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Mixed Surfactant Bilayers on Monodispersed Ferric Hydro Sols

Kunio Esumi,* Yuichi Sakamoto, Keiko Yoshikawa, and Kenjiro Meguro
Department of Applied Chemistry, Institute of Colloid and Interface Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
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The properties of mixed surfactant bilayers on monodispersed ferric hydro sol were studied by measuring the amount of surfactant adsorbed, particle size, and pyrene fluorescence spectra. The positively charged sols flocculated upon addition of sodium dodecyl sulfate (SDS) or lithium perfluoro-1-octanesulfonate (LiFOS) were redispersed by further addition of poly(oxyethylene) nonyl phenyl ether (NP7.5) due to the formation of a mixed surfactant bilayer on the sols. The mixed surfactant bilayer of SDS–NP7.5 on the sols was more easily formed than LiFOS–NP7.5. Fluorescence fine structure of pyrene gave information on the polarity of the microenvironment in the mixed surfactant layer on the sols.

The dispersion behavior of particles upon addition of surfactants has been extensively investigated[1–7] in order to elucidate the interaction between surfactants and particles and further to apply to many fields such as flotation, oil recovery, and paints etc. It has been demonstrated[1] in the past by measuring the zeta potential and particle size that positively charged particles flocculate upon addition of anionic surfactants and that on further addition, the particles redisperse due to formation of surfactant bilayers.

Recently, the structural characteristics of the surfactant layer on solids have been elucidated by fluorescence[8–11] and electron spin resonance probing methods.[12] Chandar et al.[8] have reported that highly organized surfactant aggregates of sodium dodecyl sulfate at alumina–water interface are formed by the association of hydrocarbon chains from pyrene and dinaphthylpropane fluorescence probes. A similar experiment for Triton X-100-silica has been studied.[11]

On the other hand, Meguro et al.[13] have demonstrated that positively charged particles flocculated upon addition of an anionic surfactant can be redispersed upon addition of another surfactant owing to the formation of a mixed surfactant adsorbed layer. Their results have not, however, been discussed in detail.

In this work we studied the formation of mixed surfactant layers on monodispersed ferric hydro sols by measurements of the zeta potential, particle size, adsorbed amount, and fluorescence probe. The surfactants used were two different mixed systems: sodium dodecyl sulfate–poly(oxyethylene)nonyl phenyl ether and lithium perfluoro-1-octanesulfonate–poly(oxyethylene) nonyl phenyl ether.

Experimental

Materials. As surfactants, sodium dodecyl sulfate (SDS), lithium perfluoro-1-octanesulfonate (LiFOS), and poly(oxyethylene) nonyl phenyl ether having average oxyethylene chains of 7.5(NP7.5) were used. SDS and LiFOS were synthesized in our laboratory and purified. NP7.5 was obtained from Nikko Chemical Co. Ltd. and used without further purification. The cmc's of these surfactants in the presence of 10 mmol·dm^{-3} nitrates were 3.0 for SDS, 3.4 for LiFOS, and 3.0×10^{-2} mmol·dm^{-3} for NP-7.5, respectively. The water used in all experiments was purified by passing through a Milli-Q system until its specific conductivity fell below $10^{-7}\,\Omega^{-1}\,\mathrm{cm}^{-1}$.

Hydro sols consisting of spherical hematite particles with a narrow size distribution were prepared by essentially the same procedure as Matijević et al.[14] described. The final stock sol had a concentration of 3.17 mg·cm^{-3}, as determined directly by dry-weight measurement, and was kept at pH 5.8. The mean particle size was determined by a Particle analyser (Autosizer Model 700, Malvern Co. Ltd.); the average diameter was 160 nm with a polydispersity of 0.03. Alumina was supplied by Showa Denkou Co. The surface area and the average diameter of the alumina particles were 10.1 m^2·g^{-1} and 500 nm, respectively.

Methods. As the ferric hydro sol had an isoelectric point of pH 7.9, the ferric hydro sol was allowed to flocculate upon addition of LiFOS or SDS at pH 3.5. Then, NP7.5 was added into the flocculated sol. The concentration of the sol in all the experiments except the fluorescence measurement was 3.17 mg/5 cm^3. In order to keep the ionic strength constant, all the measurements were carried out in 10 mmol·dm^{-3} sodium nitrate or lithium nitrate solution at 25 °C. Nitric acid was used to adjust the pH of the mixtures.

For the fluorescence experiments, pyrene dissolved in ethanol was first introduced into a flask and the solvent allowed to evaporate. Then, the ferric hydro sol (the concentration of the sol; 0.32 mg/5 cm^3) was added and sonificated.

Measurements. The amount of anionic surfactants adsorbed on the ferric hydro sol was determined from the difference in concentrations before and after the adsorption. The concentration of anionic surfactants was determined by means of isotachophoresis (Shimadzu Co. Ltd.). That of NP7.5 was also determined by means of a UV spectrophotometer (200A, Hitachi Co.). The zeta potential of the ferric hydro sol was measured by means of an electrophoresis apparatus Laser-Zee meter Model-500 (Pen Kem Inc.).

Steady-state emission spectra were obtained using a Hitachi 650-10S fluorescence spectrophotometer. A portion of the dispersion sample was transferred to a 1 cm quartz cell. The concentration of pyrene ranged from 1×10^{-6} to 1×10^{-7} mol·dm^{-3}. The pyrene containing samples were excited at 335 nm.

Results and Discussion

In order to characterize the ferric hydro sols, the zeta potential was measured as a function of pH. Since the isoelectric point of the sol was estimated to be pH 7.9, the interaction between the sol and the anionic surfactants due to electric attraction forces plays an important role in the range below pH 7.9. Accordingly, in this study, all the measurements were conducted at pH 3.5 where the zeta potential of the ferric hydro sols was about +25 mV.

Figure 1 shows the adsorption isotherms of anionic surfactants on the ferric hydro sols. In both cases, the amount adsorbed increased gradually and then sharply, following a plateau level. This behavior has been observed by other workers.[8,15] At the same time, the dispersion behavior of the ferric hydro sols was observed: the sol flocculated upon addition of SDS or LiFOS (flocculation region pointed by the arrow) and then redispersed by further addition of the same surfactant.[16] Here, the optimum additive concentration for the flocculation of ferric hydro sol was about 0.2 $\mathrm{mmol \cdot dm^{-3}}$ for both cases, although the amount of SDS adsorbed was twice that of LiFOS.

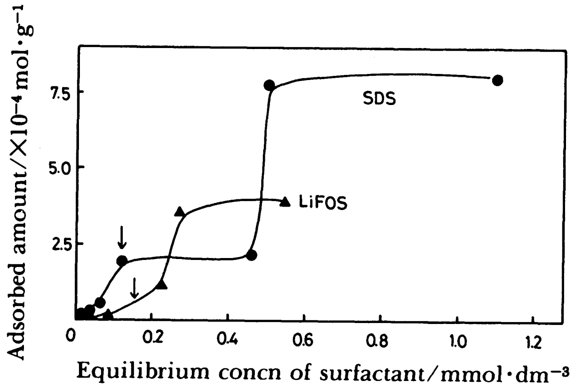

Fig. 1. Adsorption isotherms of anionic surfactants on ferric hydro sols at pH 3.5 in 10 $\mathrm{mmol \cdot dm^{-3}}$ nitrates.

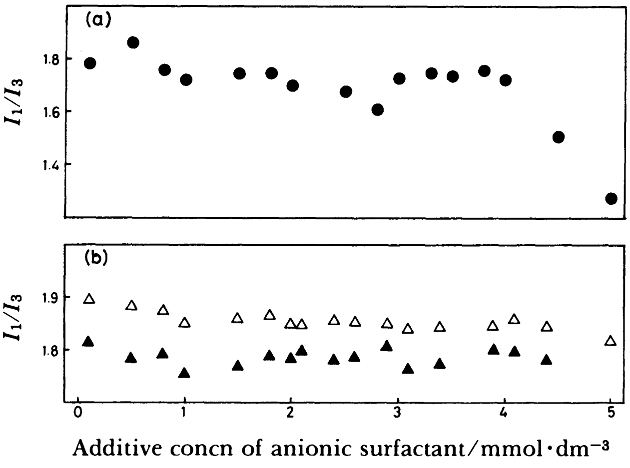

Fig. 2. (a) I_1/I_3 ratio of pyrene in SDS-ferric hydro sols. (b) I_1/I_3 ratio of pyrene in LiFOS-ferric hydro sols: ▲, in dispersion; △, in supernatant.

The pyrene fluorescence fine structure has been found to be remarkably dependent on the solvent: the intensity ratio of I_1/I_3(I_1, first vibrionic and I_3 third vibrionic bands at 373 and 383 nm, respectively) is sensitive to the solvent polarity.[17] This fluorescence method was applied to the dispersion system in order to obtain the polarity of environment of surfactant adsorbed layer on the ferric hydro sol. The change in intensity ratio of, I_1/I_3, of pyrene in SDS-sol and LiFOS-sol dispersion as a function of additive concentration of anionic surfactant is given in Fig. 2. In the case of SDS-ferric hydro sol, no pyrene was detected in the supernatants of the dispersion, which suggests that pyrene is almost solubilized in the adsorbed layer. The I_1/I_3 values of the probe were constant up to 4 $\mathrm{mmol \cdot dm^{-3}}$ SDS, corresponding to the region of the cmc, and then decreased rapidly to a value of 1.30. The above result suggests that the solubilization site for pyrene above 4 $\mathrm{mmol \cdot dm^{-3}}$ SDS is probably the hydrocarbon region which is formed by association of SDS hydrocarbon chains on the surface. A similar result has been reported on SDS-alumina system using pyrene steady-state fluorescence.[8] On the other hand, in the LiFOS-ferric hydro sol, the I_1/I_3 values were almost constant(1.80) over the whole concentration region of LiFOS, whose values coincide with that for pyrene in water. The I_1/I_3 values in the supernatants were also constant (1.86). This indicates that the pyrene is only very weakly solubilized in the fluorocarbon chain layer of LiFOS on the sol. This speculation is also supported by the fact that the I_1/I_3 value of pyrene solubilized into the LiFOS micelles is about 1.51[18] and the amount of adsorbed pyrene in the adsorbed layer is negligibly low.

In order to elucidate the interaction of the anionic surfactant and NP7.5 on the ferric hydro sols, NP7.5 was added to the sol which had been flocculated upon addition of 0.2 $\mathrm{mmol \cdot dm^{-3}}$ anionic surfactant.

Figure 3 shows the amount of the anionic surfactant adsorbed and of NP7.5 on the ferric hydro sols as a function of the additive concentration of NP7.5. As can be seen, the amount of the anionic surfactant adsorbed on the sols is almost constant even after addition of different concentrations of NP7.5. This indicates that the anionic surfactant required for flocculation is adsorbed strong enough on the sol due to the electric attraction between the charged head group of the surfactant and the charged site of the sol. Upon addition of NP7.5, the amount of NP7.5 adsorbed increased for both the SDS-NP7.5 and the LiFOS-NP7.5 systems, although the amount adsorbed was larger for SDS-NP7.5 than for LiFOS-NP7.5. This result can be interpreted as follows: In

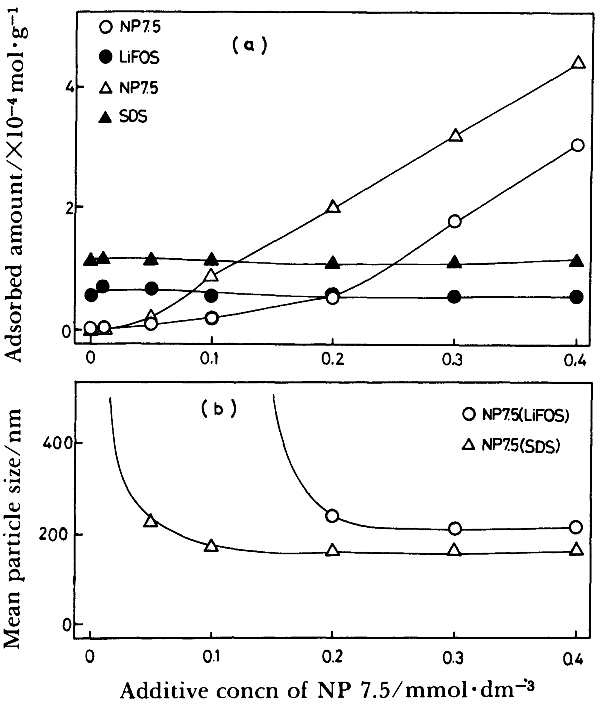

Fig. 3. (a) Amount adsorbed of anionic surfactant and of NP7.5 on ferric hydro sol in presence of 0.2 mmol·dm^{-3} of anionic surfactant as a function of additive concentration of NP7.5. (b) Particle size of ferric sols flocculated by addition of anionic surfactant (0.2 mmol·dm^{-3}) as a function of additive concentration of NP7.5.

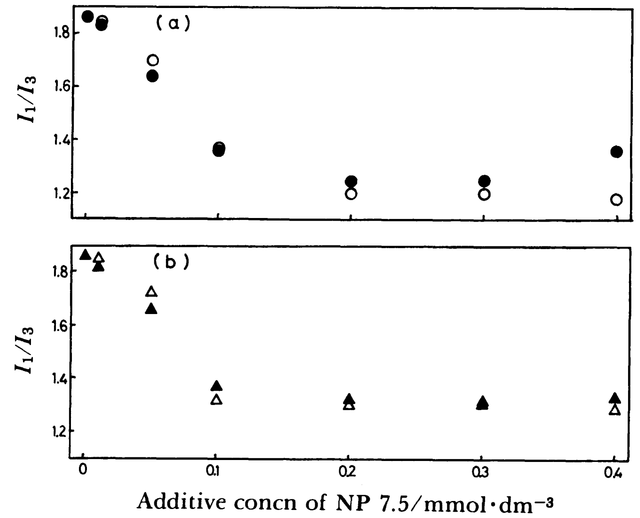

Fig. 4. I_1/I_3 ratio of pyrene for systems shown in Fig. 3. (a) SDS–NP7.5–ferric hydro sols: ●, in dispersion; ○, in supernatant. (b) LiFOS–NP7.5–ferric hydro sols: ▲, in dispersion; △, in supernatant.

SDS–NP7.5, the flocculated ferric sol, upon addition of SDS is fully covered with SDS molecules, orienting their hydrocarbon chain to the aqueous solution. This dense hydrocarbon layer allows the adsorption of NP7.5 easily where the hydrocarbon chains of NP7.5 forms hydrophobic bond with the hydrocarbon layer of SDS, resulting in the formation of a mixed surfactant bilayer. Scamehorn et al.[19] studied the adsorption of mixtures of anionic and nonionic hydrocarbon surfactants on kaolinite and alumina and they reported the adsorption amount of mixed surfactant, but not the interaction between the mixed bilayer. On the other hand, due to a lower adsorption density of LiFOS, NP7.5 can not easily be adsorbed on the LiFOS layer. Further, since it is known[20] that the interaction between the hydrocarbon and fluorocarbon is weaker than that between hydrocarbon and hydrocarbon, this factor also governs the magnitude in the adsorption of NP7.5 on LiFOS layer.

In order to examine the dispersing state of ferric hydro sols for SDS–NP7.5 and LiFOS–NP7.5, the particle size of the sol was also measured (Fig. 3). Upon addition of SDS or LiFOS to the positively charged sol, the sol flocculated and its particle size became too large to detect by the Autosizer. When NP7.5 was added to the flocculated sol, the particle size decreased remarkably upon addition of more than some concentration of NP7.5: 0.05 mmol·dm^{-3} for SDS–NP7.5 and 0.2 mmol·dm^{-3} for LiFOS–NP7.5. These concentrations of NP7.5 were above the cmc of NP7.5(3.0×10^{-2} mmol·dm^{-3}). The decrease in the particle size corresponds to the redispersion state of the sol. Compared to the amount of NP7.5 adsorbed required to attain the redispersion of the sol, the amount for SDS–NP7.5 decreases to one third of that for LiFOS–NP7.5. This result also supports the view that the hydrocarbon–hydrocarbon interaction is preferred to the fluorocarbon–hydrocarbon interaction.

The properties of the mixed surfactant adsorbed layer on the sol were also examined using the pyrene probe method. Figure 4 shows the changes in intensity ratio of I_1/I_3 of pyrene in the SDS–NP7.5 and LiFOS–NP7.5 containing sols. The I_1/I_3 values decreased and then became constant (1.34) above 0.1 mmol·dm^{-3} NP7.5 for both cases. This value is almost the same as that in micelles of NP7.5. Accordingly, pyrene is solubilized into mainly hydrocarbon chains of NP7.5 for both cases, but there is no strict distinction whether pyrene is solubilized in aqueous micelles of NP7.5 or in mixed bilayer on the sols. So, in order to clarify this point, a highly concentrated dispersion system is necessary to obtain information from the bilayer on the solids. In this case, we used an alumina instead of a ferric hydro sol because alumina does not significantly scatter fluorescence light, compared with ferric hydro sol. Figure 5 shows the I_1/I_3 ratios of pyrene for SDS–NP7.5–alumina and LiFOS–NP7.5–alumina. Here, the amount of alumina used was 0.3 g/10 ml. The I_1/I_3 values for pyrene in SDS–NP7.5–alumina ranged between 1.05 and 1.34

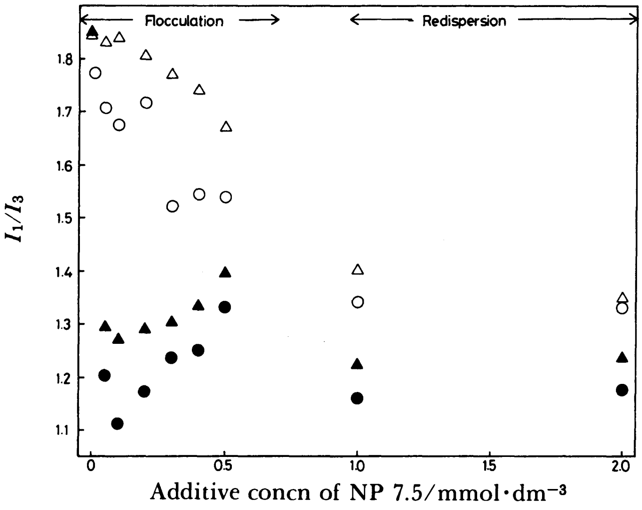

Fig. 5. I_1/I_3 ratio of pyrene for SDS–NP7.5–alumina (●, ○) and LiFOS–NP7.5–alumina (▲, △): filled symbols, in dispersion; empty symbols, in supernatant.

where the alumina particles were flocculated. Above 1 mmol·dm^{-3} of NP7.5, the alumina particles were redispersed due to formation of a mixed bilayer on the alumina and the I_1/I_3 values became constant (1.17). On the other hand, the I_1/I_3 values in the supernatants decreased with an increase of concentration of NP7.5 and reached a constant value (1.34). This suggests that the mixed bilayer of SDS and NP7.5 on the alumina is more densely compact than that of their mixed micelles. In the case of LiFOS–NP7.5–alumina, the I_1/I_3 values of pyrene decreased steeply from 1.85 to 1.30 upon an addition of 0.05 mmol·dm^{-3} NP7.5 and ranged between 1.27 and 1.39 below 0.5 mmol·dm^{-3} NP7.5 where the alumina particles were flocculated. Upon further addition of NP7.5, the alumina particles were redispersed and the I_1/I_3 values decreased to 1.23. The I_1/I_3 values in the supernatants decreased with an increase of concentration of NP7.5 and reached a value of 1.35. The I_1/I_3 value of pyrene(1.17) in SDS–NP7.5–alumina, for the redispersion state is smaller than that (1.23) in LiFOS–NP7.5–alumina, suggesting that pyrene is solubilized in the higher polarity environment of the mixed bilayer for LiFOS–NP7.5–alumina than for SDS–NP7.5–alumina. The isoelectric points of alumina and ferric hydro sol are 9.0 and 7.9, and the zeta potential values at pH 3.5 are +30 mV for the former, +25 mV for the latter. It might be expected from these values that alumina and ferric hydro sol would show a similar interaction behavior against the surfactants. Consequently, these microenvironment results obtained from the dispersion systems containing alumina would reflect the dispersion system containing ferric hydro sol.

From the above results, it is concluded that ferric hydro sols flocculated upon addition of SDS or LiFOS redisperse by further addition of NP7.5 due to formation of a mixed surfactant bilayer and the difference in mixed surfactant bilayer on the sols between SDS–NP7.5 and LiFOS–NP7.5 are characterized by measuring the amount adsorbed and the pyrene fluorescence spectra.

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