

FEATURE ARTICLE

Interactions between Surfactants and Particles: Dispersion, Surface Modification, and Adsolubilization

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Interactions of surfactants and polymers at solid–liquid interfaces can be correlated with many interfacial processes. In this study, we discuss dispersion of particles, surface modification of particles, and adsolubilization using various surfactants and particles. © 2001 Academic Press

1. INTRODUCTION

Adsorption of surfactants onto solid particles controls many interfacial processes, such as stabilization of solid dispersions, selective flotation of minerals, detergency, protection of metal surfaces, and lubrication. Surfactant adsorption at the solid–liquid interface is a major event in which the surfactant molecules can interact with the solid surface. On the basis of the results of conventional measurements such as adsorbed amount of surfactant, zeta potential, and dispersion stability, three models of adsorption of ionic surfactant onto oxides have been proposed. The reverse orientation model suggested by Somasundaran and Fuerstenau (1) consists of four distinct regions of the adsorption isotherm, while the bilayer model presented by Harwell *et al.* (2) differs slightly from the reverse orientation model. Gu and Huang (3) have proposed the surface micelle model, and recent work has shown (4, 5) that the shape, size, and lateral organization of ionic surfactant aggregates at the solid–liquid interface can be determined directly by atomic force microscopy. Thus, the interactions between surfactants and solid particles have been studied using various techniques.

When ionic surfactants adsorb onto metal oxide particles, the stability of dispersed particles is often altered by the surfactant concentration; a high dispersion stability without surfactants decreases by addition of low concentrations of surfactants, but at high surfactant concentration the dispersion stability becomes high. This process is called “dispersion–flocculation–redispersion” and is very useful for fundamen-

tal study of aqueous dispersion of particles by surfactants. Also, this process illustrates surface modification of particles by surfactants.

Surfactant adsorbed layers formed by the adsorption of surfactants onto particles constitute a hydrophobic environment, so that water-insoluble compounds are incorporated into the layers, which has been referred to as adsolubilization (6). This adsolubilization phenomenon has been used to modify surface properties of particles as well as to eliminate toxic substances in aqueous media.

In the present report, the interactions between surfactants and particles are discussed on the basis of conventional measurements such as particle size and zeta potential. Then, surface modification of particles using polymerizable surfactants is described. The results of adsolubilization are summarized from the standpoint of surfactant structure. Finally, simultaneous adsorption of polymers and surfactants onto particles is described.

2. INTERACTION AMONG SOME LYOPHOBIC SOLS AND SURFACTANTS

To study the interaction between surfactants and particles it is very important to use a well-dispersed particle system without surfactants. Ferric oxide sol is well known to be a positively charged sol (7) and is well dispersed in aqueous solution.

Such a ferric oxide sol is coagulated upon addition of sodium alkyl sulfates, such as sodium butyl sulfate (SBS), sodium octyl sulfate (SOS), and sodium dodecyl sulfate (SDS). The coagulation behavior of ferric oxide sol with the alkyl chain length is summarized as follows: (i) The longer the alkyl chain length of the sulfates, the smaller the coagulation value, which is the critical concentration required to coagulate the sol. (ii) When the alkyl chain of the sulfates reaches C12, peptization is observed in addition to the coagulation action. (Peptization is the redispersion of coagulated sol.) Upon addition of SDS, the precipitate of ferric oxide sol being coagulated can be easily transferred into an organic phase such as benzene, toluene, and chloroform

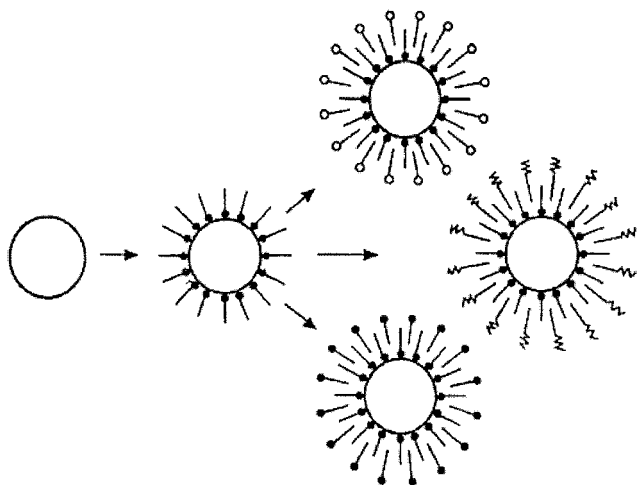


FIG. 1. Model for hydrophobic coagulation and peptization of negatively charged sol by surfactants: (—●) cationic surfactant; (—○) anionic surfactant; (—◊) nonionic surfactant.

simply by shaking. The sol particles transferred into an organic phase disperse perfectly in that phase. It is observed that the precipitate of a ferric oxide sol coagulated by SDS is peptized again upon addition of a concentrated SDS solution. Similar peptization phenomena can be observed in the case of addition of cationic or nonionic surfactants to this precipitate. Hydrophobic coagulation can be observed similarly in the combination of a negative sol, such as arsenic sulfide (8) or silver iodide (9), and a cationic surfactant, such as dodecylpyridinium bromide.

The model for hydrophobic coagulation and peptization is shown in Fig. 1. When an oppositely charged surfactant is added to a sol, the sol is coagulated (see the middle of Fig. 1). Then, the coagulated sol is peptized by further addition of the same surfactant as the first one, a surfactant charged oppositely to the first one, or a nonionic surfactant (right side of Fig. 1). From the experimental evidence in several adsorption systems, it has been found that ionic surfactants adsorb in appreciable amounts onto oppositely charged solids and the zeta potential of solids converts from positive to negative or vice versa. In addition, the dispersion state of solids after addition of surfactants can be correlated with the formation of a surfactant monolayer or bilayer.

3. ADSORPTION OF OLIGOMERIC SURFACTANTS ON PARTICLES

Although oligomeric surfactants with multichained and multihydrophilic groups show weaker hydrophilicity than conventional single-chain surfactants, it has been demonstrated (10–12) that they provide strong amphiphilicity and high orientation at interfaces when a small amount of them is used. These excellent properties may be derived from the enhancement of the interfacial density of oligomeric surfactants. On the other hand, polysoaps are known as one type of surfactant with multichained and multihydrophilic groups (13). However, the orientation of

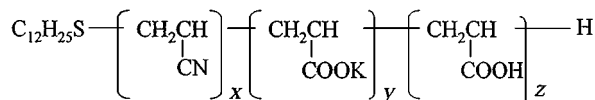
hydrophobic groups of polysoaps is often limited due to blocking and steric hindrance by the main polymer chains so that their interfacial orientation becomes lower than that of surfactants with lower molecular weight.

Two kinds of oligomeric surfactants have been synthesized and their adsorption characteristics on iron oxide or silica have been studied.

The chemical structure and analytical properties of synthesized acrylic oligomeric surfactants (14, 15) are given in Table 1. A well-dispersed system is obtained upon addition of 0.5 mmol dm⁻³ iron(III) chloride to the iron oxide suspension. The addition of a small amount of oligomeric surfactant (I) to aqueous suspensions of iron oxide particles in 0.5 mmol dm⁻³ iron(III) chloride makes the iron oxide particles flocculate, but the flocs redisperse on further addition of the same surfactant. The mean particle size of the iron oxide increases with the increasing concentration of oligomeric surfactant (I), reaches a maximum value at 0.016 mmol dm⁻³, and then decreases on further addition of oligomeric surfactant (I), as shown in Fig. 2a. The positively charged iron oxide particles in an aqueous iron(III) chloride solution are neutralized in the presence of oligomeric surfactant (I). The charge is reversed to negative on further addition of this oligomeric surfactant (Fig. 2b). The zero point of charge of iron oxide is about 0.016 mmol dm⁻³ of oligomeric surfactant (I); this value corresponds to the concentration of oligomeric surfactant (I) at which the maximum mean particle size is observed. The flocs formed on addition of this surfactant can be easily suspended in toluene by shaking, which indicates that the surface of the solids becomes hydrophobic by adsorption of oligomeric surfactant (I). The behavior of the other oligomeric surfactants (II)–(V) is analogous to that of oligomeric surfactant (I). The redispersion of the iron oxide flocs has been investigated by the further addition of oligomeric surfactant (I). Figure 2a shows that the mean particle size of iron oxide flocs decreases with increasing concentration of oligomeric surfactant (I). Complete redispersion occurs at about 0.029 mmol dm⁻³ of oligomeric surfactant (I). In the case of the other oligomeric surfactants (II)–(V), similar results are obtained. To study the effects of different compositions of oligomeric surfactants on

TABLE 1
Chemical Structure and Composition of Oligomer-Type Surfactants

Oligomer	x	y	z	Mol wt
I	0	9.5	3.8	1530
II	3.6	7.0	2.2	1325
III	6.8	2.8	11.4	1700
IV	6.5	5.7	2.0	1320
V	11.9	4.5	2.9	1539



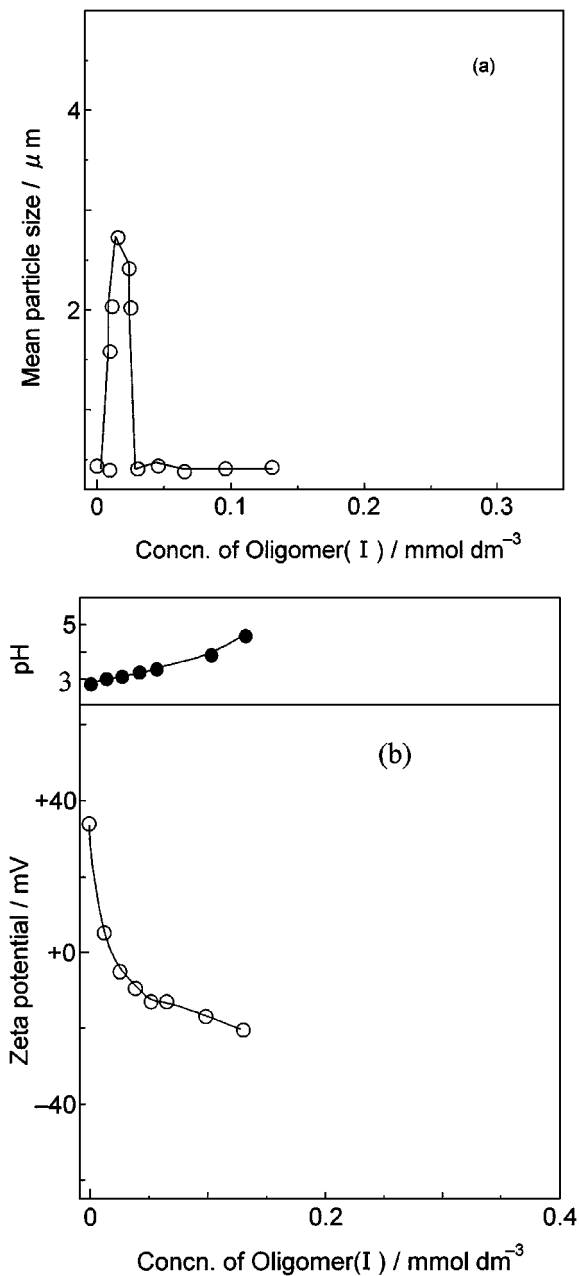


FIG. 2. The variation of (a) the mean particle size and (b) zeta potential of iron oxide in the presence of 0.5 mmol dm^{-3} iron(III) chloride as a function of added oligomer surfactant (I).

the dispersion of iron oxide, the maximum flocculation and redispersion concentration values are plotted in Fig. 3. As the ionizable acrylic content in the oligomeric surfactant molecule increases, the maximum flocculation concentration decreases gradually, while the redispersion concentration decreases more steeply. These results suggest that the oligomeric surfactant with higher ionizable acrylic content adsorbs effectively onto the positively charged iron oxide, thus lowering the maximum flocculation concentration. However, since oligomeric surfactants with lower ionizable acrylic content may be coiled in the solution

more closely than the oligomeric surfactant with a higher ionizable acrylic content, the adsorption of a second layer due to hydrophobic-hydrophobic interaction may not occur effectively. Furthermore, oligomeric surfactants with lower ionizable acrylic content would not contribute as strongly to electrostatic repulsion. Accordingly, to attain redispersion by adding an oligomeric surfactant with lower ionizable acrylic content, more dense adsorption at the second layer is required. Thus, the redispersion concentration of the oligomeric surfactant with lower ionizable acrylic content becomes higher. The mechanism of flocculation and redispersion processes using oligomeric surfactants is also consistent with monolayer or bilayer formation, similar to the case for conventional single-chained surfactants.

Other oligomeric surfactants have been synthesized and their structures are shown in Fig. 4 (16). The adsorption behavior of the oligomeric surfactants at the solid/liquid interface has been studied using silica particles. Since silica particles are negatively charged at neutral pH, it is expected that adsorption of the oligomeric surfactants would occur mainly due to electrostatic attraction between negatively charged sites of silica and quaternary pyridinium groups of the oligomeric surfactant as a first adsorption process. Figure 5 show the adsorption isotherms of the oligomeric surfactants on silica. It is apparent that the adsorbed amounts of the oligomeric surfactants increase sharply at very low concentrations and reach a plateau, suggesting that the interaction between the oligomeric surfactants and the surface of silica is appreciably strong. At low oligomeric surfactant concentrations, the oligomeric surfactant molecules adsorb onto the negatively charged silica surface by orienting their hydrocarbon chains to the aqueous solution so that the surface of the silica becomes hydrophobic. With further increase of the oligomeric surfactant concentration, a bilayer adsorption

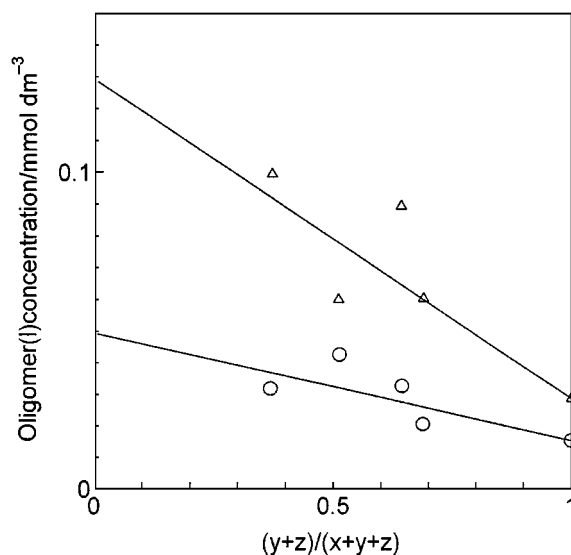


FIG. 3. The variation of the maximum flocculation and the redispersion concentration as a function of acrylic content in oligomer surfactants: (○) maximum flocculation concentration; (△) redispersion concentration.

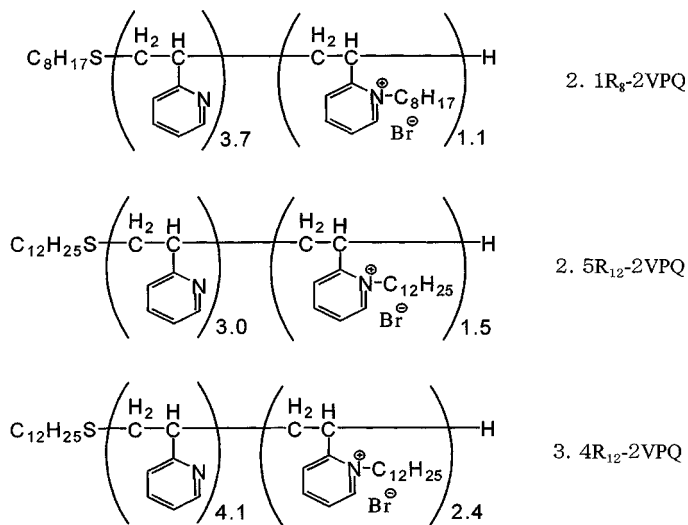


FIG. 4. Structures of cationic oligomers.

will occur. These adsorption behaviors reflect the changes in the zeta potential of silica. In Fig. 5, the zeta potential of silica in the absence of the oligomeric surfactants is negative, but it increases rapidly with increasing oligomeric surfactant concentration. This alternation from negative to positive in the zeta potential supports the formation of a bilayer. Since the areas occupied by the oligomeric surfactant adsorbed (the surface area of the silica/the saturated amount of oligomeric surfactant adsorbed) are quite large compared to those at the air/aqueous solution interface, it is conceivable that patchlike bilayers are sparsely formed at even high oligomeric surfactant concentrations. The sedimentation rate of silica by adsorption of the oligomeric surfactants is significantly affected by the change of zeta potential: it increases rapidly at low oligomeric surfactant concentrations, reaches a maximum, and then decreases with further increase of the oligomeric surfactant concentration. The maximum sedimentation rate corresponds to almost zero zeta potential, where the order of the rate is $3.4R_{12}-2VPQ > 2.5R_{12}-2VPQ > 2.1R_8-2VPQ$ (Fig. 6). This indicates that the chain length and the number of hydrocarbon chains, along with the pyridinium group and the main hydrocarbon chains of the oligomeric surfactants, play important roles in the flocculation of silica. Thus, the silica suspension shows a dispersion–flocculation–redispersion sequence as the oligomeric surfactant concentration increases, which is very similar for oppositely charged systems of surfactants and particles.

4. SURFACE MODIFICATION BY POLYMERIZABLE SURFACTANTS

As already described, upon addition of ionic surfactants to oppositely charged particles, a bilayer of the surfactant is formed on the particles. In this bilayer, the interaction between the first and second layers is attributed only to hydrophobic forces be-

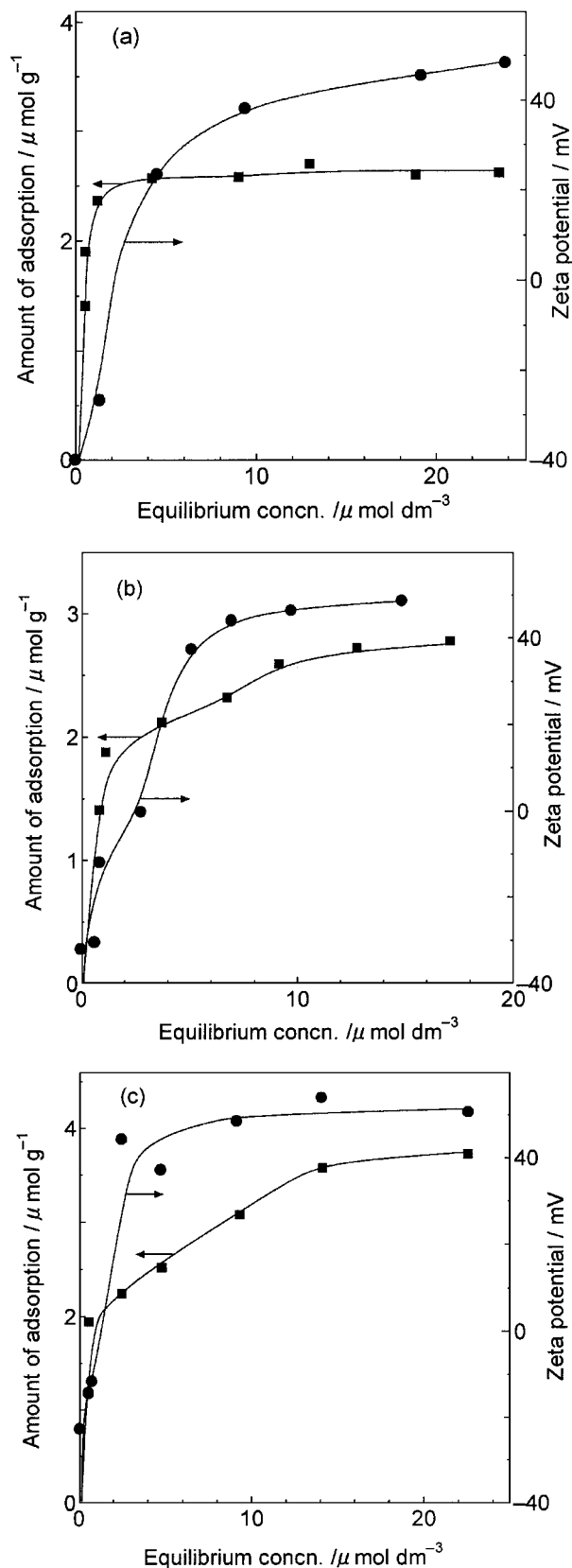


FIG. 5. Adsorption isotherms and zeta potential change for (a) $2.1R_8-2VPQ$ -silica, (b) $2.5R_{12}-2VPQ$ -silica, and (c) $3.4R_{12}-2VPQ$ -silica systems.

tween the surfactants, so that this bilayer is easily broken by dilution. Using a polymerizable surfactant, there is a possibility of fixing the bilayer by polymerization.

Polymerization of sodium 10-undecenoate micellar solutions either by irradiation or by free radical initiators has been shown to yield low-molecular-weight oligomers (17–19). Fixation of bilayers onto alumina particles using polymerizable surfactants such as sodium 10-undecenoate and sodium 10-undecenyl sulfate has been performed (20–22). Since the alumina has an isoelectric point of 9.1, all studies have been carried out at pH 8.0 because sodium 10-undecenoate dissociates fully as an anionic surfactant and the alumina shows an appropriate positive zeta potential, +30 mV. Suspensions which provide an appropriate redispersion state of the alumina by adsorption of sodium 10-undecenoate are transferred to a quartz beaker with a cover and polymerization of the suspensions is carried out under irradiation by a UV lamp (40 W). The major differences in the IR spectra of alumina before and after the polymerization are in bands at 3100 (=CH stretch) and 1640 cm^{-1} (C=C stretch). These bands are present before the polymerization but absent after the polymerization. Measurement of the mean particle size shows that the mean particle size of alumina is not changed even after the polymerization. It is crucial to elucidate how strongly the polymerized layer on particles is fixed. After the washing of the polymerized dispersions, the zeta potential and the percentage of retained surfactant have been determined (Fig. 7). Without polymerization, the percentage of retained surfactant is only about 33%, whereas with irradiation of 6 h or more, the percentage of retained surfactant is more than 90%. In addition, the zeta potential of polymerized suspensions shows appreciable negative values in a wide pH region. These results indicate that

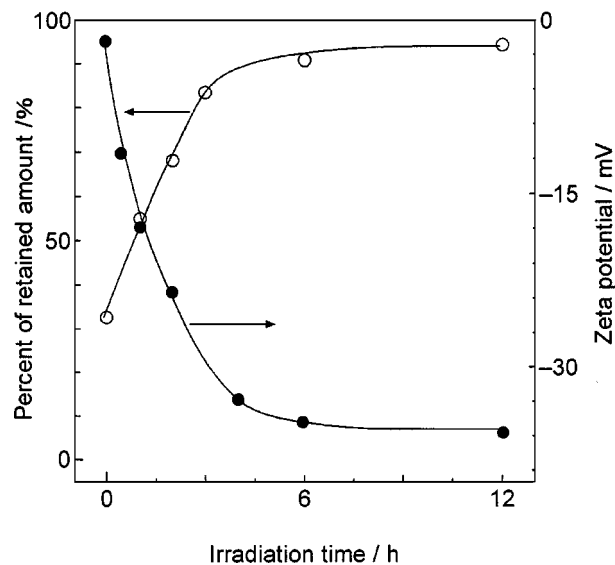


FIG. 7. Change in zeta potential and retained amount of sodium 10-undecenyl sulfate on alumina by polymerization and subsequent washing.

the layer polymerized by UV irradiation enhances the fixation of the bilayer. This method can be applied to microcapsulation of particles by polymerizable surfactants, which is one of several surface modification techniques.

5. ADSOLUBILIZATION

Surfactant adsorbed layers formed on particles exhibit hydrophobic properties which have been characterized by many techniques including ESR and fluorescence spectroscopy (23–27). Accordingly, water-insoluble compounds can be incorporated into the surfactant adsorbed layers, which is called adsolubilization. Factors influencing adsolubilization behavior are as follows: (a) surfactant structure; (b) kind of water-insoluble compound; (c) kind of particles.

In this section, we will discuss adsolubilization behavior of single surfactants and mixed surfactants. Then, adsolubilization using chemically modified titanium dioxide particles is also described.

5.1. Adsolubilization Using Single Surfactant Systems

For adsorption of ionic surfactants, oppositely charged systems of ionic surfactants and particles are well known to show strong interactions between the first surfactant layer and the surfaces of particles. The amount of ionic surfactants adsorbed onto oppositely charged particles increases accompanying the formation of monolayer and bilayer. For adsolubilization studies, two systems have been mainly investigated: silica-cationic surfactant systems (28, 29) and alumina-anionic surfactant systems (30–32).

Adsolubilization of hexanol for silica-cationic surfactant systems such as dodecylpyridinium chloride (DPCl) and

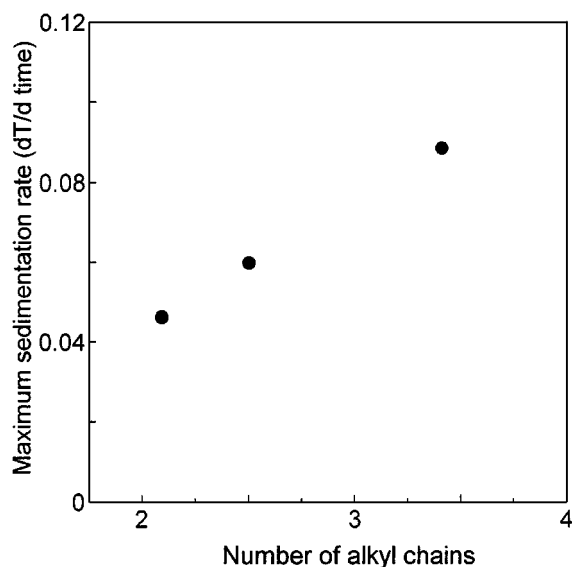


FIG. 6. Maximum sedimentation rate against the number of alkyl chains of oligomers for the oligomer-silica systems: 2.1 for 2.1R₈-2VPQ, 2.5 for 2.5R₁₂-2VPQ, 3.4 for 3.4R₁₂-2VPQ.

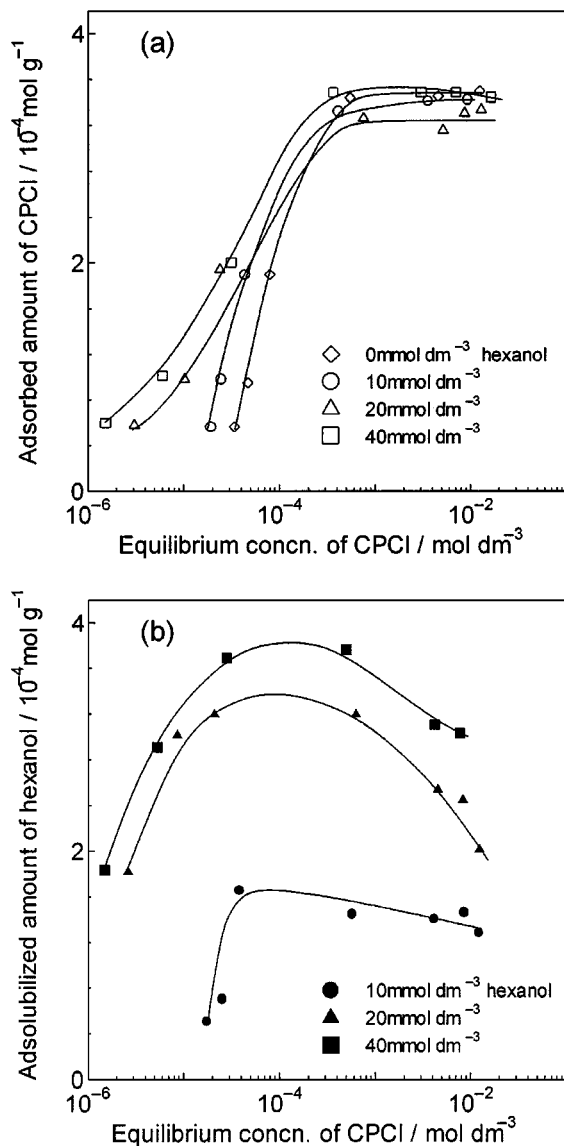


FIG. 8. (a) Adsorption isotherms of CPCl and (b) adsolubilization of hexanol on silica in the presence of various concentrations of hexanol.

cetylpyridinium chloride (CPCl) has been studied (24). Figure 8 shows the adsorption isotherm of CPCl and adsolubilization of hexanol for the silica–CPCl system. The adsorbed amount of CPCl increases slightly with increasing feed concentration of hexanol. The increase in the adsorption of CPCl is due to an increase of the surface activity of CPCl in the presence of hexanol. A similar trend is observed for the silica–DPCl system. The adsolubilized amount of hexanol increases with the adsorbed amount of CPCl and decreases above the critical micelle concentration of CPCl. Also, the adsolubilized amount of hexanol increases with the feed concentration of hexanol. However, for the silica–DPCl system, hexanol is hardly adsolubilized. Microenvironmental properties such as micropolarity and microviscosity of adsorbed layers have been estimated using the fluo-

rescence probe and spin probe techniques. The micropolarity of the CPCl layer on silica is lower than that of the DPCl layer on silica, while the microviscosity of the former is greater than that of the latter. It is reasonable to correlate the adsolubilization behavior with the microenvironmental properties of the adsorbed surfactant layer.

It is interesting to study the effect of surfactant chemical structure on adsolubilization behavior. For that purpose, two kinds of cationic surfactants have been selected (33, 34). One is quaternary ammonium cationic surfactants with one, two, or three dodecyl chains and the other is monomeric, dimeric, or trimeric quaternary ammonium surfactants. Their chemical structures are shown in Fig. 9. The amount of adsorbed surfactants and the adsolubilization of 2-naphthol are shown in Figs. 10 and 11. The adsolubilized amount of 2-naphthol increases and reaches a maximum and then decreases with the surfactant concentration for all the systems, while the adsorbed amount of surfactant increases and reaches a plateau with the surfactant concentration. The ratios of maximum amount of 2-naphthol adsolubilized to the adsorbed amount of surfactant on silica for the double-chain and triple-chain surfactants are not so different and are quite large compared to that for the single-chain surfactant. On the other hand, the ratio increases with an increase in the

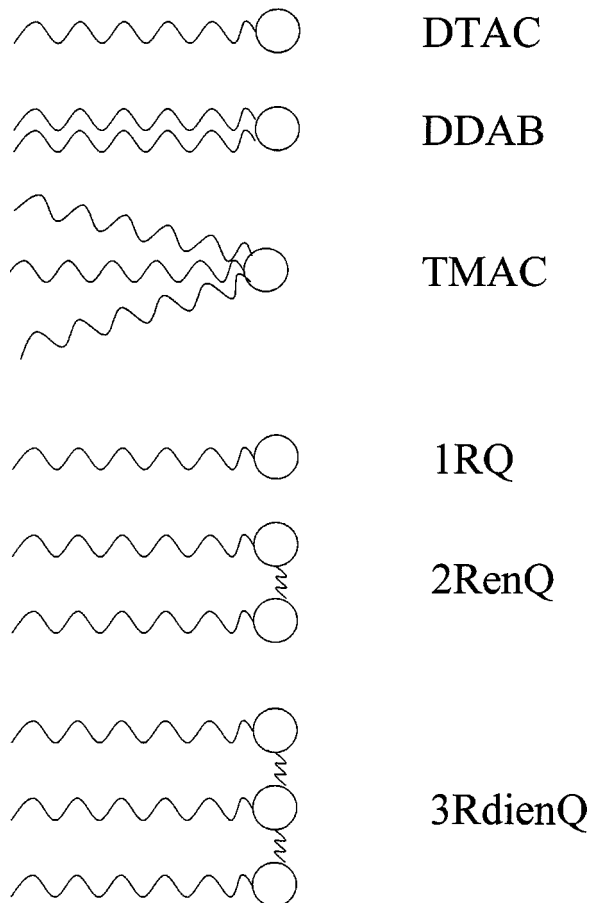


FIG. 9. Structures of multichained and polymeric surfactants.

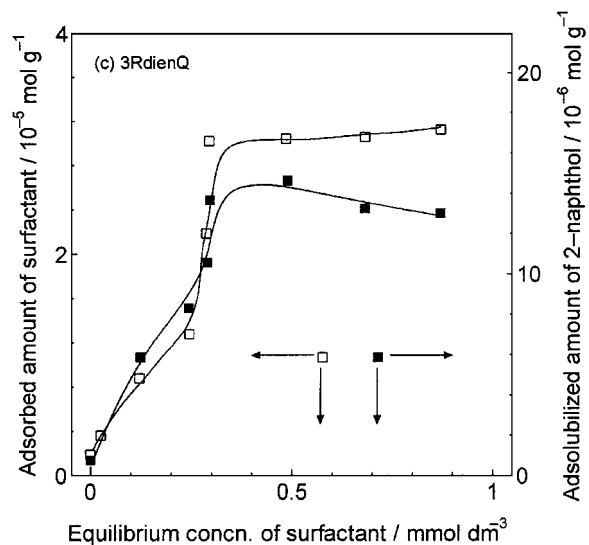
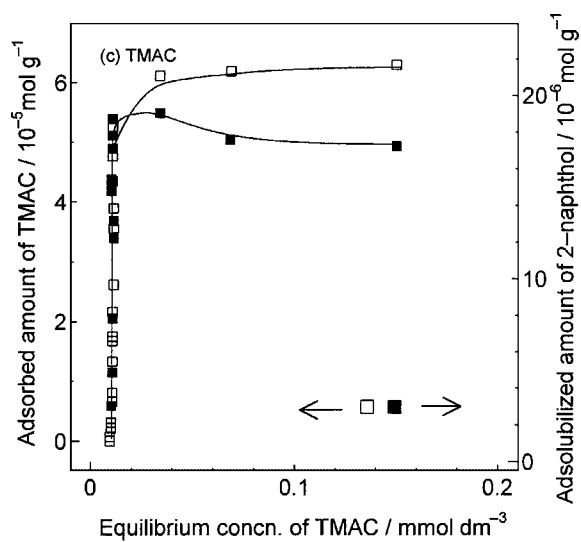
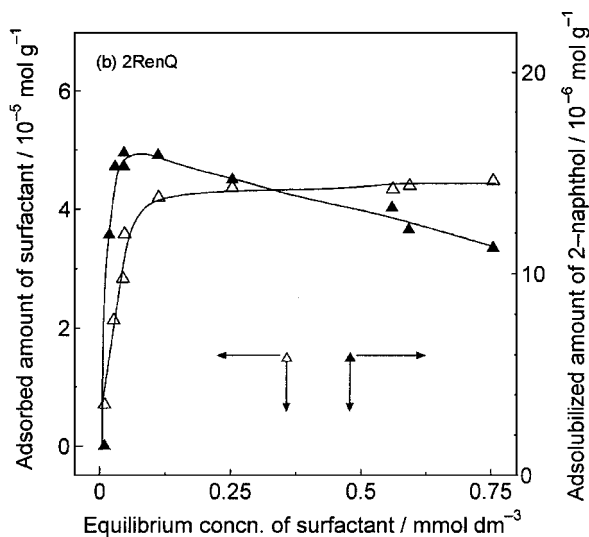
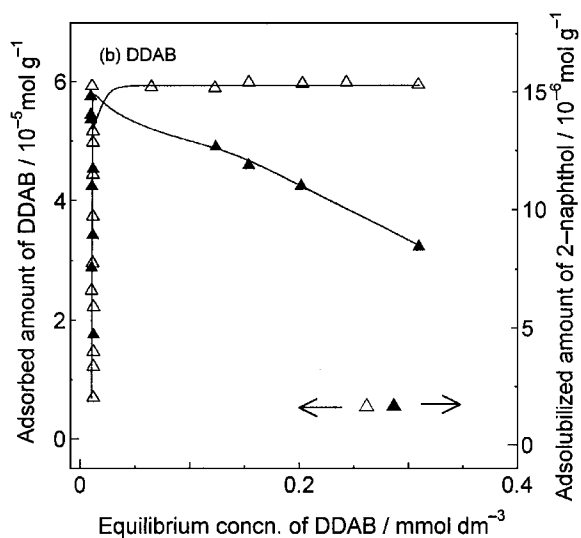
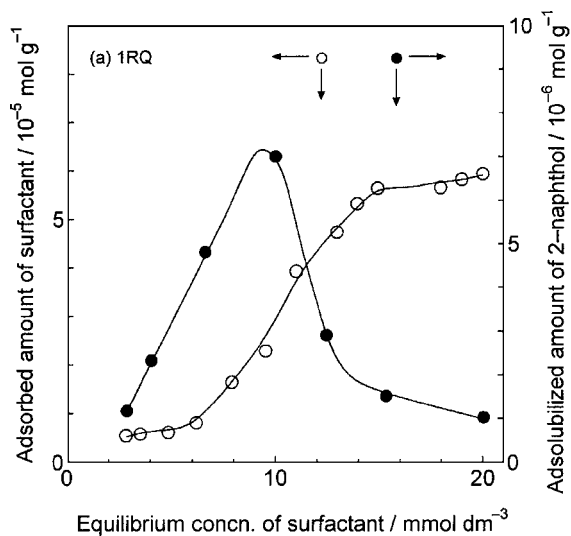
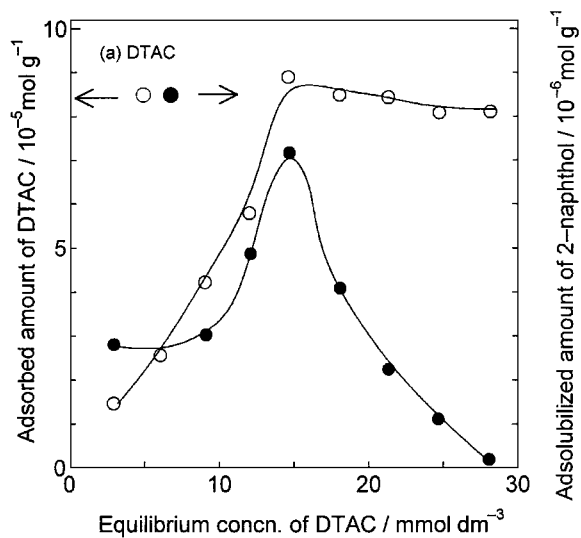


FIG. 10. Change in adsolubilized amount of 2-naphthol and in adsorbed amount of surfactant by adsorption of cationic multichained surfactants on silica.

FIG. 11. Change in adsolubilized amount of 2-naphthol and in adsorbed amount of surfactant by adsorption of cationic polymeric surfactants on silica.

TABLE 2

Effect of Surfactant Structure on Adsorption and Adsolubilization

Surfactant	(A)	(B)	(C)	(C)/chain
	Adsolubilized amount (mmol/g)	Adsorbed amount (mmol/g)		
DTAC	7.1	85	0.08	0.08
DDAB	15.4	50	0.31	0.15
TMAC	19.8	50	0.40	0.13
1RQ	7.1	32	0.22	0.22
2RenQ	16.5	28	0.59	0.29
3RdienQ	16.4	25	0.66	0.22

dodecyl chain number of the surfactants from 1RQ to 2RenQ and 3RdienQ. Thus, these results indicate that multiple-chained surfactants have an adsolubilization capacity larger than that of single-chained surfactants. Furthermore, to compare the difference in the adsolubilization between two systems, the ratios of maximum adsolubilized amount of 2-naphthol per dodecyl chain of the surfactants adsorbed are calculated and their values are shown in Table 2. One can see that the ratios for multichained surfactants are smaller than those for polymeric surfactants. In particular, in both systems, the surfactants having two dodecyl chains give higher ratios than the others. Since adsolubilization of 2-naphthol is strongly affected by microproperties of the surfactant adsorbed layer formed on silica, the order parameters (S) of 12-doxylstearate in the surfactant-adsorbed layer have been calculated from the maximum hyperfine splittings and the known hyperfine crystal tensors. The order parameters increase with increasing surfactant concentration and remain constant for all the systems (Fig. 12). Among the three surfactants such as 1RQ, 2RenQ, and 3RdienQ, the order parameters for 1RQ are much lower than those of 2RenQ and 3RdienQ, whereas those for 2RenQ are slightly greater than those for 3RdienQ. In the case of multichained surfactants such as DTAC, DDAB, and TMAC, the order parameters for DTAC are considerably lower than those for DDAB and TMAC. Since the order parameter represents the mobility of the probe in the adsorbed layer, which can be correlated with the microviscosity, it is inferred that the microviscosities of the adsorbed surfactant layers for surfactants having two or three dodecyl chains are higher than those for single-chained surfactants such as DTAC and 1RQ. This higher microviscosity is probably derived from the highly packed surfactant layer. In addition, the small difference in the order parameters between the surfactants having two or three dodecyl chains may arise from the increasing difficulty in packing alkyl chains linked by two and by three. The data for the adsolubilization have been obtained from mixtures of surfactant and 2-naphthol on silica. To evaluate the interaction of surfactants with the silica surface for 2-naphthol adsolubilization a two-step adsorption-adsolubilization process has been carried out: after the adsorption of the cationic surfactant alone onto silica, the supernatant obtained by centrifugation of the suspensions was removed and then an aqueous solution containing

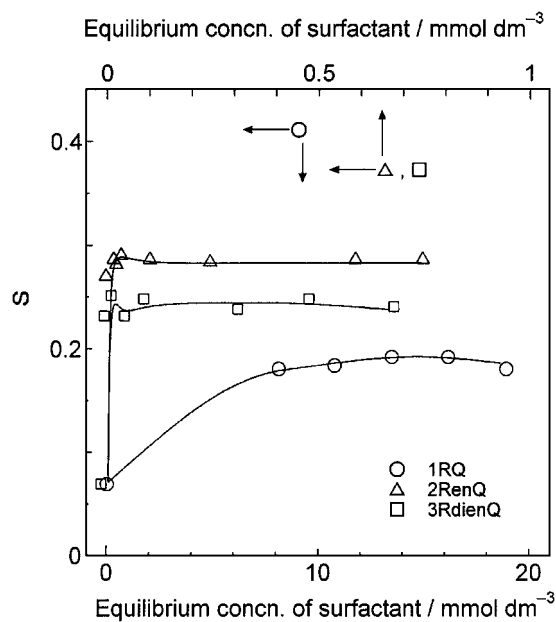


FIG. 12. Order parameter vs surfactant concentration.

2-naphthol was added to the cationic surfactant-adsorbed silica. Then, the amount of surfactant remaining on silica and the adsolubilized amount of 2-naphthol have been measured. The results are shown in Fig. 13. In the case of 1RQ, the adsolubilized amount of 2-naphthol markedly decreases accompanying the desorption of 1RQ, suggesting that a second layer of 1RQ at the bilayer would desorb due to weak hydrophobic interaction between the hydrocarbon chains of 1RQ. On the other hand, in the cases of 2RenQ and 3RdienQ, the adsorbed amount of the

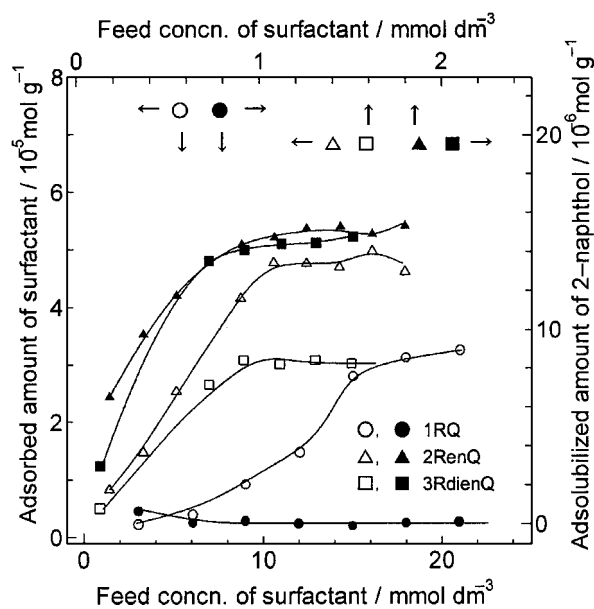


FIG. 13. Change in amount of 2-naphthol adsolubilized and surfactant adsorbed on silica by the process of adsorption-adsolubilization.

surfactant, as well as the adsolubilized amount of 2-naphthol, is almost unchanged by the two-step process. Since no micelles are present in the suspensions, no reduction in the adsolubilized amounts of 2-naphthol in the 2RenQ- and 3RdienQ-adsorbed layer is observed. Interestingly, it is suggested that 2RenQ and 3RdienQ adsorb strongly onto the silica surface, incorporating 2-naphthol more firmly than 1RQ. Similar behavior has been observed for adsorption and adsolubilization using multichain surfactants such as DTAC, DDAB, and TMAC.

Adsolubilization of water-insoluble compounds for the anionic surfactant-alumina systems has also been investigated (35–37). It is generally thought that the decrement in the adsolubilization occurs at above the cmc of the surfactant because the adsolubilize is partitioned between the adsorbed-surfactant layer and the micelles in solution. However, since the decrement in the adsolubilization in some cases begins below the cmc, adsolubilization behavior of 2-naphthol on alumina with adsorption of sodium dodecyl sulfate (SDS) at pH 3.5 in the presence of 10 mmol dm^{-3} NaCl has been reexamined (38). Figure 14 shows the adsorption isotherm of SDS as well as the adsolubilization of 2-naphthol at pH 3.5. It is seen that the isotherm of SDS consists of four adsorption regions in the linear-linear plot. The adsolubilized amount of 2-naphthol increases significantly at low SDS concentration, reaches a maximum, and then decreases with further increase of SDS concentration. It is found that the decrement in the adsolubilization begins at below the cmc. Accordingly, it is unlikely that the decrement in the adsolubilization is due to the partition of 2-naphthol between the SDS adsorbed layer and SDS micelles in solution. To confirm the effect of the adsorption of SDS on the adsolubilization, the dispersion stability of alumina suspensions has been monitored using a Turbiscan. Figure 15 shows that the dispersion stability of the alumina suspensions in the absence of SDS is very high because the intensity

of backscattering does not change during the running time. In the region below 1.6 mmol dm^{-3} SDS concentration, the transmittance of the entire length of the suspensions increases with the running time, indicating that flocculation of alumina particles occurs. It is suggested that SDS adsorbs onto positively charged alumina particles, orienting its hydrocarbon to aqueous solution at low SDS concentration so that the alumina surface becomes hydrophobic, resulting in flocculation between the hydrophobic surface particles. Thus, in SDS concentrations below 1.6 mmol dm^{-3} , it can be concluded that SDS adsorbs onto alumina as a monolayer and 2-naphthol molecules can be incorporated into the hydrophobic layer of SDS. Further, in the flocculation region the adsolubilized amount of 2-naphthol increases sharply, whereas the adsorbed amount of SDS increases gradually. This increase in the adsolubilization may proceed by incorporation and penetration of 2-naphthol into the flocs consisting of hydrophobic alumina particles. At a SDS concentration of 3 mmol dm^{-3} , the transmittance of the suspensions increases a little only in the upper portion of the samples, suggesting that admicelles are formed to some extent and the dispersion stability becomes increased due to electrostatic repulsion between the admicellar surfaces. If the number or size of admicelles increases at the SDS concentration region between 3 and 4.8 mmol dm^{-3} and the efficiency at adsolubilization by admicelles is lower than that of adsolubilization by monolayer, the adsolubilized amount of 2-naphthol would be reduced. As a result, the SDS concentration at the maximum adsolubilization is situated below the cmc of SDS. Above the cmc of SDS, it is likely that 2-naphthol can be partitioned into the SDS adsorbed layer and SDS micelles. Accordingly it can be suggested that the decrement in the adsolubilization of 2-naphthol is mainly due to the change in the surfactant adsorbed state on alumina rather than the partition of 2-naphthol between the adsorbed layer and SDS micelles in solution.

To enhance the adsolubilization of 2-naphthol, surfactant-clay systems have been studied. In the case of cationic surfactant-laponite clay systems (39), the surfactants adsorb extraordinarily on the clay and layer broadening of laponite occurs. As a result, the adsolubilization of 2-naphthol is considerably enhanced. A similar enhancement in the adsolubilization of 2-naphthol has been observed for SDS-hydrocalcite systems (40).

For surface modification of particles, adsolubilization and subsequent polymerization have been performed. After adsolubilization of styrene into SDS adsorbed layers on metal oxides such as titanium dioxide (41), iron oxide (41), and alumina (42), the adsolubilized styrene is polymerized by addition of initiator at 70°C . This polymerization process can be explained by the Smith-Ewart theory for emulsion polymerization.

5.2. Adsolubilization Using Mixed Surfactant Systems

Adsorption from surfactant mixtures onto solids includes the adsorption of binary surfactant mixtures of anionic surfactants, anionic-nonionic surfactants, and cationic-nonionic surfactants

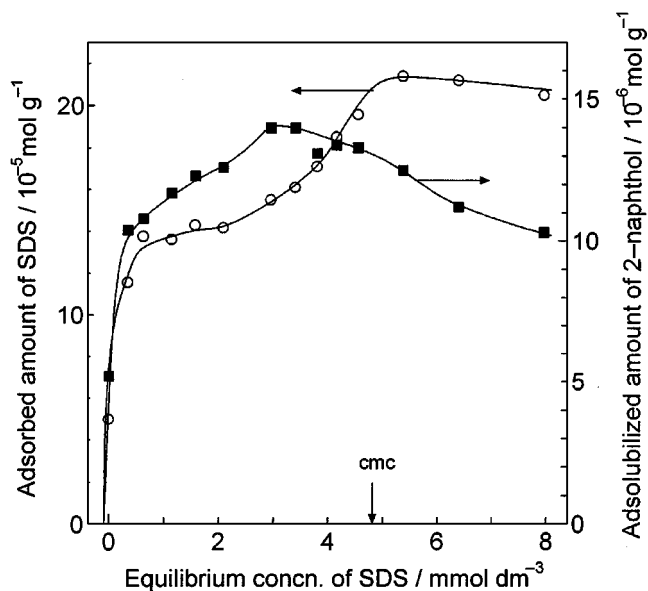


FIG. 14. Adsorption of SDS and adsolubilization of 2-naphthol on alumina.

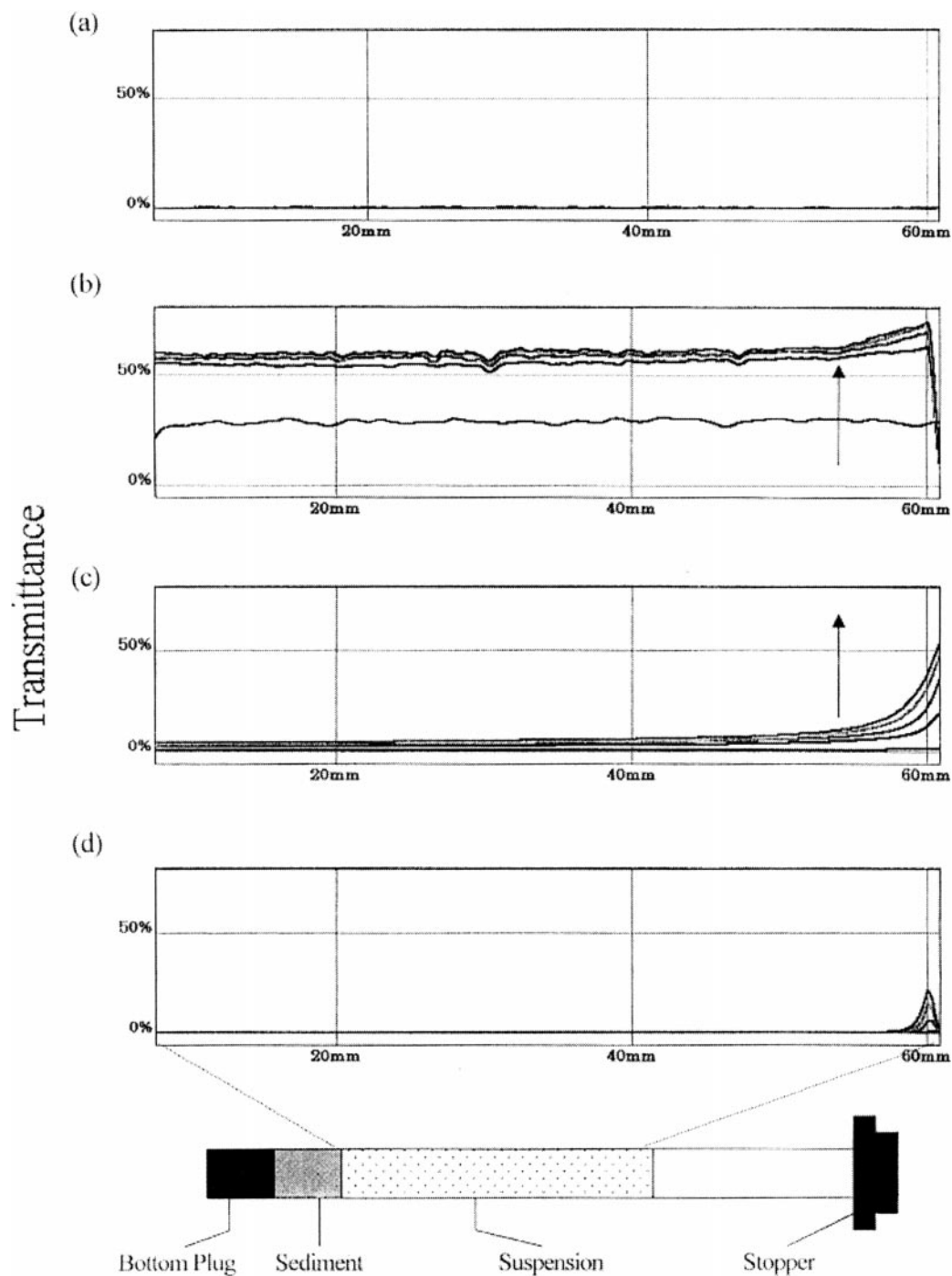


FIG. 15. The dispersion state of an alumina suspension with SDS adsorption (a) without SDS, and at (b) 1.6, (c) 3.0, and (d) 3.4 mmol dm^{-3} SDS (equilibrium concentration). The arrow indicates running time within 1 h, and the interval is 10 min.

(43–47). In particular, it is interesting that in ionic–nonionic surfactants, the adsorption of one surfactant is often enhanced by the addition of a small amount of the other surfactant. Surfactant mixtures provide several advantages over single surfactants, because the adsorption of surfactants onto particles can be controlled using appropriate surfactants and solution prop-

erties. The adsolubilization of 2-naphthol onto alumina by surfactant mixtures of an anionic surfactant (SDS) and a nonionic surfactant (hexaoxyethylenedodecyl ether, C_{10}E_6) has been investigated (48). In aqueous solution, the interaction parameter of SDS/ C_{10}E_6 mixed systems calculated using regular solution theory is about -3.4 , suggesting that the mutual phobicity between

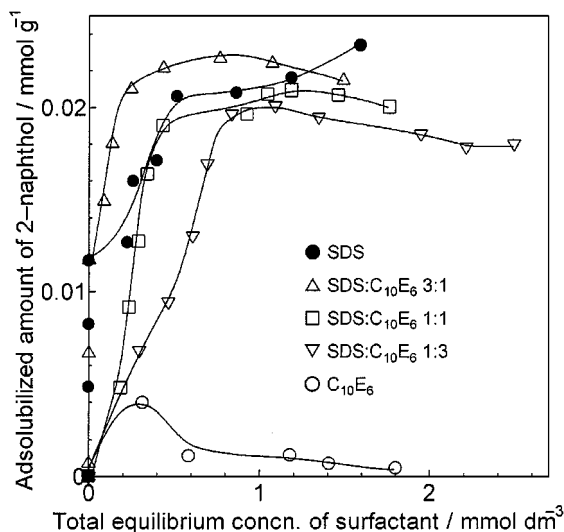


FIG. 16. Adsolubilization of 2-naphthol on alumina for SDS- $C_{10}E_6$ mixtures as a function of total surfactant equilibrium concentration: 25°C, 0.4 mmol dm⁻³ 2-naphthol, 10 mmol dm⁻³ NaCl, pH 3.5.

the hydrocarbon chains, as well as the reduction in coulombic repulsion between the headgroups, dominates the interactions between SDS and $C_{10}E_6$. Figure 16 shows the adsolubilized amount of 2-naphthol as a function of total surfactant equilibrium concentration. Because the adsolubilization of 2-naphthol is not observed on alumina without surfactants, it is apparent that 2-naphthol is incorporated into the surfactant adsorbed layer that exhibits a hydrophobic property. It is seen that the amount of 2-naphthol adsolubilized by adsorption of $C_{10}E_6$ alone is very low, but becomes greater with an increase in the SDS content of the initial mixtures, from SDS : $C_{10}E_6 = 1 : 3$ to 3 : 1. The adsolubilized amount of 2-naphthol by adsorption of SDS alone ranges between SDS : $C_{10}E_6 = 1 : 1$ and 3 : 1.

To compare the efficiency of adsolubilization by surfactants, we compare the ratio of adsolubilized amount to adsorbed surfactant amount. The ratios of adsolubilized amount (mmol g⁻¹) to adsorbed surfactant amount (mmol g⁻¹) are plotted with the total adsorbed amount of surfactant in Fig. 17. In the case of SDS, the ratios are about 0.1 for the whole SDS adsorption concentration range, whereas those for $C_{10}E_6$ range between 0.02 and 0.06, suggesting that the efficiency of adsolubilization is low for both SDS and $C_{10}E_6$ single adsorption. On the other hand, the ratios for both SDS : $C_{10}E_6 = 1 : 3$ and 1 : 1 decrease with an increase in the total adsorbed amount of surfactant and approach 0.1, while those for SDS : $C_{10}E_6 = 3 : 1$ increase gradually and also approach 0.1. It is suggested that for SDS : $C_{10}E_6 = 3 : 1$, the efficiency of adsolubilization is predominantly controlled by the adsorption of SDS. It is also found that the efficiency of adsolubilization increases when the SDS content in the initial mixtures drops below surfactant adsorption of 0.2 mmol g⁻¹. Interestingly, a relationship exists between the efficiency of adsolubilization and the ratio of SDS to $C_{10}E_6$ in

the adsorption; when the ratio of SDS to $C_{10}E_6$ in the adsorption becomes small, the efficiency of adsolubilization becomes greater. This result might be explained by a view that the mixed surfactant adsorbed layer is more compact because of a shield of electrostatic repulsion of SDS adsorbed by incorporation of $C_{10}E_6$, in particular for the case of SDS : $C_{10}E_6 = 1 : 3$. Thus, surfactant mixtures of anionic and nonionic surfactants with low concentrations have great possibilities for enhancing adsolubilization of water-insoluble compounds. A similar enhancement of 2-naphthol adsolubilization has been observed for hexadecyltrimethylammonium bromide/ $C_{10}E_6$ /silica systems.

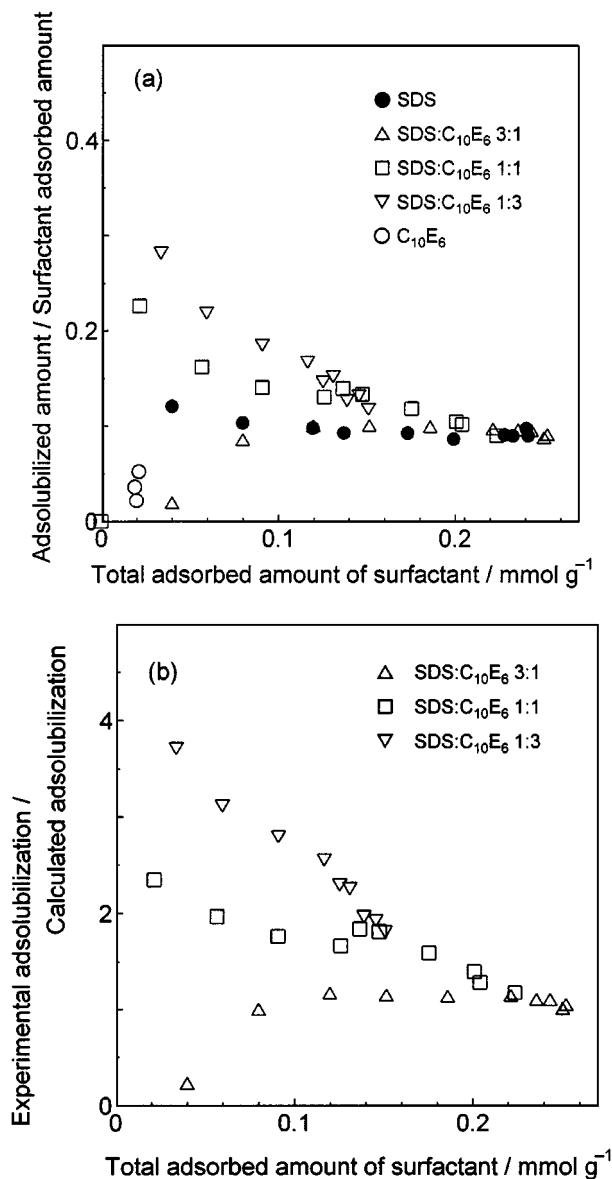


FIG. 17. (a) Ratio of adsolubilized amount and surfactant adsorbed amount on alumina for SDS- $C_{10}E_6$ mixtures as a function of total surfactant adsorbed amount; (b) ratio of experimental and calculated adsolubilization on alumina for SDS- $C_{10}E_6$ mixtures as a function of total surfactant adsorbed amount.

5.3. Adsolubilization by Surfactants Using Surface Chemistry Modified Particles

Until now, particles used for adsolubilization have been limited to hydrophilic particles such as alumina, silica, titanium dioxide, and clay. It is expected that the adsolubilization behavior can be altered by using modified hydrophilic particles with chemical bonding of surfactant or surfactant-like molecules. Various oxides have been modified by chemical vapor deposition using 1,3,5,7-tetramethylcyclotetrasiloxane, followed by hydrosilylation to graft functional groups on the oxides (49). Usage of such grafted oxides can provide information to develop new types of particles for adsolubilization (50).

Titanium dioxide has been modified by grafting dodecyl chains onto the surface (51, 52). The concentrations of dodecyl

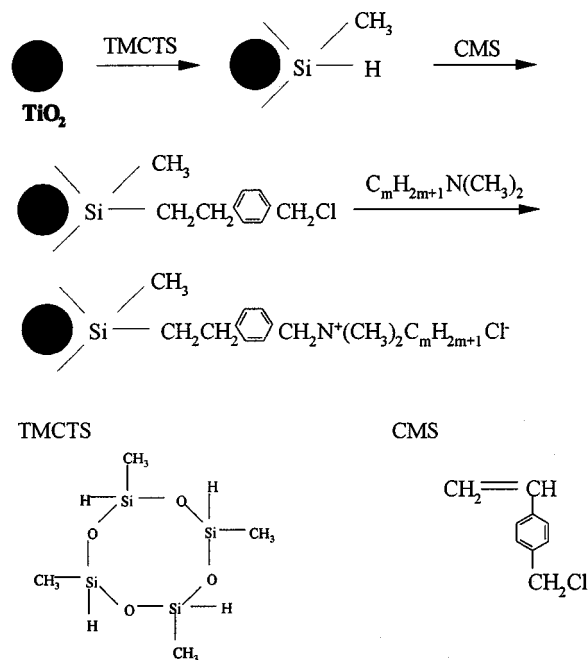


FIG. 19. Scheme of reaction for XNm.

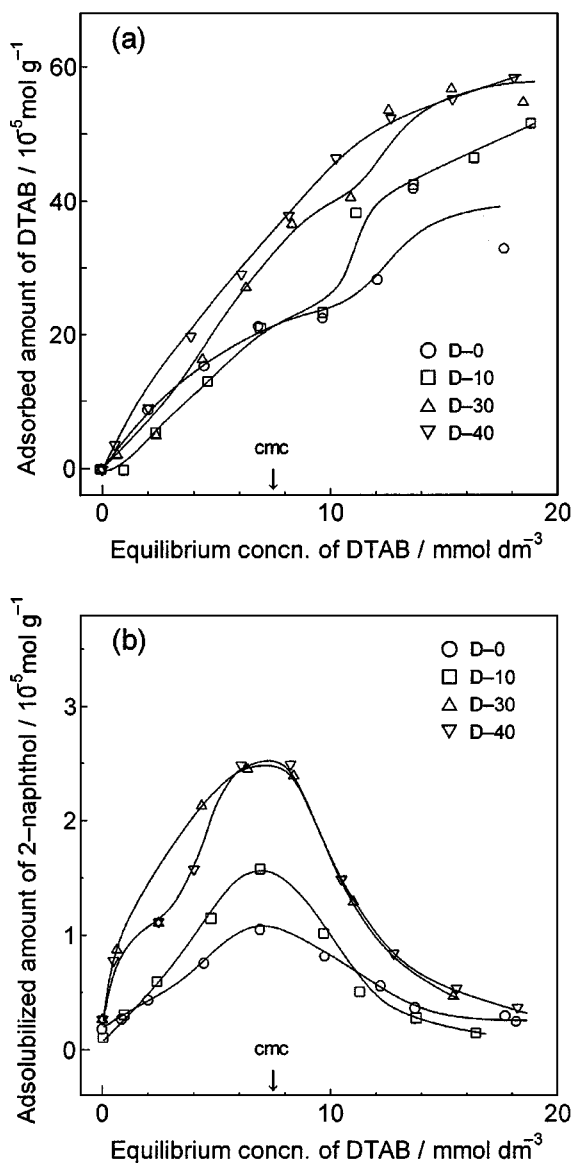


FIG. 18. (a) Adsorption isotherms of DTAB on titanium dioxide with dodecyl chain anchor; (b) adsolubilization of 2-naphthol with adsorption of DTAB.

chains grafted on the surface are 11.8, 26.3, and 47.2 $\mu\text{mol g}^{-1}$, respectively, and these samples are referred to as D-10, D-30, and D-40 (D-0 is the untreated sample). Figure 18a shows the adsorption isotherms of dodecyltrimethylammonium bromide (DTAB) on the modified titanium dioxide in the presence of 0.4 mmol dm^{-3} 2-naphthol. The adsorption of DTAB on D-0 and D-10 increases gradually with DTAB concentration, whereas that of DTAB on D-30 and D-40 increases rather sharply. These differences are probably derived from the different hydrophobicities of the samples, which increase with increasing dodecyl chain concentration as the anchor. Assuming that DTAB is adsorbed on the treated samples through hydrophobic interaction between the hydrocarbon chain of DTAB and dodecyl chain on titanium dioxide, aggregation of about five to eight molecules of DTAB is obtained for adsorption per one dodecyl chain on titanium dioxide at the saturation. Figure 18b shows the adsolubilization of 2-naphthol with adsorption of DTAB. It is apparent that the amounts of 2-naphthol adsolubilized increase, reach a maximum, and then decrease with the DTAB concentration for all the samples. It is interesting to note that the amount adsolubilized is markedly dependent on the dodecyl chain concentration. In particular, the maximum amount of 2-naphthol adsolubilized by D-40 is 2.5 times that adsolubilized by D-0. Thus, an enhancement in the adsolubilization of 2-naphthol by introducing the dodecyl chain onto the titanium dioxide is clearly demonstrated. In addition, the ratios of the maximum amount of 2-naphthol adsolubilized to the amount of DTAB adsorbed are 0.048 for D-0, 0.046 for D-10, 0.078 for D-30, and 0.065 for D-40. In the absence of DTAB, the incorporation of 2-naphthol on the surface-modified samples increases with increasing dodecyl chain concentration, probably due to hydrophobic interaction

between 2-naphthol and the dodecyl chain on titanium dioxide. The ratio of 2-naphthol incorporated to dodecyl chains is about 0.10–0.15.

Another surface modification of titanium dioxide has been performed, as shown in Fig. 19. The modified samples are referred to as XNm , where m is the carbon number of the alkyl chain, 4–16. Titanium dioxides modified with various chain lengths from 4 to 16 exhibit good wetting behavior in water because cationic quaternary ammonium groups are grafted on the surfaces (53, 54). Figure 20 shows the adsolubilization of 2-naphthol in the adsorbed layers of ionic surfactants on XNm and untreated titanium dioxide. Here, the ionic surfactants used are SDS, DTAC, and 1,2-bis(dodecyldimethylammonio)ethane dichloride (2RenQCl). Interestingly, in the absence of ionic surfactants, 2-naphthol molecules adsorb appreciably on XNm surfaces, whereas a negligible amount is observed on the untreated titanium dioxide. The amounts of 2-naphthol adsorbed increase with increasing alkyl chain length on XNm , and the ratios of 2-naphthol molecule adsorbed to alkyl chains are calculated to be 0.18, 0.25, 0.31, and 0.46 from $XN4$, $XN8$, $XN12$, and $XN16$, respectively. In the case of $XN0$ (only chloromethyl-treated), the ratio of 2-naphthol to chloromethyl groups is calculated to be about 0.04, which is very small compared to those for XNm . The great adsorption of 2-naphthol on XNm without ionic surfactants may occur because of a good polarity matching between 2-naphthol and the ammonium chain anchor on XNm . The amount of 2-naphthol adsolubilized on XNm increases slightly with increasing SDS or DTAC concentration except for $XN16$ in which the amount adsolubilized rather decreases. Here, the adsolubilization experiments for both SDS and DTAC have been carried out below their cmcs. In the case of 2RenQCl, the amount of 2-naphthol adsolubilized increases sharply with 2RenQCl concentration and reaches a maximum and then gradually decreases for XNm and untreated titanium dioxide. The magnitude in the increment of 2-naphthol adsolubilization becomes small with increasing alkyl chain length on XNm .

To compare the adsolubilization behavior of 2-naphthol on XNm , the admicellar partitioning coefficient K_{adm} can be obtained from

$$K_{adm} = X_{adm}/X_{aq},$$

$$X_{adm} = C_{adm}/(C_{adm} + S_{ads}),$$

and

$$X_{aq} = C_{eq}/(C_{eq} + S_{eq} + 55.55),$$

where C_{adm} and C_{eq} are the adsolubilized amount and the equilibrium concentration of the organic solute, and S_{ads} is the adsorbed amount of the surfactant. The moles of water per liter is 55.55 and S_{eq} is the equilibrium concentration of the surfactant in aqueous solution. Figure 21 shows the admicellar partitioning coefficients with surfactant concentrations for (a) SDS- XNm , (b) DTAC- XNm , and (c) 2RenQCl- XNm . In the

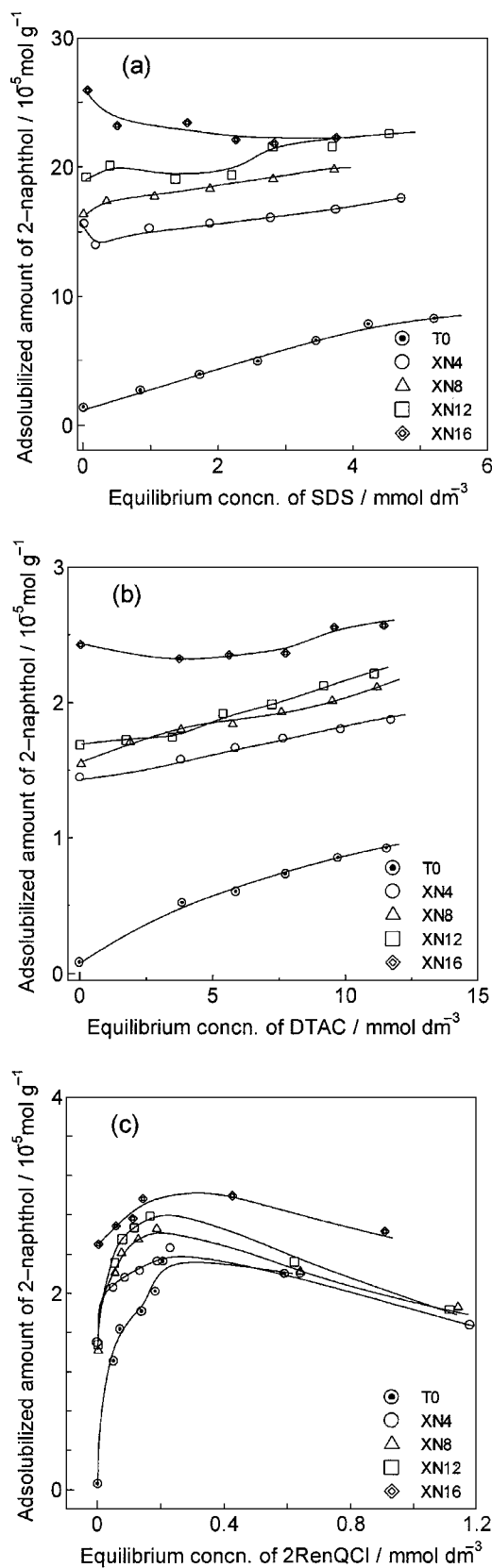


FIG. 20. Adsolubilization of 2-naphthol on titanium dioxide with quaternary ammonium groups with adsorption of surfactant: (a) SDS; (b) DTAC; (c) 2RenQCl.

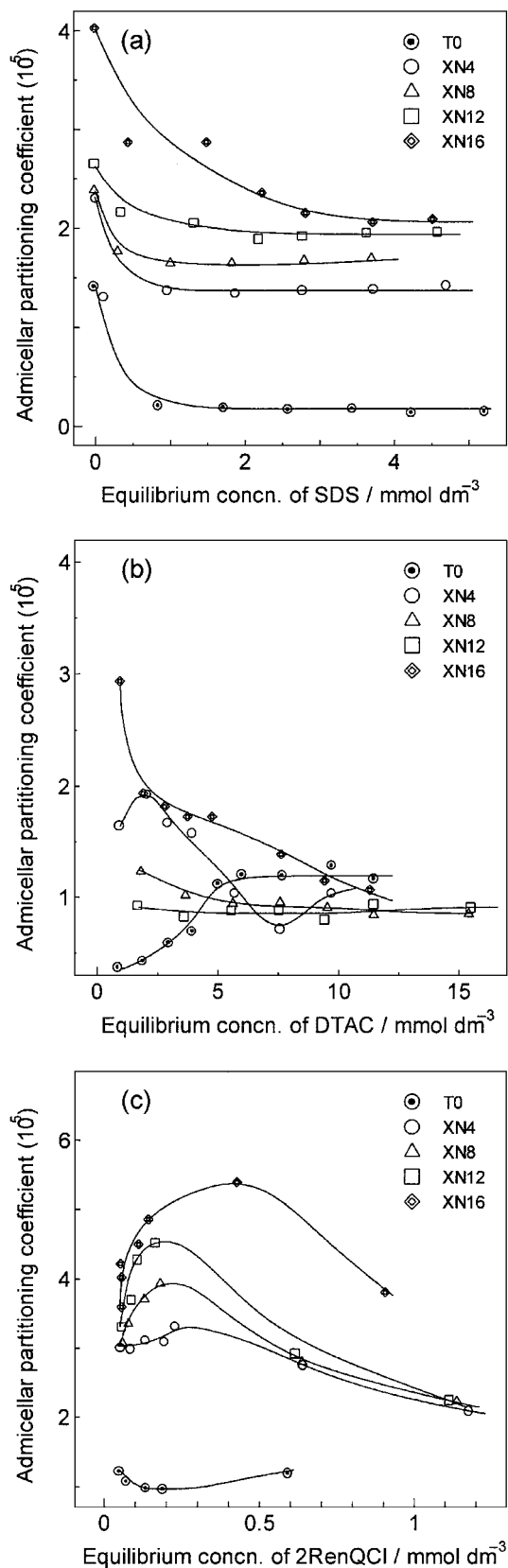


FIG. 21. Admicellar partitioning coefficients of 2-naphthol with surfactant concentration for (a) SDS-XNm, (b) DTAC-XNm, and (c) 2RenQCl-XNm.

case of the SDS-XNm system, K_{adm} becomes larger as the alkyl chain length increases from 4 to 16, whereas K_{adm} for untreated titanium dioxide is very small. This small value of K_{adm} for untreated titanium dioxide is similar to the values of K_{adm} for 2-naphthol/SDS/alumina and 2-naphthol/DTAB/titanium dioxide. In the case of the DTAC-XNm system, the values of K_{adm} range between 1×10^5 and 1.5×10^5 , irrespective of the alkyl chain length for XNm at 10 mmol dm^{-3} DTAC. On the other hand, for the 2RenQCl-XNm system, K_{adm} increases gradually and reaches a maximum and then decreases with 2RenQCl concentration, while K_{adm} for untreated titanium dioxide decreases gradually and reaches a constant level. Further, the magnitude of K_{adm} increases with increasing alkyl chain length on XNm, indicating that the alkyl ammonium chain groups for XNm play an important role in enhancing the adsolubilization of 2-naphthol. In addition, it is found that adsolubilization of 2-naphthol is considerably altered by a combination of surfactant and modified titanium dioxide.

6. SIMULTANEOUS ADSORPTION OF SURFACTANTS AND POLYMERS ON PARTICLES

Simultaneous adsorption of surfactants and polymers from their mixed solutions onto solid particles, as well as adsorption of surfactants alone, has been studied (55–70). Depending on the surface properties of solids as well as the aqueous properties of polymers and surfactants, the adsorption can be described as follows. When the interactions between polymers and surfactants in aqueous solution are weak, competitive adsorption may occur. If the interactions are strong and the polymer or surfactant has a strong affinity with the solid surface, enhancement in the adsorption of the other occurs.

A remarkable enhancement of polymer adsorption by surfactant has been observed for the poly(vinylpyrrolidone) (PVP)/SDS/alumina system (71). The result is shown in Fig. 22. The adsorption of PVP and SDS at an initial concentration of PVP (0.8 g dm^{-3}) has been measured as a function of the SDS equilibrium concentration at pH 3.5. One can see that the amount of PVP adsorbed increases markedly with the SDS equilibrium concentration, achieves a maximum, and then decreases, while the adsorption of SDS also increases with the SDS equilibrium concentration and reaches a plateau. The amount of SDS adsorbed in the presence of PVP is greater than that for SDS alone at low SDS equilibrium concentration, but less at high SDS concentration. It is suggested that since the PVP–SDS complexes are formed in the bulk, they adsorb to some extent onto the surface of the alumina and free PVP is adsorbed onto the preadsorbed SDS due to the hydrophobic interaction of SDS and PVP, resulting in a remarkable enhancement in PVP adsorption at low SDS concentration. The decrease in the PVP adsorption at high SDS concentration is due to the decrease in the adsorption of PVP–SDS complexes, which are less surface active than SDS. Such a mechanism of PVP and SDS adsorption onto alumina is supported by an adsorption kinetics study (72). Furthermore, the conformation change in adsorbed PVP due to simultaneous

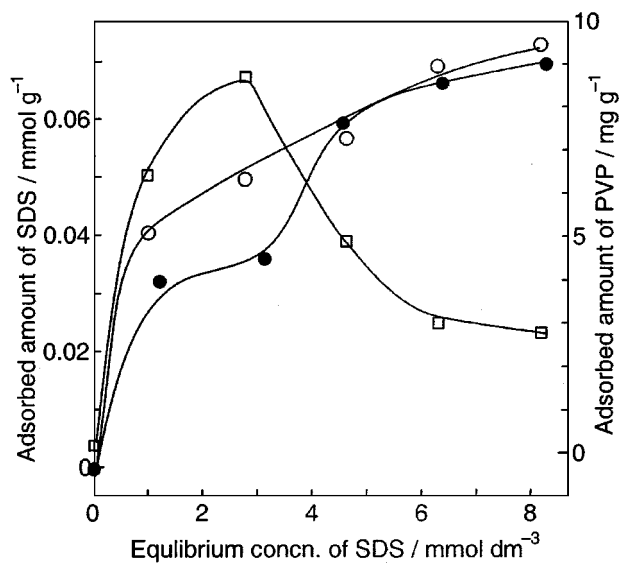


FIG. 22. Adsorption isotherm of SDS (●) and simultaneous adsorption of SDS (○) and PVP (□) onto alumina. The initial concentration of PVP is 0.8 g dm^{-3} .

adsorption of SDS has been estimated using spin-labeled PVP (71, 73–75).

Many studies of simultaneous adsorption of surfactants and polymers have been limited to linear polymers. Dendrimers, being highly branched polymers, have become the subject of extensive studies (76–79) because their functional groups and specific shapes have unique properties compared to those of conventional linear polymers. We have been studying the simultaneous adsorption of poly(amidoamine) dendrimers with surface carboxyl groups and an anionic surfactant at the alumina/water interface (80) and of poly(amidoamine) dendrimers with surface amino groups and cationic surfactants at the silica/water interface (81). In both systems involving the same charged dendrimers and surfactants against oppositely charged particles, competitive adsorption of the dendrimers and surfactants has been observed. From comparison between the dendrimers and linear polymers such as poly(acrylic acid) and poly(ethyleneimine) it is found that the number of linear polymers is much smaller than that of dendrimers and the replacement of the linear polymers by the surfactants occurs more easily than that of the dendrimers by the surfactants.

Enhancement in dendrimer adsorption by surfactant adsorption has been observed for sugar-persubstituted poly(amidoamine) dendrimers (sugar ball) and anionic surfactants and alumina systems (82). Figure 23 shows simultaneous adsorption of SDS and SB5 (sugar ball with generation 5) onto alumina. Here, the initial concentrations of SB5 are fixed at 0.10 and 0.25 g dm^{-3} . It is very interesting to note that the amount of SB5 adsorbed increases markedly at low SDS concentrations, shows a maximum, and then decreases with an increase of SDS concentration, while the amount of SDS adsorbed is greater in the presence than in the absence of SB5. Such an enhancement

in the adsorption of SB5 is probably due to interaction between SDS and SB5 on the alumina surface. Actually, the surface tensions of mixtures of SDS and SB5 are very low compared to that of SDS alone, suggesting formation of some complex of SDS and SB5 in which the hydrophilic groups of SDS might be adsorbed onto the residue of glycoside of SB5, resulting in the orientation of the hydrocarbon chain of SDS to the aqueous phase (83). When mixtures of SDS and SB5 consisting of their complexes and SDS monomer contact alumina particles, SDS monomer adsorbs first, orienting its hydrocarbon chain to the alumina surface, followed by adsorption of SDS–SB5 complex on the surface. As a result, adsorption of SB5 is enhanced at low SDS concentration. With an increase of SDS concentration,

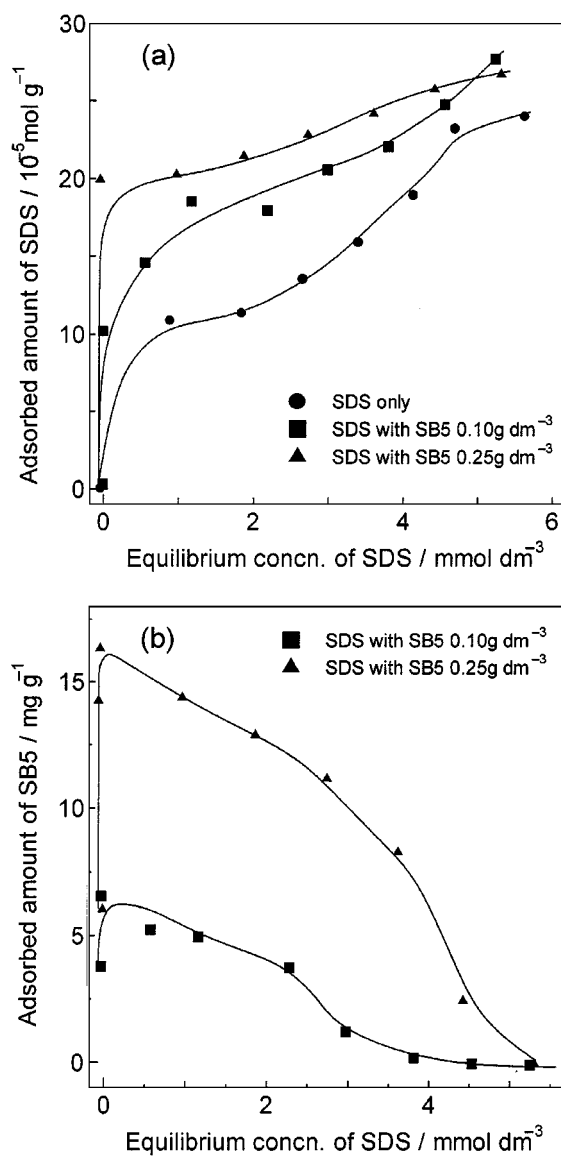


FIG. 23. Simultaneous adsorption of SDS and SB5 onto alumina: (a) SDS adsorption; (b) SB5 adsorption. The initial concentrations of SB5 are 0.10 and 0.25 g dm^{-3} . The adsorption isotherm of SDS alone is also given.

competitive adsorption between SDS monomer and SDS–SB5 complex against SDS-covered alumina surface occurs, and at the same time the state of the SDS–SB5 complex changes from monolayer coverage to bilayer coverage of SDS on the SB5 surface. Then, adsorption of SB5 onto alumina will decrease. The enhancement in the adsorption of SB5 by SDS is clearly observed when the initial concentration of SB5 is higher. A similar enhancement in the adsorption of SB5 on alumina has been observed by addition of an anionic fluorinated surfactant.

7. CONCLUDING REMARKS

The interactions between surfactants and particles can be correlated with many interfacial processes. Surfactant adsorbed layers formed on particles using various surfactants exhibit characteristic adsolubilization behaviors. In addition, the adsolubilization is also enhanced using surfactant mixed systems and surfactant-modified particles. By addition of surfactant, adsorption of polymer onto particles is considerably affected, depending on a combination of kinds of surfactants and polymers. To understand these interactions in detail, analysis of the adsorbed surfactant layer is required using several techniques including AFM and neutron scattering. Furthermore, future studies of the effect of particle size on the interaction between surfactants and particles are necessary, in the range between micrometer and nanometer size.

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