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Interaction between Disodium 1,14-Tetradecanediyl Disulfate and Sodium Dodecyl Sulfate or Poly(oxyethylene) Nonyl Phenyl Ether on Alumina

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The interactions between disodium 1,14-tetradecanediyl disulfate ($\alpha,\omega C_{14}$) and sodium dodecyl sulfate (SDS) or poly(oxyethylene) nonyl phenyl ether (NP 7.5) on α-alumina have been studied by measuring the zeta potential, the mean particle size, the amounts of surfactants adsorbed, and the fluorescence spectra of pyrene. When $\alpha,\omega C_{14}$, SDS, or NP 7.5 as a second additive is added to alumina previously flocculated by the addition of SDS or $\alpha,\omega C_{14}$, as a first additive, the flocculated alumina redisperses in the $\alpha,\omega C_{14}$-SDS and $\alpha,\omega C_{14}$-NP 7.5 systems. For the $\alpha,\omega C_{14}$-SDS and $\alpha,\omega C_{14}$-NP 7.5 systems, the redispersion of alumina proceeds in such a manner that the hydrophobic parts of SDS or NP 7.5 are in contact with the $\alpha,\omega C_{14}$-coated alumina and the hydrophilic polar groups direct out to aqueous solution, resulting in the formation of mixed bilayers on the alumina, while for the $\alpha,\omega C_{14}$-SDS system the adsorption of SDS on the $\alpha,\omega C_{14}$-coated alumina is not enough to attain the redispersion of alumina. The measurement of the ratio I_1/I_3 of intensities of the first and third vibrionic bands of the pyrene monomer fluorescence spectra indicates that pyrene is solubilized in a much lower polar site for the $\alpha,\omega C_{14}$-SDS mixed bilayer than for the mixed bilayer of $\alpha,\omega C_{14}$-NP 7.5.

Recently, we have studied the properties of mixed bilayers[1-3] of surfactants formed on monodispersed ferric hydro sols and on alumina by measuring the zeta potential, the mean particle size, the amounts of surfactants adsorbed, and the fluorescence spectra of pyrene. The formation of the mixed bilayers depends on the combination of surfactants used: the mixed bilayers are more preferentially formed for anionic hydrocarbon-nonionic hydrocarbon surfactants than for anionic fluorocarbon-anionic hydrocarbon surfactants. All of the studies of the mixed bilayers have been limited to combinations of conventional surfactants consisting of a straight-hydrocarbon chain or a fluorocarbon chain and one hydrophilic group.

A bolaform surfactant is composed of a hydrocarbon chain with one ionic or polar head group attached at each of its two ends. Ionic bolaform surfactants show several important differences from conventional surfactants with the same head group.[4-8] The bolaform surfactants have been reported to take a folded, wicket-like conformation at the air-water interface.[5,8] Zana et al.[9] have reported the mixed micellization in mixtures of α,ω-bis(trimethylammonio)alkane dibromide and alkyltrimethylammonium bromide, and they have found that the mixed micellization depends on the matching of the hydrocarbon chain length between bolaform and conventional surfactants, and on their concentrations. This study would lead the possibility of the formation of a mixed bilayer between bolaform and conventional surfactants on particle surfaces.

This work will extend the above approach to the solid/aqueous solution interface. In this paper, the interactions between disodium tetradecanediyl disulfate ($\alpha,\omega C_{14}$) and sodium dodecyl sulfate (SDS) or poly(oxyethylene) nonyl phenyl ether (NP7.5) will be studied through the redispersion behavior of alumina by measuring the zeta potential, the mean particle size of alumina, the amounts of surfactants adsorbed, and the fluorescence spectra of pyrene.

Experimental

Materials. The disodium 1,14-tetradecanediyl disulfate was synthesized as follows. Tetradecanedioic acid supplied by the Tokyo Kasei Co. was reduced to 1,14-tetradecanediol with borane-THF complexes following the esterization of the diol with chlorosulfuric acid. The product was then neutralized by the addition of sodium hydrogencarbonate. The final product was recrystallized twice with mixtures of 2-propanol-water and then with diethyl ether. Sodium dodecyl sulfate was also synthesized and purified. Poly(oxyethylene) nonyl phenyl ether with average oxyethylene chains of 7.5 was obtained from the Nikko Chemicals Co., Ltd., and was used without further purification.

The water used in all experiments was purified by passing it through a Mill-Q system (Nihon Millipore Co.) until its specific conductivity fell below $10^{-7}\ \Omega^{-1}\ cm^{-1}$.

The alumina used was α-alumina of a 99.995% purity supplied by Showa Denko K.K. The specific surface area and the average particle diameter of the alumina were 10.1 $m^2\ g^{-1}$ and 500 nm respectively.

Procedure. As the alumina had an isoelectric point of pH 9.0, the alumina flocculated upon the addition of anionic surfactants at pH 3.5, where the alumina showed an appropriate positive zeta potential value. Then, a second surfactant, different from the first one, was added to the flocculated alumina. After the mixture had reached an adsorption equilibrium, the interaction between first and second surfactants on the alumina was characterized by measuring the zeta potentials and the particle size of the alumina. The zeta potential of alumina was measured using an electrophoresis apparatus (Pen Kem, Laser Zee 500). The particle size of alumina was measured using photocorrelation spectroscopy (Autosizer, Malvern Co.). Further, after the centrifugation of the suspension, the concentrations of all the surfactants except NP7.5 in the supernatant were determined by means of an isotachophoresis method. The concentration of NP7.5, which has an absorption band at 275 nm, was determined by means of a UV spectrophotometer. The amounts of surfactants adsorbed on the alumina were determined from the difference in the concentration before and after the adsorption.

For the measurement of the fluorescence spectra, the suspension was added to a flask in which pyrene dissolved in ethanol had first been introduced, after which the solvent had been allowed to evaporate. The steady-state emission spectra of the suspensions were obtained using a Hitachi 650-10S fluorescence spectrophotometer. The concentration of pyrene ranged from 1×10^{-6} to 1×10^{-7} mol dm^{-3}. The excitation wavelength of pyrene was at 335 nm.

In order to keep the ionic strength constant, all the measurements were carried out at 25 °C in 10 mmol dm^{-3} sodium nitrate. Nitric acid was used to adjust the pH of the suspension.

Results and Discussion

Figure 1 shows the adsorption isotherms of SDS and $\alpha,\omega C_{14}$ on the alumina. The amounts of SDS and $\alpha,\omega C_{14}$ adsorbed increased at first gradually and then sharply, following a plateau level. This adsorption behavior has been reported by many workers.[10–13]

In order to study the dispersion state of the alumina upon the addition of SDS or $\alpha,\omega C_{14}$, the zeta potentials and the mean particle sizes of the alumina were measured.

Figure 2 shows that the zeta potentials of the alumina decrease with the concentration of both SDS and $\alpha,\omega C_{14}$, then they are reversed, the zeta potential of the alumina upon the addition of SDS being much smaller than that upon the addition of $\alpha,\omega C_{14}$. The mean particle size measurement suggests that the alumina is flocculated by the addition of $\alpha,\omega C_{14}$ above 0.5 mmol dm^{-3} and that it is not redispersed anywhere in the whole concentration region studied, whereas the alumina is flocculated and then redispersed with an increase in the concentration of the SDS additive. By the addition of $\alpha,\omega C_{14}$, the alumina might be covered with $\alpha,\omega C_{14}$ molecules orienting their hydrocarbon chains toward the aqueous solution, resulting in the hydrophobic surface of the alumina and flocculation. This mechanism may be supported by the view that α,ω surfactants generally adopt a folded, wicket-like conformation at an air-water interface.[5,8] On the other hand, SDS molecules are adsorbed on the alumina, orienting their hydrophobic chains toward the aqueous solution, and with an increase in the concentration the bilayer of SDS[14] on the alumina is formed, resulting in a redispersion of the alumina. In this study, it is found that the optimum flocculation con-

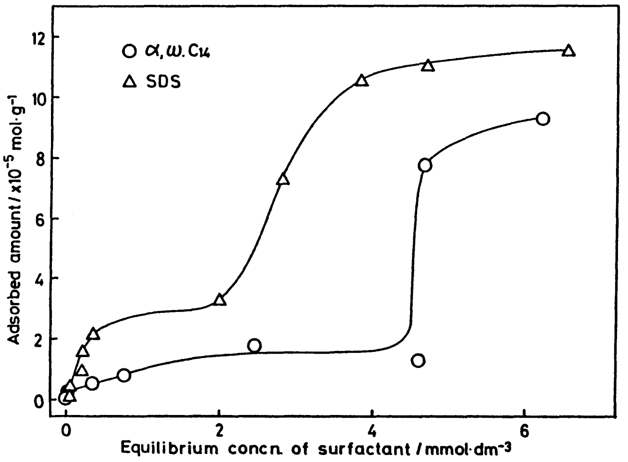

Fig. 1. Adsorption isotherms of SDS and α,ω C_{14} on alumina at 25 °C.

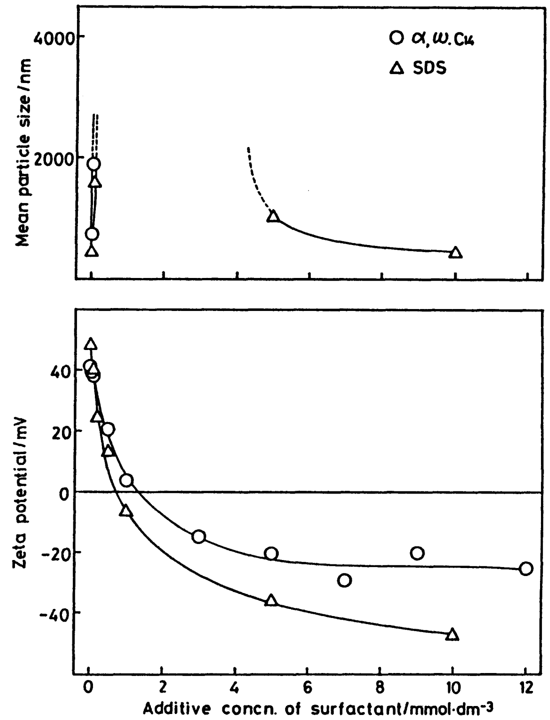

Fig. 2. Changes in mean particle size and zeta potential of alumina with additive concentration of SDS or $\alpha,\omega C_{14}$.

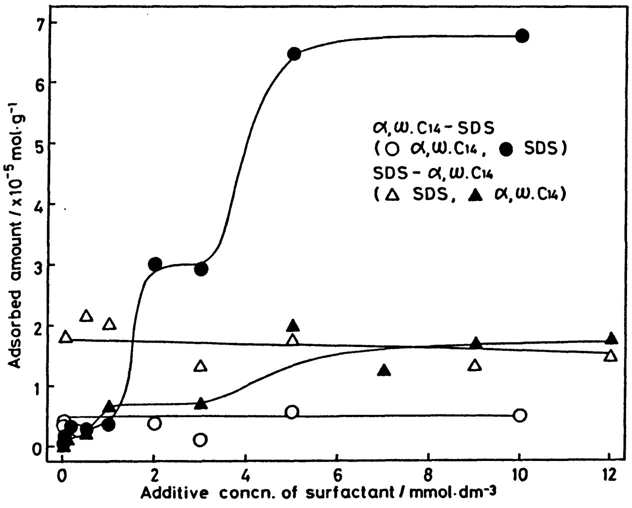

Fig. 3. Amount adsorbed of SDS and α,ω C_{14} on alumina with additive concentration of anionic surfactant for SDS–$\alpha,\omega C_{14}$ and $\alpha,\omega C_{14}$–SDS systems.

centrations of SDS and $\alpha,\omega C_{14}$ for the alumina are about 1 mmol dm^{-3}.

In order to elucidate the interaction between $\alpha,\omega C_{14}$ and SDS or NP7.5 on the alumina, SDS, $\alpha,\omega C_{14}$ or NP7.5 was added to alumina which had been flocculated by the addition of SDS or $\alpha,\omega C_{14}$ at its optimum flocculation concentration.

Figure 3 shows the amounts of SDS and $\alpha,\omega C_{14}$ adsorbed on the alumina for the SDS-$\alpha,\omega C_{14}$ and $\alpha,\omega C_{14}$-SDS systems. Here, the SDS-$\alpha,\omega C_{14}$ system means that in which the alumina is flocculated by the addition of 1 mmol dm^{-3} SDS as a first additive and then $\alpha,\omega C_{14}$ as a second additive to the flocculated alumina. The other systems are studied by the same procedure as the SDS-$\alpha,\omega C_{14}$ system. In the SDS-$\alpha,\omega C_{14}$ system, it is clear that the amount of SDS adsorbed is nearly constant after the addition of $\alpha,\omega C_{14}$, while the amount of $\alpha,\omega C_{14}$ adsorbed is relatively small. This result may imply that the hydrophobicity of the hydrocarbon chain of $\alpha,\omega C_{14}$ is not strong enough to form hydrophobic bonding between SDS and $\alpha,\omega C_{14}$. On the contrary, in the $\alpha,\omega C_{14}$-SDS system, the amount of $\alpha,\omega C_{14}$ adsorbed is almost constant, while the amount of SDS adsorbed increases gradually with the concentration of the SDS additive, suggesting that, with the concentration of the SDS additive, SDS is adsorbed on the hydrocarbon chains of $\alpha,\omega C_{14}$ covering on the alumina, resulting in the formation of a mixed bilayer between SDS and $\alpha,\omega C_{14}$. These differences in adsorption behavior between $\alpha,\omega C_{14}$ and SDS as the second additive may be supported by the fact that the surface activity of a bolaform surfactant[9] is considerably smaller than that of alkyl hydrogensulfate because of the lower hydrophobicity of the bolaform surfactant.

Figure 4 shows that the amount of $\alpha,\omega C_{14}$ adsorbed on the alumina is nearly constant, even after the addition of various concentrations of NP7.5, while the amount of NP7.5 adsorbed increases with an increase in the concentration of the NP7.5 additive. These results imply that with an increase in the concentration of the NP7.5 additive, the $\alpha,\omega C_{14}$ adsorbing on the alumina is not replaced by NP7.5, but a subsequent adsorption of NP7.5 forms mixed bilayers of $\alpha,\omega C_{14}$-NP7.5 on the alumina. This mixed bilayer is probably formed in such a manner that the hydrophobic parts of NP7.5 are in contact with the $\alpha,\omega C_{14}$-coated alumina and the hydrophilic polar groups, i.e., oxyethylene chains, directed out toward the aqueous solution.

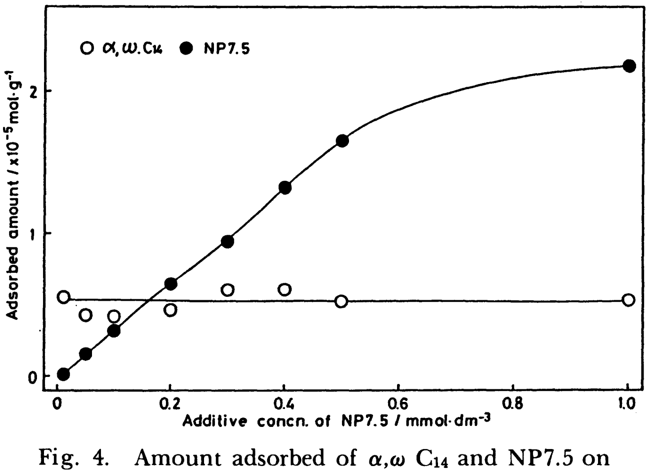

Fig. 4. Amount adsorbed of α,ω C_{14} and NP7.5 on alumina with additive concentration of NP7.5.

Furthermore, in order to characterize the properties of layers adsorbed between $\alpha,\omega C_{14}$ and SDS or NP7.5, pyrene fluorescence experiments were carried out. 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.[15] Typically, the I_1/I_3 ratio for pyrene

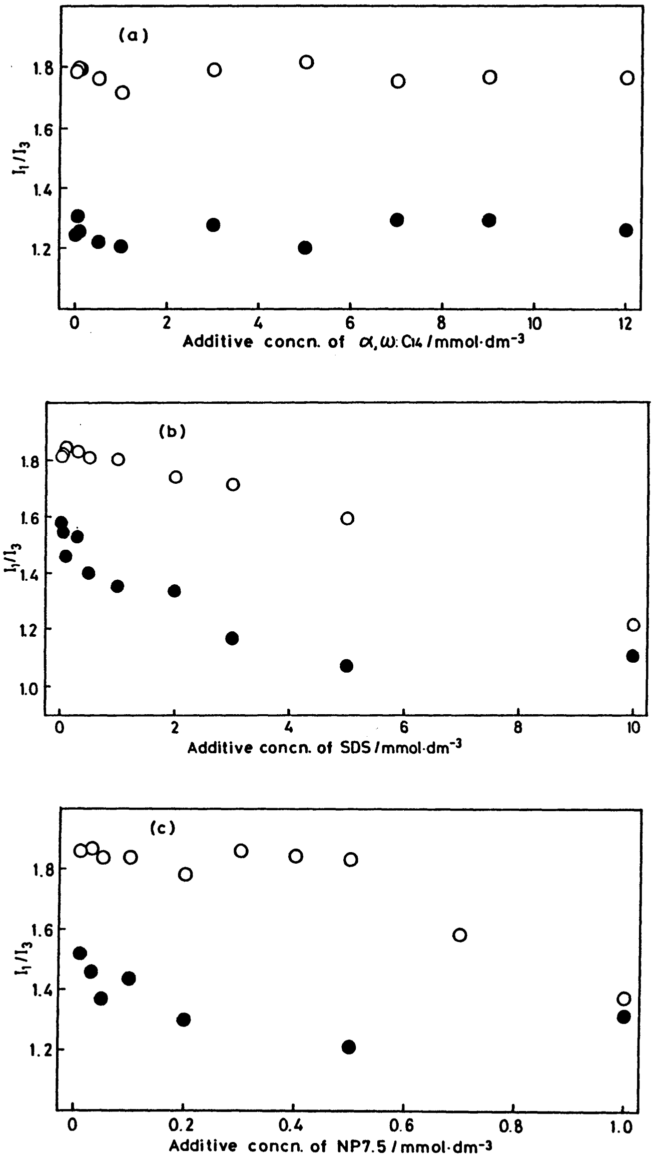

Fig. 5. Changes in I_1/I_3 value of pyrene for(a) SDS-α,ω C_{14}, (b) α,ω C_{14}-SDS, and (c) α,ω C_{14}-NP7.5 systems: open mark, in supernatant; closed mark, in suspension.

changes from 1.8 in water to 0.6 in hydrocarbon media.[16] This fluorescence technique, when applied to an aqueous system[17—20] containing solid particles, has given useful information on the microenvironmental properties of surfactants adsorbed on particles. Figures 5(a) and (b) show the changes in the I_1/I_3 values of pyrene for the SDS-$\alpha,\omega C_{14}$ and $\alpha,\omega C_{14}$-SDS systems. It may be seen that in the SDS-$\alpha,\omega C_{14}$ system, the I_1/I_3 values of the suspension are nearly constant, i.e., 1.2—1.3, even after the addition of various concentrations of $\alpha,\omega C_{14}$ while the I_1/I_3 values of the supernatant range from 1.8 to 1.7. This result indicates that the pyrene is located in hydrocarbon chain of SDS adsorbed on the alumina, for the I_1/I_3 values are very close to that in the SDS micelles. On the other hand, in the $\alpha,\omega C_{14}$-SDS system, the I_1/I_3 values of the suspension decreased from 1.6 to about 1.1 with an increase in the concentration of the SDS additive, while the I_1/I_3 values of the supernatant decreased gradually, reaching about 1.2 at the concentration of the SDS additive, 10 mmol dm^{-3}. This result can be interpreted by the view that pyrene, solubilized in hydrocarbon chains of $\alpha,\omega C_{14}$ adsorbed on the alumina, becomes located at the hydrocarbon chains of SDS, taking into consideration the fact that the I_1/I_3 values of pyrene are about 1.6 for $\alpha,\omega C_{14}$ micelles[8] and about 1.1—1.2 for SDS micelles. It is noteworthy that, on the redispersion state of alumina, the I_1/I_3 values of the suspension are much lower than that of the supernatant, indicating that the mixed bilayer of $\alpha,\omega C_{14}$ and SDS formed on the alumina is much more compact than in the case of the micelle in an aqueous solution.

Figure 5(c) shows that,in the $\alpha,\omega C_{14}$-NP7.5 system, the I_1/I_3 values of pyrene for the suspension decrease with the concentration of the NP7.5 additive until they reach a constant value (1.3), while those for the supernatant also decrease. Above 0.2 mmol dm^{-3} of NP7.5, the mixed bilayer of $\alpha,\omega C_{14}$-NP7.5 begins to be formed, but the amount of NP7.5 adsorbed is not enough to obtain a redispersion state of the alumina below 1 mmol dm^{-3} of NP7.5. In the redispersion state of alumina, the I_1/I_3 values of the suspension are not very different from those of the supernatant, suggesting that the compactness in the mixed bilayer and the mixed micelle is almost the same. The comparison with the I_1/I_3 values for the bilayers shows that the I_1/I_3 value for the $\alpha,\omega C_{14}$-SDS bilayer is lower than that for mixed bilayer of $\alpha,\omega C_{14}$-NP7.5, indicating that the pyrene is solubilized in much a lower polar site for the former than for the latter.

In order to ensure a dispersion state of the alumina for the three systems, the zeta potential and the mean particle size of the alumina were measured. Figure 6 shows that, in the $\alpha,\omega C_{14}$-SDS system, the zeta potential of the alumina decreases with an increase in the concentration of the SDS additive, reaching about −50 mV, while above the concentration of 5 mmol dm^{-3}, the mean particle size is detectable by the Autosizer. The redispersion state of the alumina is found to be achieved by the concentration of the SDS additive above 5 mmol dm^{-3}. However, although not shown in the figure, in the SDS-$\alpha,\omega C_{14}$ system, the mean parti-

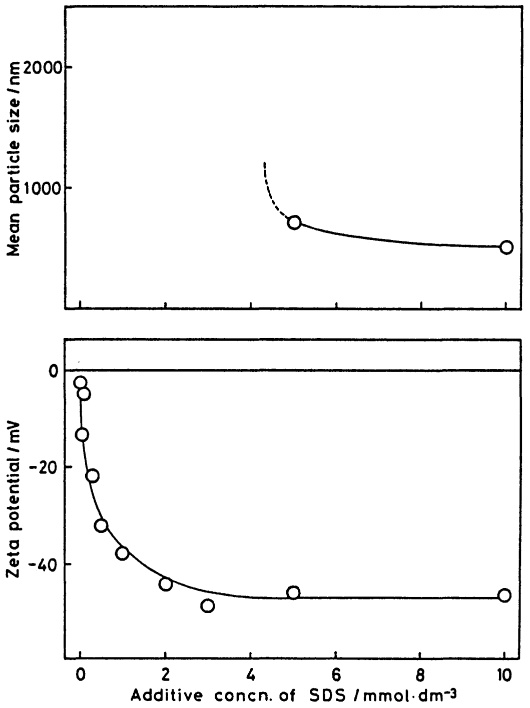

Fig. 6. Changes in zeta potential and mean particle size of alumina with additive concentration of SDS for $\alpha,\omega C_{14}$-SDS system.

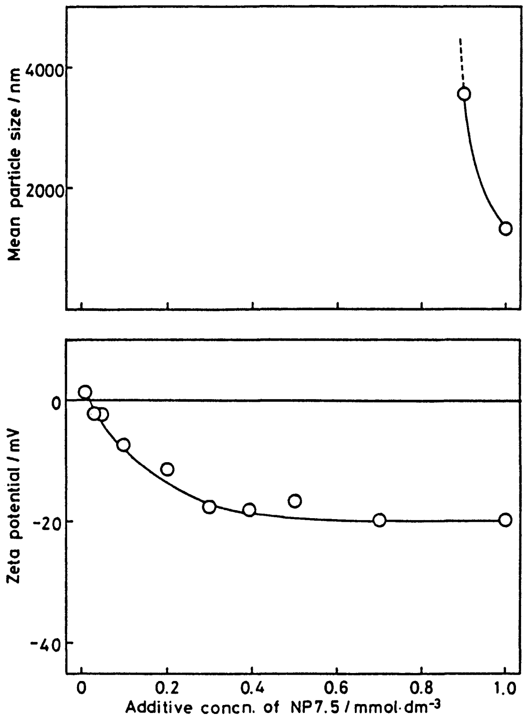

Fig. 7. Changes in zeta potential and mean particle size of alumina with additive concentration of NP7.5 for $\alpha,\omega C_{14}$-NP7.5 system.

cle size of the alumina could not be measured because of the flocculated alumina, and the zeta potential value of the alumina was not significantly changed. Figure 7 demonstrates that,in the $\alpha,\omega C_{14}$-NP7.5 system, the mean particle size of the alumina decreases with the concentration of the NP7.5 additive, while the zeta potential also decreases. The reason why the zeta potential value is negative, although NP7.5, which is a nonionic surfactant, is adsorbed on the $\alpha,\omega C_{14}$-covered alumina, can not be explained at the present time. It is found that the redispersion state of the alumina can be attained by the addition of more than 1 mmol dm^{-3} of NP7.5.

Thus, these changes in the zeta potential and the mean particle size of the alumina are well correlated with those in the amounts of surfactants adsorbed and in the I_1/I_3 values for the three systems.

This study shows that the alumina previously flocculated by the addition of $\alpha,\omega C_{14}$ redisperses upon the addition of SDS and NP7.5 due to the formation of mixed bilayers of $\alpha,\omega C_{14}$-SDS and $\alpha,\omega C_{14}$-NP7.5 on the alumina, while the alumina previously flocculated by the addition of SDS hardly redisperses upon the addition of $\alpha,\omega C_{14}$ judging from the measurements of the zeta potential, the mean particle size of alumina, and the amounts of surfactants adsorbed. From the measurement of the I_1/I_3 ratio of pyrene, it is found that pyrene is solubilized in a much lower polar site of the $\alpha,\omega C_{14}$-SDS mixed bilayer than in the mixed bilayer of $\alpha,\omega C_{14}$-NP7.5.

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