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Flocculation of Iron(III) Oxide Hydrate Sols Induced by α,ω-Type Surfactants

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The interactions of disodium salt of bis(3-sulfopropyl) α,ω-alkanedicarboxylate(C10-α,ω and C12-α,ω) with monodispersed spherical particles of iron(III) oxide hydrate sols were studied by measuring the mean particle size, the zeta-potential and the amounts of adsorption. The sols were flocculated by the addition of small amounts of C10-α,ω and C12-α,ω. The flocks thus formed were redispersed by the further addition of these surfactants. The flocculation of sols upon the addition of α,ω-type surfactants occurred over a wider concentration range than upon the addition of an ordinary surfactant, such as sodium dodecyl sulfate(SDS). Furthermore, the mechanism of redispersion upon the addition of α,ω-type surfactants is different with the two-fold adsorption layer in SDS.

Studies of the interactions between surfactants and solid particles in an aqueous solution are very important from the point view of the dispersion stability of solids.[1–4)] For this reason, the mechanism of the flocculation and redispersion of sol particles in the presence of surfactants[5,6)] has been reported. However, the surfactants used in these works were ordinary ones which have a hydrophilic group at one end of the hydrophobic chain.

Recently, some reports on α,ω-type surfactants, which have a hydrophilic group at each end of a long hydrocarbon chain, have been published.[7–9)] It seemed that it would be interesting to study the interactions of solid particles with α,ω-type surfactants, because α,ω-type surfactants could be expected to interact with solid particles differently from ordinary ones because of their structure.

In this work, the interactions between α,ω-type surfactants and monodispersed spherical particles of iron(III) oxide hydrate sols were investigated by measuring the mean particle size, the zeta-potential, and the amounts of adsorption. The results obtained were compared with those of an ordinary surfactant.

Experimental

Materials. (a) Surfactant: Disodium salt of bis(3-sulfopropyl)-α,ω-alkanedicarboxylate[7–9)] was prepared from the corresponding dimethyl α,ω-alkanedicarboxylate, sodium hydroxide, and 1,3-propanesulfone, which had all been purified by vacuum distillation. The crude product was recrystallized three times from methanol and then further extracted for 100 h with acetone by means of a Soxhlets extractor.

The chemical formulae of the α,w-type surfactants were as follows:

$$NaO_3S(CH_2)_3OOC(CH_2)_nCOO(CH_2)_3SO_3Na \quad (n=10,\ 12)$$

(b) Monodispersed Spherical Particles of Iron(III) Oxide Hydrate Sol: Hydro-sols consisting of spherical hematite particles with a narrow size distribution were prepared by essentially the same procedure as Matijevic et al.[10,11)] described. 6.66 cm^3 of a 2.97 M† $FeCl_3$ solution was diluted to 1000 cm^3 with HCl(pH 3.1). Approximately 200 cm^3 of this solution was then passed through a 0.22 μm Nuclepore filter in order to equilibrate the membrane, after which the filtrate was discarded. The rest of the solution was filtered and distributed in 10 cm^3 screw-capped test-tubes, which were then aged for 24 h at 100 °C in an air-convection oven controlled at a constant temperature (Model DN-61, Yamato Science Co.). After cooling to room temperature, the collected particles were diluted with $HClO_4$ (pH 3.1) and then centrifuged at 8000 rpm for 30 min. The supernatant solution was discarded, and the particles were again diluted with the same $HClO_4$ solution and centrifuged. This procedure was repeated eight times. Upon the completion of the washing, the particles were redispersed in ion-exchanged water to be used as a stock sol. The washing process was repeated until no chloride or iron(III) ions could be detected in the supernatant solution. The final stock sol had a concentration of 1.31 mg cm^{-3}, as determined directly by dry-weight measurement, and was kept at pH 5.8.

The mean particle size was determined by the use of a particle analyzer(Autosizer Model 700, Malvern Co., Ltd.). The average diameter was 130 nm. X-ray diffraction measurements showed that the nearly spherical particles of α-Fe_2O_3 were paracrystalline; they consisted of very uniform globular crystallites.

Methods. The pH and the ionic strength of mixtures containing given amounts of ferric oxide sol and a surfactant were adjusted to make then suitable; then the mixture was agitated at a constant temperature(25 °C) for 2.5 h. In order to keep the ionic strength constant, all the measurements were carried out in 1×10^{-2} M sodium chloride: hydrochloric acid and sodium hydroxide were used to adjust the pH of these mixtures.

Measurements. (1) Zeta-Potential: The zeta-potential of the sols was measured at 20 °C by means of an electrophoresis apparatus, Laser-Zee meter Model-500(Pen Kem, Inc.). The zeta-potential values were calculated by using the Helmholtz-Smoluchowski

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† 1 M=1 mol dm^{-3}.

equation:

$$\zeta = K\eta V/\varepsilon E,$$

where ζ is the zeta potential, K is a constant, η is the viscosity of the medium, V is the mobility, ε is the dielectric constant of the medium, and E is the electric field.

(2) Amount of Adsorption: Sixty cm^3 of the sol dispersion was mixed with the solution of the α,w-type surfactant solutions of various concentrations, and the mixture was stirred for 2.5 h at 25 °C. After the adsorption was reached an equilibrium, the dispersion was separated by centrifugation at 10000 rpm for 30 min. A Methylene Blue acidic solution was added to the supernatant solution, and then the anionic surfactant–Methylene Blue complex thus formed was extracted in the chloroform phase.[12,13] The absorbance of the extract was measured at 652 nm by means of a double-beam spectrophotometer (220A, Hitachi Co.). The amount of adsorption was calculated from the difference in the absorbance before and after the adsorption.

(3) Stability Ratio: As soon as the sols had been mixed with the surfactant solution, the turbidity of the mixture was recorded and the initial slope of the optical density vs. time curve was obtained. The measurements were carried out at 25 °C and at a wavelength of 540 nm. The stability ratio(W) was calculated from the ratio of the rapid-coagulation rate(k_o) to the slow-coagulation rate(k) of sols:[14]

$$W = k_o/k$$

(4) Flushing: The sols flocculated by the addition of the surfactant solution were added to organic solvents, and then the mixture was shaken. The behavior of flushing for sols was observed with the naked eye.

Results and Discussion

In order to characterize the iron(III) oxide hydrate sol, the zeta-potential and the mean particle size of single sol were measured as a function of the pH. The isoelectric point of sol was estimated to be pH 7, which agreed fairly well with the literature value.[10]

On studying the interactions between iron(III) oxide hydrate sol and each surfactant, the values of the zeta-potential and the mean particle size of sols at various pH values were measured as a function of the concentration of each surfactant. Further, the amounts of surfactant adsorbed on sols were determined at two different pH values, i.e., pH 3.5 and pH 5.8. As it is considered that the interactions between the sol and anionic surfactant in an alkaline solution seem less significant because the surface of sol is negatively charged in alkaline solution, the pH values described above were employed.

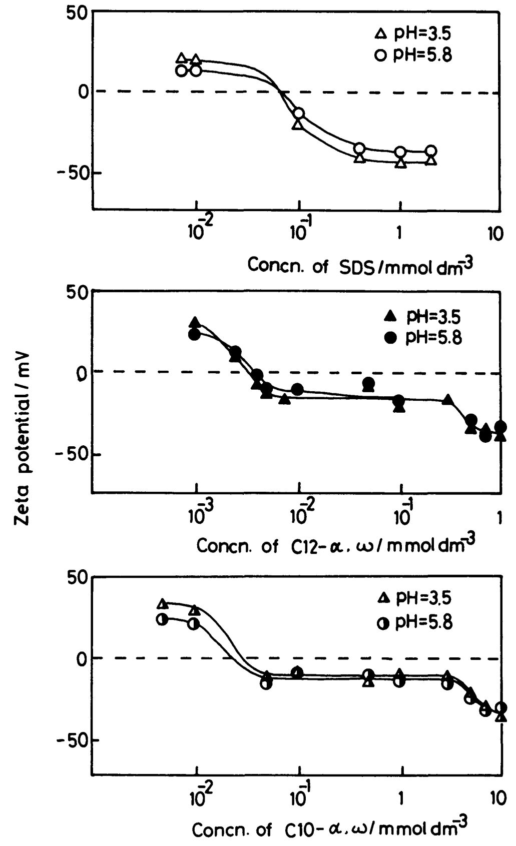

Fig. 1. The change in zeta-potential of sols as a function of concentration of surfactant.

Figure 1 shows the change in the zeta-potential of sols as a function of the concentration of the surfactant at pH 3.5 and pH 5.8. In the case of SDS, the surface of the sol charged positively at the initial stage became negative with an increase in the concentration of SDS, and the value of zeta-potential reached at a constant value, −40 mV. The results obtained for α,ω-type surfactants were similar to those of SDS. However, in the case of an α,ω-type surfactant, the zeta-potential was kept constant over a wide range of concentration at about −10 mV and then, with the further addition of an α,w-type surfactant, decreased to about −40 mV for both α,w-type surfactants.

Figure 2 shows the change in the mean particle size of the sols as a function of the concentration of the surfactant at pH 3.5 and pH 5.8. The particle size of the sols increased suddenly upon the addition of the surfactant, indicating that the sols were flocculated. Upon the further addition of the surfactant, the particle size of sols decreased again. Thus, the change in the mean particle size of the sols indicates that the dispersion-flocculation-redispersion of sols occurs by means of the surfactant. It is noteworthy that the flocculation of the sols upon the addition of

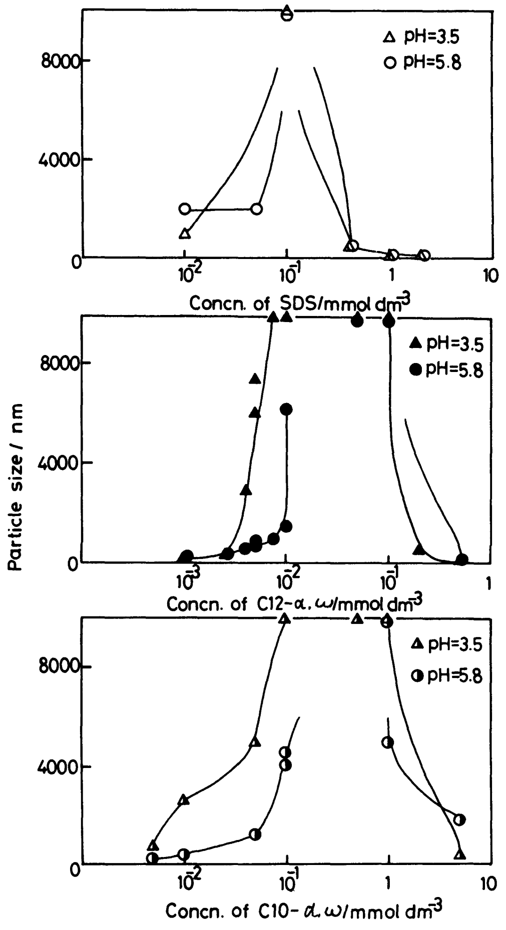

Fig. 2. The change in mean particle size of sols as a function of concentration of surfactant.

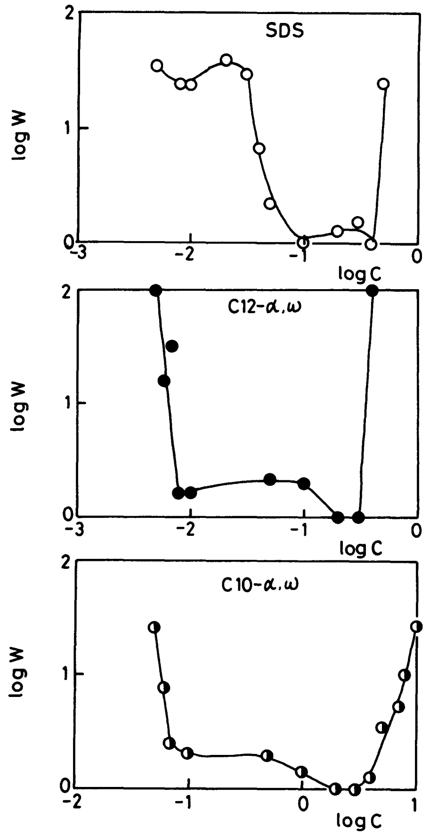

Fig. 3. Relationship between stability ratio of sols and concentration of surfactant at pH 5.8.

α,w-type surfactants occurs over a wider range of surfactant concentrations than that in SDS.

To examine the flocculation region in detail, the stability ratio of the sols was measured. The change in the stability ratio of the sols as a function of the logarithm of the concentration of the surfactant at pH 5.8 is presented in Fig. 3. In the region of rapid coagulation, log W is nearly zero. From Fig. 3, it can be seen that the region of the flocculation of the sols upon the addition of SDS ranges from 0.1 mM to 0.4 mM. On the other hand, the region of the flocculation of the sols upon the addition of C12-α,ω ranges from 0.008 mM to 0.3 mM, and that of C10-α,ω, from 0.07 mM to 4 mM. Accordingly, it was found that the flocculation region upon the addition of an α,ω-type surfactant was much wider than that by SDS. The difference between the concentrations corresponding to the flocculation regions of C10-α,ω and C12-α,ω is mainly attributing to the difference in their surface activity: The surface activity of C12-α,ω is much higher than that of C10-α,ω.[7]

Figure 4 presents the adsorption isotherms at pH 3.5 and pH 5.8 where the adsorption density(mol m^{-2}) is given as a function of the equilibrium concentration of the surfactant. The adsorption density of SDS increased gradually and then became constant. A slight inflection point appeared at about 0.1 mM of SDS. The adsorption isotherms of the α,ω-type surfactants had a plateau over a wide range and then increased suddenly. Finally, the saturated amount of adsorption was obtained. It should be noted that the concentration ranges of these plateaus are in fairly good agreement with the flocculation region of the sols caused by the surfactants. From these results on the mean particle size, the zeta-potential, and the adsorption measurements, the interactions between the sols and the α,ω-type surfactant were found to be slightly stronger at pH 3.5 than at pH 5.8, probably because of the difference in the electric interactions between them.

The properties of the sol flocks formed by the addition of the α,ω-type surfactants and SDS were characterized by the flushing process. When the flocks of the sols formed by SDS were shaken with toluene, the flocks were transferred to the toluene phase; well-dispersed sols were obtained in the toluene phase. The reason for this transfer can be explained by the mechanism of forming a hydrophobic adsorption layer on the surface of the sol particles.[5] However, the flocks formed by the addition of the α,ω-type surfactants were dispersed in neither the water phase nor the toluene phase, but moved to the water/toluene interface.

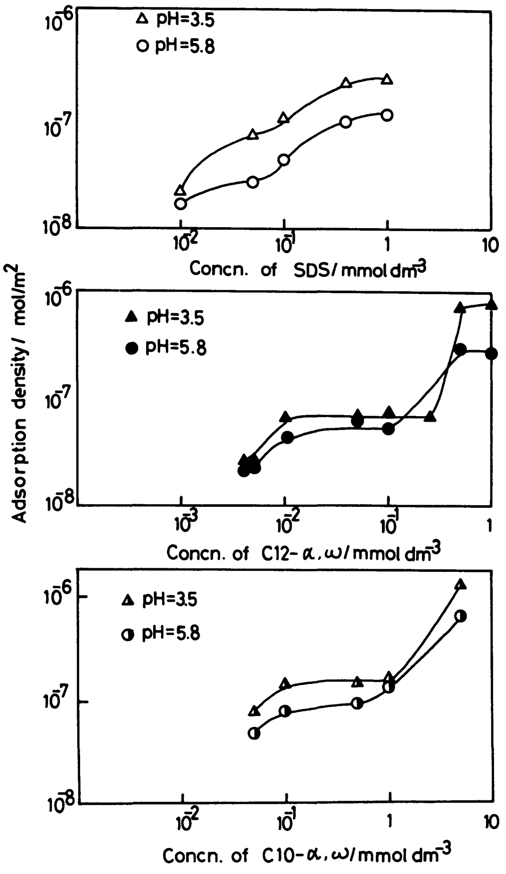

Fig. 4. Adsorption density of surfactant on sols as a function of concentration of surfactant.

Based on all the results obtained, the mechanisms of the flocculation and redispersion of sols occurring upon the addition of α,ω-type surfactants were discussed, and the results shown schematically in Fig. 5 were obtained. When low concentrations of α,ω-type surfactants are added to the sols, the surface charge of the sols is neutralized, resulting in the flocculation of the sols, much as in the case of SDS.[15] Two flocculation models by α,ω-type surfactants are proposed. The flocculation model of the left side seems unreasonable, however, because the surface of sols treated with α,ω-type surfactants does not exhibit the hydrophobic character usually obtained by flushing. On the other hand, the flocculation model of the right side indicates that α,ω-type surfactants act as bridging agents among the sols. The mechanism of bridge-forming among sols is a bimolecular process: the flocculation rate must be proportional to the product, $\theta(1-\theta)$, of the fractions covered(θ) and notcovered($1-\theta$) with the adsorbed α,ω-type surfactant. As can be seen in Fig. 3, the experimental points lie almost on a parabola, corroborating the bimolecular flocculation.[16] This bridging action renders the sols less hydrophobic than the surface of the sols flocculated by the addition of SDS. The flocculated sols thus obtained moved at the toluene/water interface and behaved like a film upon the flushing. This film-like behavior might be due to the penetration of toluene into the hydrocarbon chain of the α,ω-type surfactant, thus forming a bridge. On the further addition of an α,ω-type surfactant, the mean particle size of the sols decreased, as is shown in Fig. 2, since the redispersion of the sols was achieved. The mechanism of redispersion, which is schematically shown in Fig. 5, can be explained in terms of the monolayer

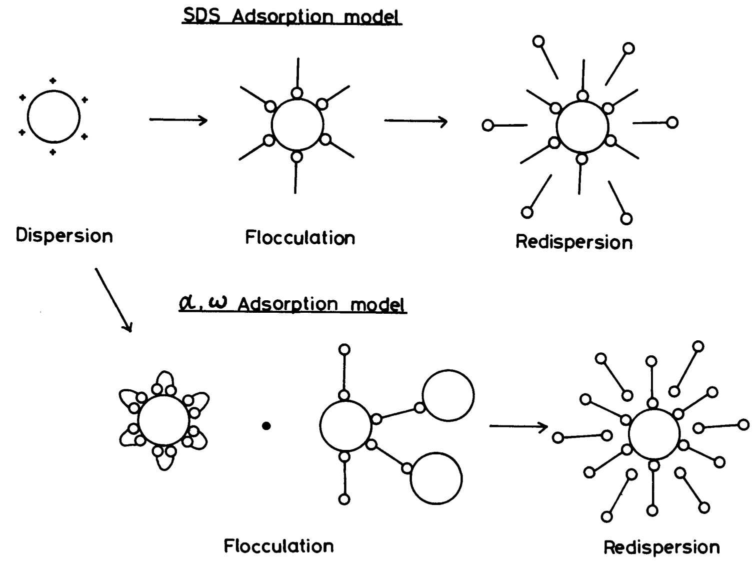

Fig. 5. A model for mechanism of flocculation and redispersion of sols by surfactant.

adsorption from the data of the zeta-potential and the amount of adsorption. Accordingly, the redispersion state of sols by α,w-type surfactants is different from the two-fold adsorption layer caused by SDS.

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