Colloid Science

The pH dependence of dispersion of TiO_2 particles in aqueous surfactant solutions

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Abstract: The pH dependence of dispersion of titanium dioxide (TiO_2) particles has been examined in the presence of surfactant molecules in water. Whereas particles were dispersed in water at acid and alkaline regions rather than at neutral region, the dispersion was enhanced at neutral region in an aqueous sodium dodecyl sulfate (SDS) solution and at acid and alkaline regions in an aqueous dodecyldimethylamine oxide ($C_{12}DAO$) solution. Considering the pH dependence of zeta potential, the adsorption models of surfactant molecules on a particle were estimated on the basis of the modes of hemimicelle and double-layer compression. While the particles that adsorbed Al^{3+} were remarkably dispersed around pH 6, their dispersion does not largely depend on pH in the addition of SDS, indicating the adsorption of SDS molecules to form double-layer compression in the whole pH region. Dynamic light-scattering measurement and electron microscopic observation suggested that the particles were dispersed in water as small flocs.

Key words: TiO_2 particle dispersion, aqueous surfactant solution, electrostatic attractive interaction, physical adhesive interaction, lateral hydrophobic interaction, hemimicelle, double layer compression.

Introduction

While small particles in colloidal suspensions are dispersed by the convection of medium and by the Brownian motion of particles, particles sometimes flocculate. Large flocs occasionally lose the stability in medium, giving rise to sedimentation. Dispersion and flocculation of particles are participated by their surface structure. In aqueous medium, when particles carry charges or hydrophilic adsorption layers are formed on their surfaces, the dispersion may be promoted and the flocculation may be restrained.

The addition of surfactants to colloidal suspensions modifies the surface structure of particles, because surfactants are adsorbed on the particle surfaces, owing to the electrostatic attractive interaction between surfactants and particles or the physical (nonelectrostatic) adhesive interaction [1]. If the surfactant concentration is lower than the critical micelle concentration (CMC), a small amount of unassociated surfactants is adsorbed on the particle surfaces. At a higher surfactant concentration than the CMC adsorbed surfactants are concentrated on surfaces and make patches. One type of patch is "hemimicelle", which is formed through the physical adhesive interaction and the lateral hydrophobic interaction between hydrocarbon chains of surfactant; another type is "double-layer compression" which is originated in the electrostatic attractive interaction and the lateral hydrophobic interaction [1–3].

In this work, we examine how the pH-dependence of dispersion of ultra-fine TiO_2 particles, with and without adsorbed Al^{+3} in water, is changed as adsorption layers of surfactants are formed on particle surfaces. The adsorption models of surfactants are assumed by the aid of the observed values of zeta potential. Flocculation of TiO_2 particles is also investigated by the dynamic light-scattering measurement and the electron microscopic observation.

Experimental section

TiO$_2$ (code no. TTO-55), which was supplied by Ishihara Sangyo Co., Ltd., is rutile crystals of 99.7% purity and has an average particle diameter of 20–50 nm. Samples of SDS and C$_{12}$DAO were purified from commercial products as before [4,5]. Commercial heptaoxyethylene dodecyl ether (C$_{12}$E$_7$) and AlCl$_3$ were used without further purification. Degas water was prepared by a routine method [5].

TiO$_2$ (5 mg) was added to water or aqueous surfactant solution of 0.5×10^{-2} g cm^{-3} (5 cm^3) in a test tube in order to obtain a TiO$_2$ or TiO$_2$-surfactant suspension. For the preparation of suspension in the presence of AlCl$_3$, that is, TiO$_2$-AlCl$_3$ and TiO$_2$-AlCl$_3$-surfactant suspensions, TiO$_2$ (5 mg) was added to aqueous AlCl$_3$ solution of 0.60 mM (2.5 cm^3), the suspension was shaken for 20 min in a water bath at 25 °C, and water or aqueous surfactant solution of 10^{-2} g cm^{-3} (2.5 cm^3) was added to it. The concentration of Al^{3+} is within the concentration region where TiO$_2$ (rutile) particles can be dispersed in water [6]. The pH of a suspension was adjusted by adding a small amount of standardized solution of HCl or NaOH. The suspension was shaken for 7 h at 25 °C and allowed to settle for 14 h. Although some amounts of TiO$_2$ gave rise to sedimentation at the tube bottom, the top of the suspension was used for the measurement.

Absorbance was measured with a 10-mm cell on a Shimadzu double-beam spectrophotometer UV-200S. The measurement of zeta (ζ) potential was carried out on a Pen Kem laser zee model 501 under the applied voltage of 100 or 150 V cm^{-1}. Mutual diffusion coefficient was measured at a 90°-scattering angle on an Otsuka Denshi dynamic light-scattering spectrophotometer DLS-700, equipped with an argon ion laser at a 488-nm wavelength. Measurements were performed at 25 °C. Electron microscopic observation was performed at room temperature on a Hitachi electron microscope 800H.

Results

As TiO$_2$ particles display turbidity in an aqueous suspension, the absorbance at 320 nm was measured as a measure of the turbidity or dispersion. Figures 1–4 show the pH-dependence of absorbance of TiO$_2$ suspensions in the absence and presence of additives, surfactants, and AlCl$_3$. The curves of the reference suspensions and the difference curves between the suspensions and the reference suspensions are also represented in the figures.

If additives are not present, the absorbance of a TiO$_2$ suspension is strong around pH 2 and 10. When the absorbance of a TiO$_2$ suspension in the presence of AlCl$_3$ is compared with that in the absence of AlCl$_3$, the difference is large: the dispersion of a TiO$_2$-AlCl$_3$ suspension is remarkable at pH 4–8, contrary to the diminution of the dispersion at pH 8–11.

When SDS is added to the TiO$_2$ suspension, the absorbance increases at pH 3–8, but decreases at pH 2–3 and above pH 8. The absorbance of a TiO$_2$-AlCl$_3$-SDS suspension is higher, on the whole, than that of a TiO$_2$-SDS suspension. It exhibits three maxima around pH 2.5, 6 and 11, as well as that of a TiO$_2$-AlCl$_3$ suspension, although the pH dependence of the absorbance decreases: the absorbance at each maximum is smaller than that of a TiO$_2$-AlCl$_3$
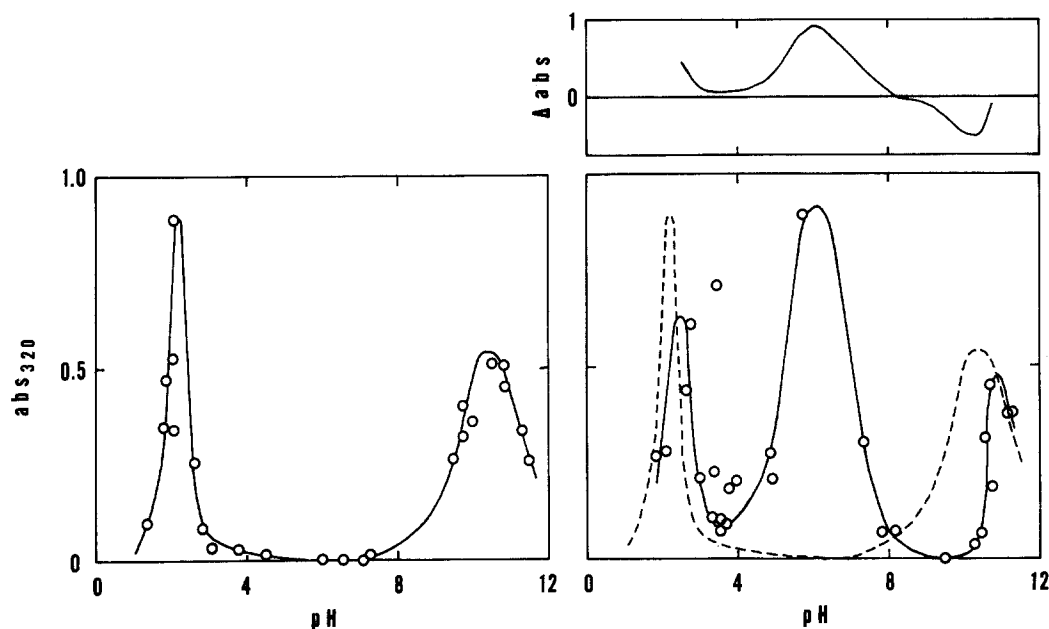

Fig. 1. The pH-dependence of absorbance of a TiO$_2$ suspension (left) and of a TiO$_2$-AlCl$_3$ suspension (right). The dotted line in the right figure represents the observed absorbance for a TiO$_2$ suspension. Δabs = abs(TiO$_2$-AlCl$_3$) − abs(TiO$_2$)
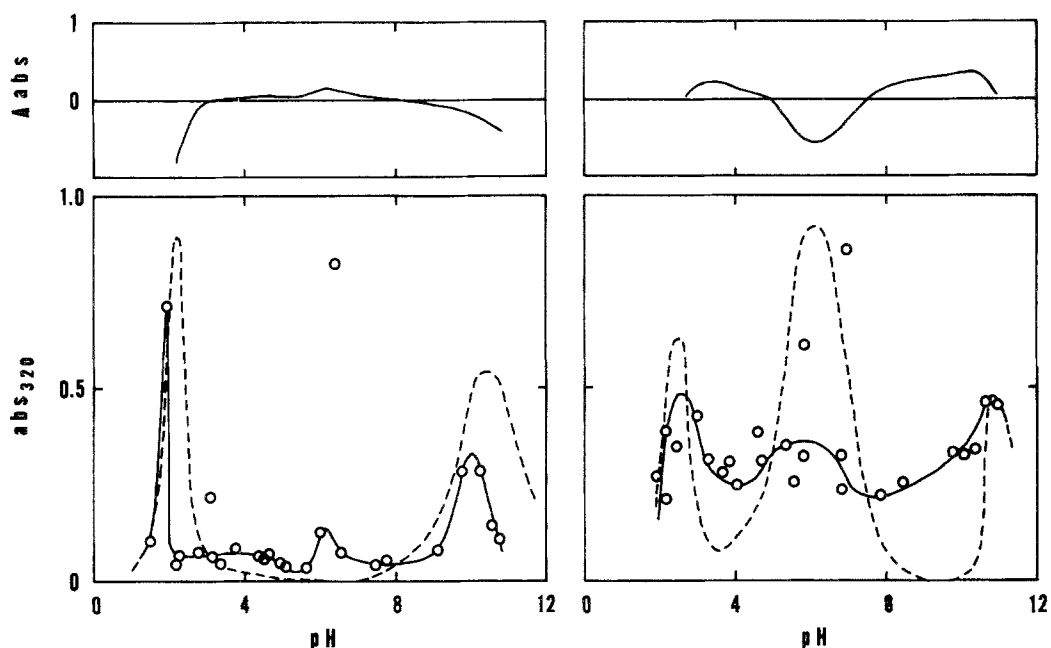
Fig. 2. The pH-dependence of absorbance of a TiO$_2$-SDS suspension (left) and of a TiO$_2$-AlCl$_3$-SDS suspension (right). The dotted lines represent the observed absorbance for a TiO$_2$ suspension (left) and for a TiO$_2$-AlCl$_3$ suspension (right). Δabs = abs(TiO$_2$-SDS) − abs(TiO$_2$) in the left figure. Δabs = abs(TiO$_2$-AlCl$_3$-SDS) − abs (TiO$_2$-AlCl$_3$) in the right figure

suspension, while the absorbance at each minimum is larger than that of a TiO$_2$-AlCl$_3$ suspension.

When the absorbance of a TiO$_2$-C$_{12}$E$_7$ suspension is compared with that of a TiO$_2$ suspension, the difference is rather small. However, the addition of

Fig. 3. The pH-dependence of absorbance of a TiO$_2$-C$_{12}$E$_7$ suspension. The dotted line represents the observed absorbance for a TiO$_2$ suspension. Δabs = abs(TiO$_2$-C$_{12}$E$_7$) − abs(TiO$_2$)

C$_{12}$DAO considerably affects the dispersion: the absorbance increases at pH 2.5–6 and above pH 10, and decreases below pH 2.5.

The zeta potential, the mutual diffusion coefficient, and the electron microscopy were examined for TiO$_2$, TiO$_2$-SDS, and TiO$_2$-C$_{12}$DAO suspensions at acid, neutral, and alkaline regions. Whereas the zeta potential of a TiO$_2$ suspension without additives changes, with an increase of pH, from positive to negative through the isoelectric point around pH 6, the addition of surfactant remarkably varies the zeta potential of a TiO$_2$ suspension, as seen in Fig. 5. While the isoelectric point is higher for a TiO$_2$-C$_{12}$DAO suspension than for a TiO$_2$ suspension, the zeta potential of a TiO$_2$-SDS suspension is always negative at pH 3–9.

The apparent hydrodynamic radius $R_{H,\,app}$ was evaluated from the mutual diffusion coefficient D and plotted in Fig. 5. The numeric values of D and $R_{H,\,app}$ are listed in Table 1, together with the values of zeta potential. It should be noted that the obtained $R_{H,\,app}$ values are larger than 85 nm. Moreover, they change with pH with a similar behavior for all three systems; the $R_{H,\,app}$ values are largest at the neutral region.
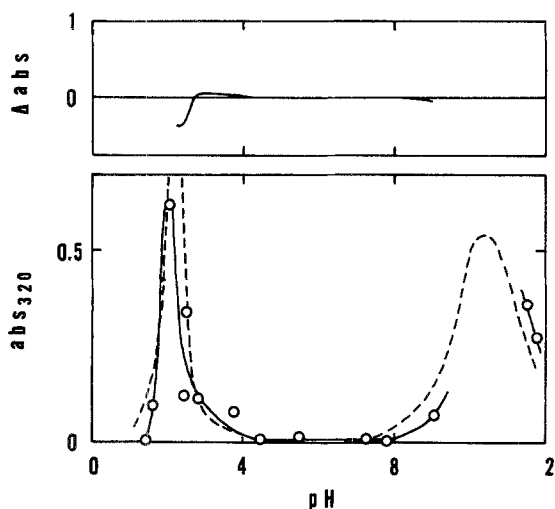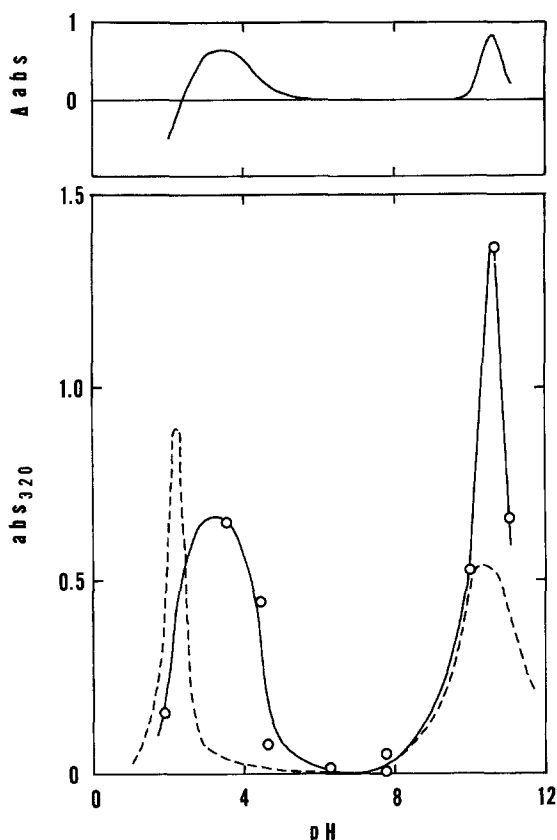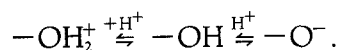
Fig. 4. The pH-dependence of absorbance of a TiO_2-$C_{12}DAO$ suspension. The dotted line represents the observed absorbance for a TiO_2 suspension. $\Delta abs = abs(TiO_2$-$C_{12}DAO) - abs(TiO_2)$

Fig. 5. The pH-dependence of zeta potential and apparent hydrodynamic radius for TiO_2, TiO_2-SDS, TiO_2-$C_{12}DAO$ suspensions. $\triangle$, TiO_2; O, TiO_2-SDS; $\square$, TiO_2-$C_{12}DAO$

An electron micrograph is represented in Fig. 6 for a TiO_2-SDS suspension at pH 5.9. Similar photographs were also obtained for the other suspensions. Although each TiO_2 particle is 20–80 nm in diameter, some of particles seem to make flocs.

Discussion

As the particle surface of metal oxide is generally covered by OH groups in aqueous medium, the ionic character of a surface varies with changing pH as follows:

$$-OH_2^+ \overset{+H^+}{\underset{}{\rightleftharpoons}} -OH \overset{H^+}{\underset{}{\rightleftharpoons}} -O^-.$$

Therefore, the surface charge is the difference between surface excess charges of the potential determing ions H^+ and OH^-. The point of zero
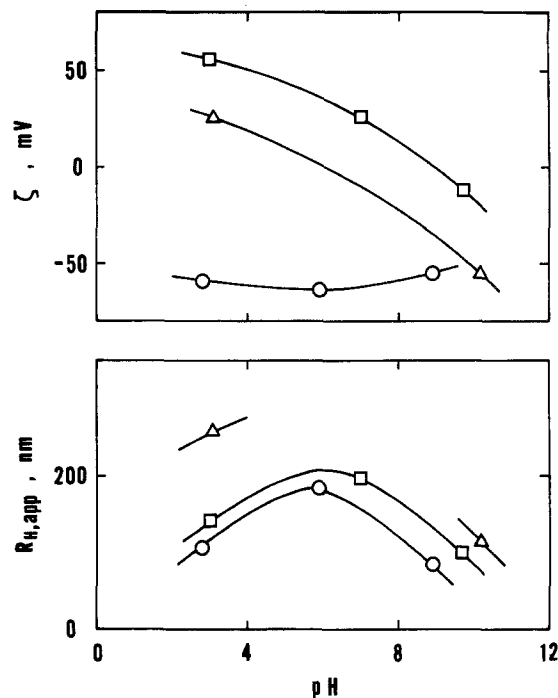
charge, which is a pH value at zero surface charge, is pH 5–7 for TiO_2 (rutile). It can be recognized from Fig. 1 that in this pH region, in which there is an isoelectric point of pH 6.1–6.2 for TiO_2 [1], the dispersion of TiO_2 in water is most diminished or is not ascertained.

If the pH is raised or lowered from this region, the surface charge of a TiO_2 particle increases and particles are dispersed in water by the electrostatic repulsion between particles. However, at very high

Table 1. Zeta potential and dynamic light-scattering measurements for TiO_2-surfactant suspensions

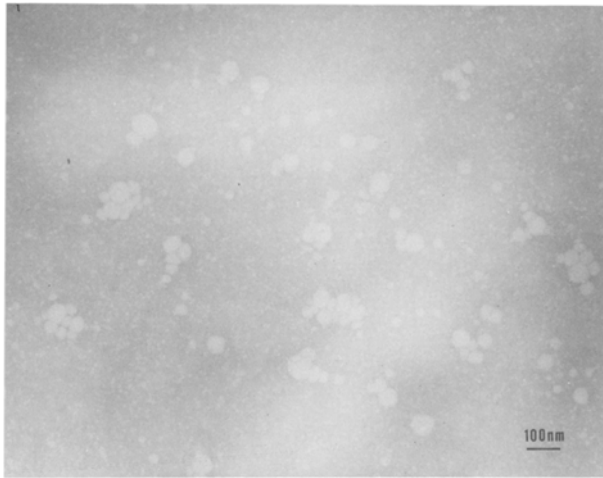| Surfactant	pH	ζ mV	D 10^{-7} cm^2 s^{-1}	$R_{H,\,app}$ nm
no	3.1	25.4	0.095	257
	10.2	−54.7	0.214	229
SDS	2.8	−59.3	0.228	107
	5.9	−63.6	0.134	184
	8.9	−54.8	0.286	85
$C_{12}DAO$	3.0	56.0	0.170	142
	7.0	26.0	0.123	183
	9.7	−12.1	0.247	99

Fig. 6. Electron micrograph of a TiO₂-SDS suspension at pH 5.9

ionic concentration, many counterions are adsorbed in the Stern layer on the particle surface and the electrostatic potential at Helmholtz plane lowers, resulting in the thin diffusion layer. Therefore, particles flocculate each other and the dispersion is diminished. This is the case below pH 2 and above pH 11 in a TiO₂ suspension.

When surfactants are added to a TiO₂ suspension, they are adsorbed on the TiO₂ surfaces, according to the adsorption modes of hemimicelle or double-layer compression at the surfactant concentrations above the CMC, which is the case with

the aqueous surfactant solutions examined here. Since particles in a TiO₂-SDS suspension at pH 2–3 carry negative charges in spite of their abundant protonation in a TiO₂ suspension, adsorbed SDS molecules must be excess and, therefore, form double-layer compression. As the pH is raised up to 6, the protonation on a TiO₂ surface lessens and the double-layer compression of SDS loosens. Above pH 6, where the TiO₂ surface charges negatively and the effective charge of particles adsorbed SDS is also negative, the electrostatic attractive interaction between TiO₂ and SDS no longer acts, but SDS molecules are adsorbed on a TiO₂ surface by the physical adhesive interaction, making the hemimicelle. Schematic representation of such adsorption is given in Fig. 7.

Since the absolute value of effective surface charge of particles at pH 2–3 in a TiO₂-SDS suspension is less than that in a TiO₂ suspension, the dispersion of particles is diminished in this pH region. At pH 3–8, an effective charge increases more than that in a TiO₂ suspension, and the dispersion is enhanced. The diminution of the dispersion above pH 8 might be the effect of high ionic concentration, as described above.

For a TiO₂-AlCl₃ suspension, although the number of $-OH_2^+$ ions on TiO₂ surfaces decreases with increasing pH up to 6, the specific adsorption of Al^{3+} on particle surfaces increases, resulting in the positive effective surface charge at neutral region. Therefore, the dispersion of particles is remarkably
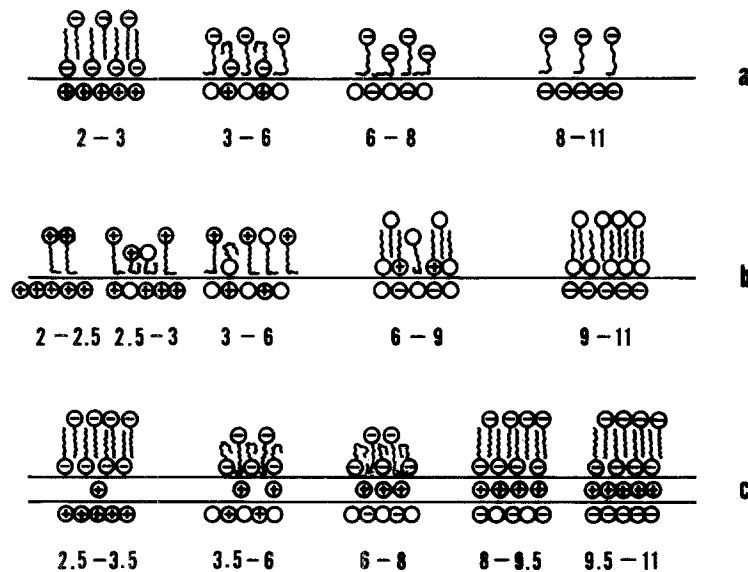

Fig. 7. Schematic representation of adsorption models for TiO₂-SDS, TiO₂-C₁₂DAO, and TiO₂-AlCl₃-SDS suspensions. a) TiO₂-SDS; b) TiO₂-C₁₂DAO; c) TiO₂-AlCl₃-SDS. The numeric values represent the pH values

enhanced at that region. At alkaline region, negative charges on TiO_2 surfaces are compensated to bound Al^{3+} ions and the effective surface charge decreases. As a result, the dispersion of particles is diminished.

When SDS is added to a TiO_2-$AlCl_3$ suspension at acid region where the effective charge of TiO_2 adsorbed $AlCl_3$ is positive, SDS molecules are adsorbed on a particle with an arrangement of double-layer compression. This arrangement is maintained even at neutral and alkaline regions, as represented schematically in Fig. 7, because the nearest-neighbor outer layers of TiO_2 surfaces are covered by Al^{3+}, even if the effective charge of TiO_2 adsorbed $AlCl_3$ changes. Then the dispersion of particles does not depend largely on pH.

It is difficult to understand the effect of $C_{12}E_7$, because the dispersion is not remarkably improved by the addition of $C_{12}E_7$ in a TiO_2 suspension, even if $C_{12}E_7$ molecules are adsorbed on a TiO_2 surface.

When TiO_2 particles adsorb $C_{12}DAO$ molecules which are protonated at acid region in water [7], the effective charge of particles changes from positive to negative through the point of zero surface charge around pH 9, which is close to the observed isoelectric point. However, the dispersion of particle adsorbed $C_{12}DAO$ is considerably enhanced at pH 2.5–6 and 9–11. Since the TiO_2 surfaces and $C_{12}DAO$ molecules are both charged positive at acid region, the protonated $C_{12}DAO$ molecules are adsorbed as hemimicelle, giving rise to the dispersion of particles. The positive charges of $C_{12}DAO$ lessen with a rise of pH, and, at pH 6–9, a large amount of noncharged and a small amount of charged $C_{12}DAO$ molecules form loose double-layer compression. However, the adsorbed positive $C_{12}DAO$ molecules are more than the negative charges of TiO_2 surfaces, because the zeta potential is still positive. Such adsorption of $C_{12}DAO$ does not bring about the dispersion of particles. Double-layer compression by noncharged $C_{12}DAO$ molecules may be formed above pH 9 where $C_{12}DAO$ molecules are well nonionic and the particles in a TiO_2-$C_{12}DAO$ suspension charge negative. The hydrophilicity of the head group of $C_{12}DAO$ might cause the dispersion of particles. Figure 7 shows the schematic representation for the adsorption of $C_{12}DAO$.

It should be noted, that the apparent particle sizes in suspensions are always larger than the size of native TiO_2 particles. Since electron micrographs guarantee the existence of TiO_2 paritcles with a native size, such large apparent particle sizes may originate in the small flocs of particles which are stabilized in a suspension. Actually, some flocs were observed in electron micrographs. Flocculation was more remarkable at neutral region than at acid and alkaline regions, and more so for a TiO_2 suspension than for TiO_2-SDS or $C_{12}DAO$ suspensions. The flocculation is consistent with the dispersion of particles: the flocculation is remarkable at neutral region where the dispersion is inferior. However, the flocculation is not necessarily related to the effective surface charge of particles: although TiO_2, TiO_2-SDS, and TiO_2-$C_{12}DAO$ suspensions are similar to each other in the pH-dependence of flocculation behavior; the zeta potential depends on pH differently for the three suspensions.

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