with a pumping speed about 200 mL/min to form a liquid jet through a nozzle which is made out of pressed copper tubing with a 1/16 in. inner diameter. The laser intercepts the center of the jet perpendicularly and passes through an approximately 2 mm thickness. Using the jet, instead of a steady cell, avoids nonlinear optical signals generated from the windows of the cell as well as accumulation and coagulation of particles/dye/surfactant on the window walls. The liquid is then collected and returned to the reservoir and forms a complete circulation loop with a circulation period of about 20 s. The solution in the reservoir is constantly stirred with a magnetic stirrer and disturbed with an ultrasound dispenser to prevent aggregation of the particles. The dye or surfactant molecules, dissolved at a known high concentration in the same solvent as the colloid, are added into the reservoir with a digital titration buret (CAT Contiburret). The titration amount is always kept below 20 mL, and the effect of the volume change is included in the analysis.

The fundamental light and the second-harmonic signal after the sample jet are collected with a 2 in. f1 lens and sent through a telescope for a 5 times beam size reduction before focusing into a monochromator (Jarrel-Ash 1/4 m). The combination of the monochromator, which is set at 423 nm with a 2 nm bandwidth and filters (Schott BG39, 2 mm × 2 mm), placed right in front of the entrance effectively eliminates fluorescence and scattering signals at other wavelengths. The second-harmonic signal is then detected with a photomultiplier tube (Hamamatsu R585). The output is preamplified with a Stanford Research Systems SR440 amplifier and processed with a photon counter (SRS SR400). The high repetition rate of the laser pulses allows phase-sensitive suppression of the noise and correlated photon counting to improve the signal/noise ratio.

(4) See for example: (a) Heinz, T. F.; Tom, H. W. K.; Shen, Y. R. *Phys. Rev. A* **1983**, *28*, 1883. (b) Tom, H. W. K.; Mate, C. M.; Zhu, X. D.; Crowell, J. E.; Heinz, T. F.; Somorjai, G. A.; Shen, Y. R. *Phys. Rev. Lett.* **1984**, *52*, 348. (c) Heskett, D.; Song, K. J.; Plummer, E. W.; Burns, A.; Dai, H. L. *J. Chem. Phys.* **1986**, *85*, 7490. (d) Heskett, D.; Urbach, L. E.; Song, K. J.; Plummer, E. W.; Dai, H. L. *Surf. Sci.* **1985**, *197*, 225. (5) (a) Wang, H. F.; Yan, E. C. Y.; Borguet, E.; Eisenthal, K. B. *Chem. Phys. Lett.* **1996**, *259*, 15–20. (b) Wang, H. F.; Yan, E. C. Y.; Liu, Y.; Eisenthal, K. B. *J. Phys. Chem. B* **1998**, *102*, 4446–50.

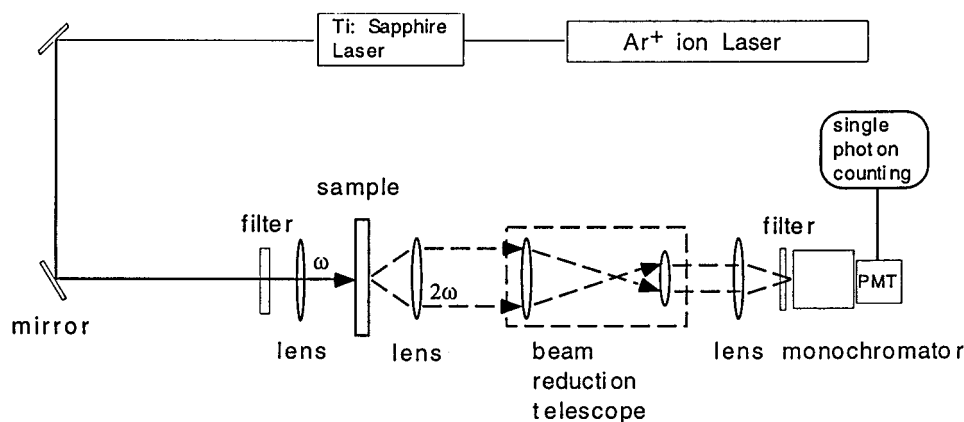


Figure 1. Experimental setup for the particle surface SHG measurement. A continuous liquid jet, shown in Figure 2, is used to ensure real time measurement and avoid problems caused by adsorption or condensation on optical cell walls.

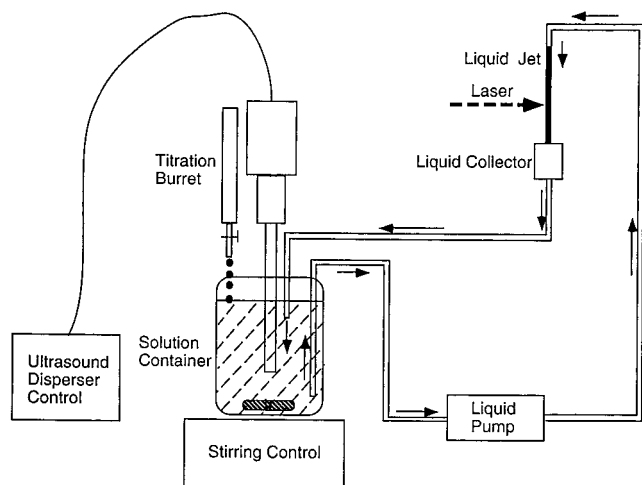


Figure 2. Liquid jet sample and circulation system. A magnetic stirrer is used to ensure effective mixing, and an ultrasonic dispenser is used to reduce coagulation of particles. A digital buret is controlled with a computer and synchronized to the data acquisition program.

For the prototypical experiment described here, the colloid is prepared with polystyrene (latex) sulfate (PSS) microspheres (Polysciences) in water. The PSS particle surface is negatively charged due to the presence of sulfate (SO_4^-) groups. The particles are uniformly spherical and supplied monodispersed in aqueous solution (diameter $1.05 \pm 0.03 \mu\text{m}$). The w/w concentration of the stock solution is 2.67%. In the experiment, 1.90 mL of the stock solution is mixed with 5.0 mL of 0.01 N HCl aqueous solution and diluted up to a total volume of 500 mL with a pH value measured to be 4.0 ± 0.2 . The dye molecule used here is Malachite Green (MG) from an aqueous solution of malachite green chloride (Aldrich, used without further purification) at a concentration of $100.0 \mu\text{M}$ at $\text{pH} = 4.0 \pm 0.2$. The surfactant, provided by the DuPont Marshall Laboratory, is a methacrylate-based, water soluble polymer mixture with a distribution of hydrocarbon chain lengths. The number-averaged molecular weight of the surfactant is $M_n = 3300 \text{ g/mol}$, while the weight-averaged molecular weight is $M_w = 8500 \text{ g/mol}$. The stock surfactant solution concentration is 5.00 g/L with $\text{pH} = 4.0 \pm 0.2$. The solution pH is controlled at around 4.0 because MG is in its single-charged (green) form between pH 2.0 and 6.5.⁶

To demonstrate the general utility of this approach, an experiment was also performed to monitor adsorption of the surfactant using another dye molecule, bromocresol purple (BCP, Aldrich, indicator grade), on talc particles. Talc itself is a phyllosilicate with a mica-like layered crystal structure. In a

typical experiment, about 100 mg of talc powder (Aldrich, $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, $< 10 \mu\text{m}$) was dispersed in 3 mL of acetone and added to 500 mL of water. To maximize the second-harmonic signal, all talc experiments reported here were performed at $\text{pH} = 3.0 \pm 0.2$. At this pH, BCP exists in the enol form in solution, employing a strong electronic transition around 430 nm, which is in resonance with the SH wavelength. The concentration of the BCP stock solution was $570 \mu\text{M}$. During the whole adsorption/displacement experiment, the solution pH value was kept constant (within ± 0.2 units) by adding manually dropwise either 1 N HCl or 1 N NaOH solution to the dispersion to avoid signal fluctuations due to pH changes. The same stock solution of the surfactant as mentioned above was used in the second step of the displacement experiments.

All the measurements are performed at 22°C .

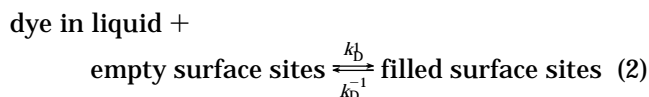
III. Theoretical Analysis of SHG from Colloidal Surfaces

The SHG intensity I_{SH} is proportional to the square of the coverage θ_D of the dye molecules on the surface and can be generally represented as

$$I_{\text{SH}} = B + [b + a\theta_D \exp(i\phi)]^2 \quad (1)$$

Here b represents the bulk contribution to the second harmonic from the particles, which may interfere with the surface contribution, designated by the proportional constant a . The effect of the interference is depicted in the phase angle ϕ . All other possible contributions to the signal detected in the experiments are summarized in the background term B .

Assuming that the adsorption follows Langmuir kinetics, the coverage θ_D is rigorously related to the total concentration C_D of the dye molecules, which include both the molecules in the liquid and the ones adsorbed on the surface, the maximum number density of the adsorbed molecules N_{max}^D , and the equilibrium constant K_D , defined as $K_D = k_D^{-1}/k_D^1$ in the adsorption equation



as

$$\theta_D = \{(C_D + N_{\text{max}}^D + 55.5/K_D) - [(C_D + N_{\text{max}}^D + 55.5/K_D)^2 - 4C_D N_{\text{max}}^D]^{1/2}\} / 2N_{\text{max}}^D \quad (3)$$

This equation is used to relate the SHG signal as a function

(6) *The Sigma-Aldrich Handbook of Stains, Dyes and Indicators*; Green, F. J., Ed.; Aldrich Chemical Co., Inc.: Milwaukee, WI, 1990; pp 436–9.

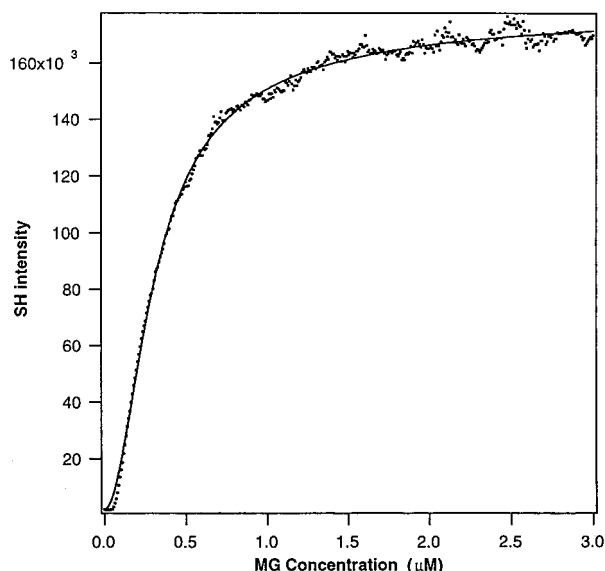
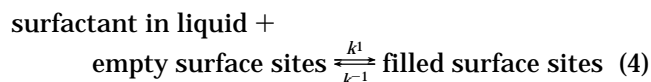


Figure 3. Adsorption isotherm of MG dye on the PSS particles (0.01%, $1.05 \pm 0.03 \mu\text{M}$, $\text{pH} = 4.0 \pm 0.2$) manifested in the SH signal. Fitting results: $N_{\text{max}}^{\text{D}} = 0.22 \pm 0.02 \mu\text{M}$, $K_{\text{D}} = (1.0 \pm 0.2) \times 10^9 \text{ M}^{-1}$, $\Delta G^{\circ} = -12.4 \pm 0.2 \text{ kcal/mol}$.

of C_{D} and subsequently for extracting $N_{\text{max}}^{\text{D}}$ and K_{D} for the dye molecule adsorption in comparison with experimental data.⁵

When the solution consists of both the dye and the surfactant molecules, in addition to the dye molecule adsorption equilibrium, there is also the surfactant adsorption equilibrium



The two equilibria coexist and are depicted by the two coupled equations

$$K_{\text{D}} \frac{(C_{\text{D}} - N_{\text{max}}^{\text{D}} \theta_{\text{D}})}{55.5} (1 - \theta_{\text{D}} - \theta_{\text{S}}) = \theta_{\text{D}} \quad (5a)$$

$$K_{\text{S}} \frac{(C_{\text{S}} - N_{\text{max}}^{\text{S}} \theta_{\text{S}})}{55.5} (1 - \theta_{\text{D}} - \theta_{\text{S}}) = \theta_{\text{S}} \quad (5b)$$

The dye molecule surface coverage θ_{D} can be straightforwardly solved using this pair of equations as a function of the dye and surfactant concentrations C_{D} and C_{S} and the surfactant properties K_{S} and $N_{\text{max}}^{\text{S}}$, given that K_{D} and $N_{\text{max}}^{\text{D}}$ are known. The result of the two equilibria is that some surfactant will displace some adsorbed dye molecules in competition for adsorption. The SHG signal is again related to θ_{D} through eq 1. A comparison of the second harmonic signal as a function of C_{S} will allow the determination of K_{S} and $N_{\text{max}}^{\text{S}}$. The former can then be used to calculate the adsorption free energy of the surfactant.

IV. Results and Analysis

A. Surfactant Adsorption on Latex Particles in Water. Before the adsorption properties of the surfactant are measured, the adsorption isotherm of the dye molecules needs to be established first. The SHG response resulting from MG adsorption on the surfaces of 0.01% PSS particles in a $\text{pH} = 4.0$ aqueous solution is shown in Figure 3. As the flow/titration system was used, the

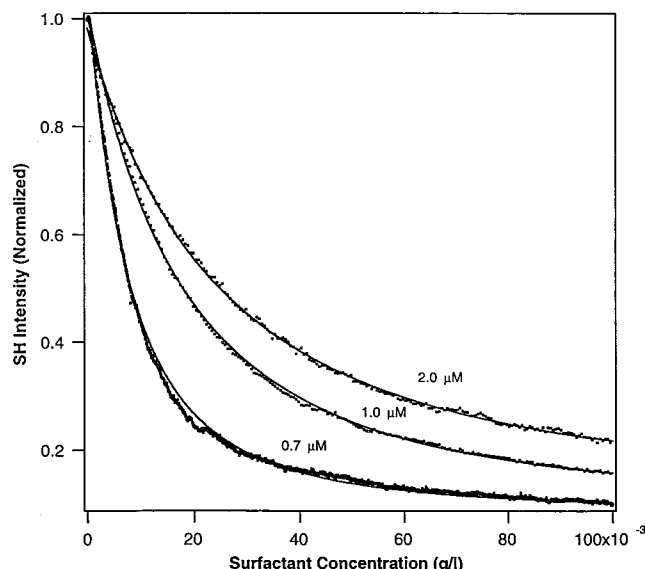


Figure 4. MG dye displacement by the surfactant manifested in the SH signal. The MG concentrations in the aqueous solution are marked by the curves. The solid points are experimental data. All curves are normalized to the zero surfactant concentration SH signal level. The dashed lines are fits to eqs 5a and 5b.

Table 1. Adsorption Free Energy and Surface Coverage of MG on the PSS Surface

$K_{\text{D}} (\text{M}^{-1})$	$\Delta G_{\text{D}}^{\circ} (\text{kcal/mol})$	$N_{\text{max}}^{\text{D}} (\mu\text{M})$	area (\AA^2)
$(1.0 \pm 0.2) \times 10^9$	-12.4 ± 0.2	0.22 ± 0.02	380 ± 40

adsorption of the dye molecules was recorded continuously with increasing dye concentration.

For the PSS particles, the bulk contribution to the SH signal is negligible, so the b parameter and the phase angle can be set as zero. A nonlinear least-squares fit using eqs 1 and 3, shown as the solid line in Figure 3, gives $N_{\text{max}}^{\text{D}} = 0.22 \pm 0.02 \mu\text{M}$ and $K_{\text{D}} = (1.0 \pm 0.2) \times 10^9 \text{ M}^{-1}$. Since the particle density of the 0.01% PSS solution is $1.6 \times 10^8 \text{ particle/cm}^3$, the average maximum surface coverage on each particle is $(0.9 \pm 0.1) \times 10^6 \text{ molecule/particle}$. This value corresponds to $380 \pm 40 \text{ \AA}^2/\text{molecule}$ surface density. The adsorption free energy is calculated from K_{D} to be $\Delta G_{\text{D}}^{\circ} = -12.4 \pm 0.2 \text{ kcal/mol}$. All these results are listed in Table 1.

The decrease in the SHG signal induced by the addition of the surfactant from 0 to 0.1 g/L to a solution prepared with 0.01% PSS and $0.7 \mu\text{M}$ MG at $\text{pH} = 4.0$ is shown in Figure 4. Note that the displacement of the dye by the surfactant is displayed in real time, which is converted into the surfactant concentration according to the titration rate. In the systems studied here, the equilibrium, indicated by the SH signal, is reached within the subsecond system response time set by the time interval between successive droplets. By using the predetermined K_{D} and $N_{\text{max}}^{\text{D}}$ values, the SHG signal is fitted to eq 5 to allow the determination of K_{S} and $N_{\text{max}}^{\text{S}}$. The nonlinear least-squares fit is shown in Figure 4 as the solid line. The fitting gives $K_{\text{S}} = (3.6 \pm 0.1) \times 10^4 \text{ L/g}$ and $N_{\text{max}}^{\text{S}} = 0.0056 \pm 0.0012 \text{ g/L}$.

This displacement model can be further tested by changing the initial concentrations and monitoring the individual system's approach to equilibrium. From the model described above, it is to be expected that when the initial MG concentration is increased, the displacement of MG by the surfactant should proceed with a slower rate. Figure 4 shows the results of this study with different

Table 2. Adsorption Free Energy and Surface Coverage of the Methacrylate Surfactant on the PSS Surface with $K_S = (2.7 \pm 0.2) \times 10^4$ L/g and $N_{\max}^S = 0.0056 \pm 0.0023$ g/L

MW	N_{\max}^S (μ M)	area (\AA^2)	K_S (M^{-1})	ΔG_S° (kcal/mol)
3300	0.51 ± 0.20	190 ± 78	$(3.0 \pm 0.2) \times 10^8$	-11.7 ± 0.1
8500	0.20 ± 0.08	480 ± 190	$(7.5 \pm 0.5) \times 10^8$	-12.3 ± 0.1

initial MG concentrations ranging from 0.7 to 1.0 to 2.0 μ M mixed with a 0.01% PSS particle solution at pH = 4.0. All these SH curves should be able to be fitted with eq 5 and yield similar K_S and N_{\max}^S values. The resulting K_S and N_{\max}^S values for the 1.0 and 2.0 μ M MG concentrations are $(2.1 \pm 0.1) \times 10^4$ L/g, 0.0091 ± 0.0030 g/L; and $(2.8 \pm 0.1) \times 10^4$ L/g, 0.0058 ± 0.0015 g/L, respectively. Accordingly, the averaged values for the surfactant adsorption constants are $K_S = (2.7 \pm 0.2) \times 10^4$ L/g and $N_{\max}^S = 0.0056 \pm 0.0023$ g/L. Since the molecular weight for the surfactant exists in a wide distribution, we have calculated K_S and N_{\max}^S , and ΔG_S° according to its M_n and M_w , respectively (see Table 2).

According to the per-unit-volume N_{\max}^S value, we can estimate the average surface coverage on each PSS particle: $(2.0 \pm 0.8) \times 10^6$ and $(0.73 \pm 0.29) \times 10^6$ molecules/particle, respectively, for M_n and M_w . From the average size of the PSS particle, we can estimate the average area occupied by each adsorbed surfactant molecule. The values are 190 ± 78 and 480 ± 190 \AA^2 /molecule, respectively, for M_n and M_w . Since each methacrylate unit occupies up to 30 to 40 \AA^2 area, these numbers indicate that only 5 to 12 units of each surfactant molecule are actually in contact with the PSS particle surface. This suggests that a very long tail extends into the solution phase, since each molecule has at least 40 to more than 100 methacrylate units, depending on its molecular weight.

B. Surfactant Adsorption on Talc Particles in Water. Another example exhibiting the successful application of this displacement strategy for determining thermodynamic properties of surfactant adsorption on micron-sized particle surfaces was obtained by measuring the displacement of bromocresol purple dye (BCP) by the surfactant on the surface of talc powder dispersed in water. Talc is a member of the phyllosilicate group, and has a mica-like structure represented by the mineralogical chemical formula ${}^2\text{Mg}^{(6)}_3\{(\text{OH})_2/\text{Si}_2\text{O}_5\}_2$. The talc powder used in these experiments was polydispersed with particle sizes < 10 μ m.

Figure 5 shows the adsorption isotherm obtained using second-harmonic generation of BCP on talc at pH = 3.0 \pm 0.2. A noticeable second-harmonic signal is already observed without the presence of BCP in the solution, which is attributed either to the talc/water interface or bulk talc. The additional signal which increases with the BCP coverage is normalized to this initial background contribution. As seen in Figure 5, once a saturated surface coverage is reached, the BCP-induced second-harmonic signal is about 10 times stronger than the initial background signal. Compared to the system of MG adsorption on PSS, the early increase of the second-harmonic signal at low BCP concentration is quite slow. This difference arises from the difference of the relative contribution of the adsorbed dye molecule and the particle itself for these two solutions, which is fully described by eq 1.

A nonlinear least-squares fit using eqs 1 and 3, including the b parameter and the phase angle, is shown with a solid line in Figure 5. From the fitting, an equilibrium constant $K_{\text{BCP}} = (2.0 \pm 0.1) \times 10^9$ M^{-1} and a maximum number of surface sites $N_{\max}^{\text{BCP}} = 11.8 \pm 0.5$ μ M were

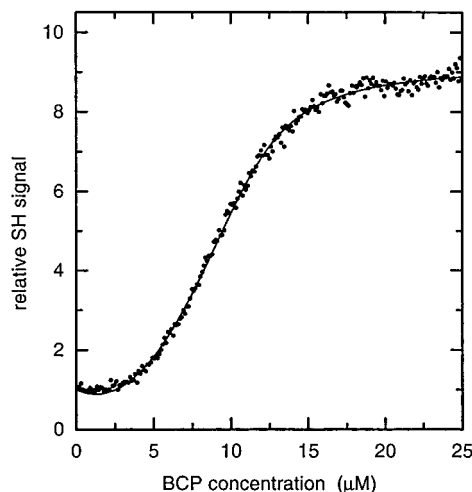


Figure 5. Second-harmonic signal due to BCP adsorption on talc in water as a function of the BCP concentration. Dots are experimental points, and the solid line is the best fit.

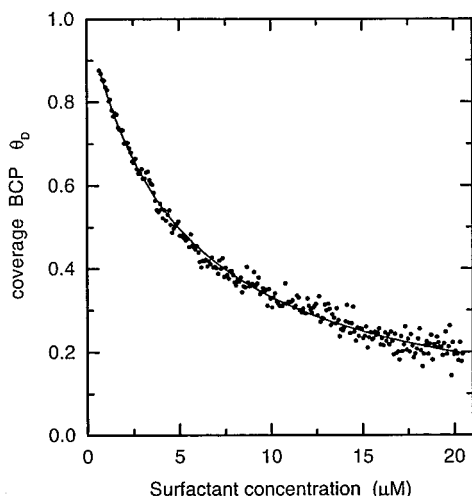


Figure 6. BCP dye coverage of talc particles in a water dispersion as a function of the surfactant concentration. The solid line represents the best fit using eqs 5a and 5b. The BCP dye concentration in this experiment is 32 μ M.

obtained. A calculation of the number of dye molecules per particle is not possible from the latter number, because of the unknown polydispersity of the talc sample. On the other hand, the adsorption free energy ΔG_{BCP} is calculated from the K_{BCP} value to be -11.2 ± 0.2 kcal/mol. The absolute value of this adsorption free energy is about 1 kcal/mol less than that of the PSS/MG system, indicating a less favorable adsorption process for the BCP adsorption on the talc surface.

When adding continuously a solution of the surfactant to the same dispersion of talc particles, which are fully covered with BCP dye molecules, a decrease of the SH signal is expected with the increasing of the surfactant concentration. Figure 6 shows the corresponding displacement trace, whereby the BCP coverage is plotted as a function of the surfactant concentration added to the dispersion. This curve was obtained from the experimentally recorded trace of the SH signal versus surfactant concentration by inverting eq 1, which describes the SH signal intensity as a function of BCP coverage given by eq 3. Thereby, we used the parameters obtained by fitting the BCP adsorption isotherm. Figure 6 shows that, at the beginning of the experiment, the signal level reached saturation due to the complete coverage of the talc particle

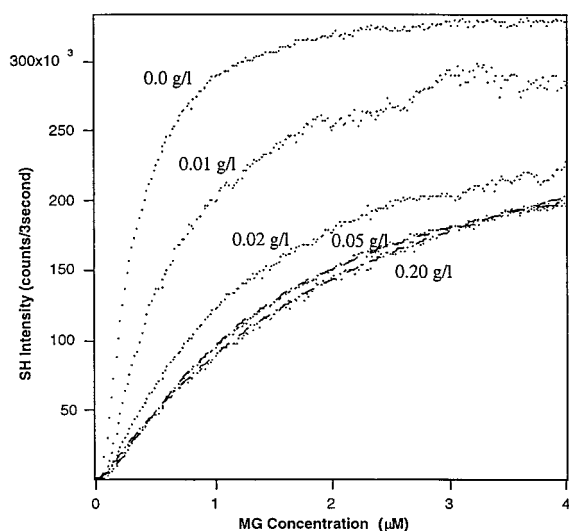


Figure 7. SH signal resulting from MG dye adsorption on the surfactant-covered PSS particle surfaces with the initial surfactant concentration set at 0.0, 0.01, 0.02, 0.05, and 0.20 g/L, respectively. (To avoid congestion, the 0.01 g/L data, which lie between the 0.05 and 0.20 g/L data, are not shown here.) Dashed lines are fitting curves using eq 3.

Table 3. Adsorption Free Energy and Coverage of BCP and the Methacrylate Surfactant on Talc

BCP on Talc	
$\Delta G_{\text{BCP}}^{\circ} = -11.2 \pm 0.2 \text{ kcal/mol}$	$N_{\text{max}}^{\text{BCP}} = 11.8 \pm 0.1 \mu\text{M}$
Surfactant on Talc (MW = 8500)	
$\Delta G_{\text{sur}}^{\circ} = -12.0 \pm 0.2 \text{ kcal/mol}$	$N_{\text{max}}^{\text{sur}} = 1.3 \pm 0.2 \mu\text{M}$

surface by BCP. The following decrease of the BCP coverage, and therefore the SH signal intensity, is explained by the displacement of the adsorbed BCP molecules by the surfactant, since the latter does not contribute any significant amount of second-harmonic intensity due to the lack of an electronic resonance in the whole visible spectral region.

Using the two adsorption equations (5a and 5b) which describe the equilibrium coverage dependence as a function of the BCP and surfactant concentrations in the solution, we were able to fit the experimental trace in Figure 7 to extract the adsorption free energy $\Delta G_{\text{sur}}^{\circ} = -12.0 \pm 0.2 \text{ kcal/mol}$, as well as the maximum surface site concentration $N_{\text{max}}^{\text{sur}} = 1.3 \pm 0.2 \mu\text{M}$, using the $M_w = 8500$ of the surfactant. All the numerical values of the adsorption parameters of this system are summarized in Table 3. It is interesting to note that the total amount of surfactant adsorbed on talc at high surfactant concentration, expressible by the fitting parameter $N_{\text{max}}^{\text{sur}}$, is about 8 times smaller than that for BCP. This indicates that one surfactant molecule displaces approximately 8 BCP dye molecules.

V. Discussion: Competition between Surfactant and Dye Molecules for Adsorption on Microparticles

We have demonstrated that, by using the strategy of displacing the adsorbed dye molecules, the adsorption of the surfactant can be monitored through the SH response of the remaining dye molecules on the particle surface. This strategy relies on a lower adsorption free energy for the surfactant than for the dye. But even with a favorable adsorption energy, the surfactant adsorption kinetics can be reversed if a sufficient dye concentration is added. In particular, in the situation where the microparticles are

first adsorbed with a layer of the surfactant, if given a sufficient dye concentration, the dye molecules should in principle be able to displace the adsorbed surfactant. This will result in an increase of the SH signal.

Figure 7 shows the results when MG is added into a solution prepared with 0.01% PSS premixed with different surfactant concentrations: 0.0, 0.01, 0.02, 0.05, and 0.20 g/L, respectively. Data for 0.10 g/L are not plotted in this figure to avoid congestion of data points. The 0.10 g/L data points all lie between the 0.05 and 0.20 g/L data points, which are already close to each other. In all curves the SH signal increases with added MG concentration. The 0.0 g/L solution behaves just like the curve shown in Figure 3. This increase slows as the surfactant concentration increases.

It is surprising that fits of the curves where surfactant is present in the solution to eq 5, with the known K_D and N_{max}^D values, result in very dissimilar surfactant adsorption constants from the ones obtained from Figure 4. The K_s values obtained here are $(1.1 \pm 0.1) \times 10^4 \text{ L/g}$ for the 0.01 g/L surfactant concentration; $(1.5 \pm 0.1) \times 10^4 \text{ L/g}$ for 0.02 g/L; $(0.8 \pm 0.1) \times 10^4 \text{ L/g}$ for 0.05 g/L; $(0.22 \pm 0.04) \times 10^4 \text{ L/g}$ for 0.10 g/L; and $(0.18 \pm 0.02) \times 10^4 \text{ L/g}$ for 0.20 g/L.

The inconsistent results indicate that equilibrium in the solution is not established by the displacement of surfactant adsorbed on the surface by the abundant dye molecules. The SH signal here actually arises from the adsorption of the MG molecule on surfactant-covered surfaces. For surfactant concentrations $\geq 0.05 \text{ g/L}$, the PSS surface is fully covered with surfactant molecules. The adsorption of MG onto the surfactant-covered surface should not be affected by, and therefore is independent from, the amount of surfactant in these solutions. The behavior of the two solutions with lower initial surfactant concentrations, namely 0.01 and 0.02 g/L, is consistent with the scenario that the PSS surface is not yet totally covered by surfactant molecules. Here, the SH signal comes from MG molecules adsorbed on both the surfactant molecules adsorbed at the surface and the uncovered part of the PSS surfaces. In this interpretation, eq 3 can be used to fit all curves in Figure 7 that have a saturated coverage of surfactant molecules (from 0.05, 0.10, and 0.20 g/L data). We noticed that these three curves actually bundle together. In this model analysis, the adsorption free energy of MG on the surfactant molecules can be determined. It is noted that all three saturated surfactant SH curves give identical ΔG° values for MG adsorption on surfactant of $-11.2 \pm 0.2 \text{ kcal/mol}$. The fitted curves are shown in Figure 7.

The above data indicate that there is no displacement of the preadsorbed surfactant by the dye molecules from the PSS particle surface. This appears to contradict the adsorption free energies of MG and the surfactant on PSS surfaces obtained earlier. As they are only different by $<1 \text{ kcal/mol}$, in these systems MG adsorption should be more favorable once its concentration is high. This contradiction can be understood from the kinetic effect caused by the structure of the surfactant-covered PSS surface. According to the N_{max} in section VI, the structure of the PSS particle with surfactant molecules adsorbed on the surface looks just like an octopus with thousands of tentacles dangling out from the particle surface into the solution. The adsorbed surfactant molecules have long tails extending into the solution phase and prevent MG molecules from getting close to the PSS surface. This presents the displacement of surfactant by the MG molecule with a high barrier. Therefore, even though it is thermodynamically plausible, displacement of surfactant by dye does

not happen on the time scale of our experiment. Our experimental measurements actually offer a direct indication of this kinetic asymmetric behavior in adsorption of polymeric molecules.

No second-harmonic signal, besides the talc background signal, was detected at all in an experiment where the surfactant was added first to cover the talc particle surface before the addition of the BCP dye. This observation indicates that BCP can no longer adsorb on the surfactant-covered talc surface. (The data show only a nearly flat line without any significant increase of the SH signal above the talc SH signal level. Therefore, they are not presented here.) This behavior is another illustration of the kinetic asymmetric behavior.

VI. Concluding Remarks

A novel approach based on a nonlinear optical phenomenon—second-harmonic generation—has been developed as an *in situ*, real time probe of adsorption kinetics of surfactant molecules on the surfaces of microparticles in colloids. The basis of theoretical analysis of the observable and the experimental setup presented here has been demonstrated for two systems: adsorption of a commercial surfactant on latex PSS and talc particles in aqueous solutions. This nonlinear optical method provides the surface sensitivity that allows the adsorption to be observed directly. The experimental time is now controlled only by the time the system would take to reach equi-

librium, not by the experimental measurement itself anymore. For the prototype systems where equilibrium, after addition of a small quantity of either the dye or the surfactant into the solution, is reached within a few seconds, the curves mimicking adsorption isotherms in Figures 4 and 6 take about 10 min each to record. (The equilibrium time can be directly observed by following the SHG signal after one titration dose is added.) This is orders of magnitude of savings in laboratory time in comparison with many other analytical techniques for colloid characterizations. Furthermore, the curves are obtained continuously so that maximum accuracy in the determination of the adsorption properties in the analysis can be obtained.

To implement this approach for monitoring surfactant adsorption and determining the adsorption constants for various kinds of surfactants, microparticles, and solvents, it is necessary to establish a library of appropriate dyes that are soluble in the selected solvent and have the comparable adsorption free energies to compete with the surfactant for adsorption. More studies are now needed to establish such a dye library.

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