

ORIGINAL

Dispersion Stability of TiO₂ Particles in Aqueous Surfactant Solutions

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The dispersion stability of TiO₂ particles was assessed in aqueous solution of spherical and rodlike micelles. In aqueous solution of alkyl hepta (oxyethylene) ethers (C_nE₇, *n*=12, 14, 16) at pH 5, this parameter was independent of coexisting micelle shape, whether spherical or rodlike. It did depend on whether rodlike micelles were in a nonentangled, entangled, or concentrated state. TiO₂ particles may be mechanically captured in compact networks consisting of rodlike micelles.

1 Introduction

In order to avoid the flocculation or coagulation of colloidal particles in medium, potential-determining ions or polymers are added to colloidal suspensions. Small ions and polymer chains are adsorbed on particle surfaces and result in particles with high charged surfaces or with adsorption polymer layers. Then the electrostatic potential of particles is changed. Furthermore, polymers bridge between particles or raise the depletion effect¹⁾.

In comparison with many investigations for the effect of small ions and polymers on dispersion stability of particles, a few works were reported for the effect of surfactant. The pH dependence of dispersion stability of titanium dioxide (TiO₂) particles has been examined in the presence of surfactant molecules in water²⁾. The adsorption of sodium dodecyl sulfate (SDS) and dodecyldimethylamine oxide (C₁₂DAO) on TiO₂ particles affected to the particle stability with the different way, depending on pH. However, when TiO₂ particles were added to aqueous solutions of dodecyl hepta (oxyethylene) ether (C₁₂E₇), the stability of a TiO₂ suspension was not improved. It

was concluded that adsorbed surfactant molecules formed hemimicelle and double-layer compression on particles^{3)~5)}, and the situation of adsorption depended on surfactant species.

Surfactant molecules are associated into spherical or rodlike micelles in bulk water. The effect of micelles on metal dioxide suspensions has never been discussed. In this work, dispersion stability of TiO₂ particles has been examined in aqueous surfactant solutions, where additive nonionic surfactant and coexisting NaCl are varied in concentrations. The dispersion stability is compared between solutions of spherical and rodlike micelles and is discussed in relation to the solution properties of coexisting micelles.

2 Experimental

2.1 Materials

Ultra-fine TiO₂ (IDEMITSU UFP-TiO₂) particles with average particle diameter of 15~20 nm were supplied by Idemitsu Kosan Co., Ltd., Japan. Alkyldimethylamine oxides (C_nDAO, *n*=12, 14) are the same samples as previously used⁶⁾. Alkyl hepta (oxyethylene) ethers (C_nE₇, *n*=12, 14, 16) were purchased from Nikko Chemicals Co., Ltd., Japan. NaCl was used after heating

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for 1 h. HCl and NaOH are the standardized solutions. Water was redistilled from alkaline KMnO_4 and then degassed *in vacuo* by an aspirator under the ultrasonication.

2.2 Solution Preparation

TiO_2 powder (5 mg) was dispersed in water or aqueous surfactant solutions (5 cm^3). If necessary, solutions were adjusted to adequate pH by adding a small amount of HCl or NaOH by a microsyringe. The suspensions were shaken for 7 h in a water bath incubator at 25°C and allowed to settle for 17 h at 25°C . This condition is based on the following reasons: the dependence of shaking time on the turbidity was examined for aqueous TiO_2 suspensions. Turbidity equilibrated after 5~7 h. After shaken for 7 h, the turbidity became independent of leaving time of 0~24 h.

2.3 Measurement

The absorbance of the top of the suspension was measured on a UV-200 S Shimadzu spectrophotometer. Since aqueous surfactant solutions exhibit no absorption bands at wavelengths above 200 nm, absorbance at 250 nm was utilized as a measure of turbidity, that is, dispersion stability.

Transmission electron microscopic observation was performed at room temperature on a Hitachi electron microscope 800 H. Replica films were prepared on a freeze fracture apparatus. Optical microscopic observation was carried out at room temperature on an Olympus optical microscope BH.

3 Results

3.1 Turbidity of TiO_2 - C_nDAO suspensions

Figure-1 shows the pH dependence of turbidity of TiO_2 suspension. The turbidity of TiO_2 suspension is lowest at pH 5 and increases at lower and higher pH. Since pH 5 is very close to isoelectric point (pH 4.3) of TiO_2 suspension, TiO_2 particles at lower and higher pH are charged as follows;

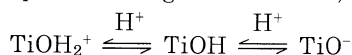
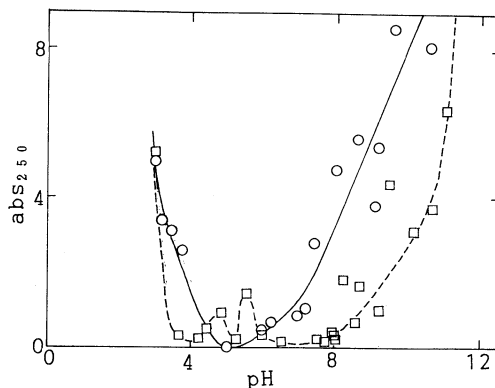


Figure-1 includes the pH dependence of



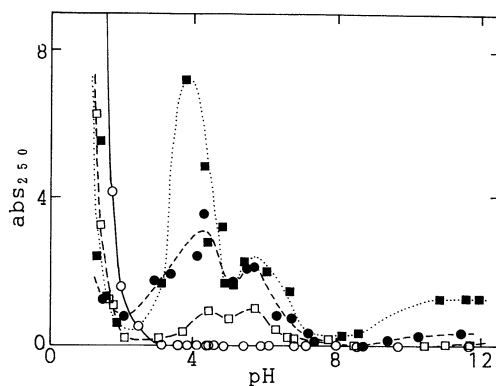
Surfactant concentration ($10^{-2} \text{ g}\cdot\text{cm}^{-3}$):

○, 0; □, 0.5.

Fig.-1 The pH dependence of turbidity of TiO_2 - C_{12}DAO suspensions.

turbidity of TiO_2 - C_{12}DAO suspension, where concentration of C_{12}DAO is fixed at $0.5 \times 10^{-2} \text{ g}\cdot\text{cm}^{-3}$ (0.022 M). Turbidity is rather lower than that of TiO_2 suspension, except at pH 4.5~6, where there are two weak peaks. Turbidity is especially low at pH 6~8.

The pH dependence of turbidity of TiO_2 - C_{14}DAO suspensions prepared at various C_{14}DAO concentrations in 0.2 M NaCl is illustrated in Figure-2. In 0.2 M NaCl solution without surfactant, turbidity is lower than that in water which is shown in Figure-1. TiO_2 particles disperse in 0.2 M NaCl only below pH 3. When the medium is changed by aqueous C_{14}DAO solution of $10^{-2} \text{ g}\cdot\text{cm}^{-3}$ (0.039 M), turbidity increases at pH 3~7,



Surfactant concentration ($10^{-2} \text{ g}\cdot\text{cm}^{-3}$):

○, 0; □, 1; ●, 3; ■, 5.

Fig.-2 The pH dependence of turbidity of TiO_2 - C_{14}DAO -0.2 M NaCl suspensions.

where there are two peaks. Turbidity increases with increasing $C_{14}DAO$ concentration. For $C_{14}DAO$ solution of $5 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}$ (0.19 M), maximum around pH 4 is more dominant than a peak around pH 5.5. The pH value where turbidity is maximum shifts from 4.7 to 4.0 with changing surfactant concentration from 0.5 to $5 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}$.

3.2 Turbidity of $TiO_2-C_nE_7-NaCl$ suspensions

Aqueous C_nE_7 solutions with different concentrations of C_nE_7 and NaCl were prepared, and TiO_2 particles were suspended in the solutions at pH 5. It should be noted that TiO_2 and TiO_2-NaCl suspensions without C_nE_7 are not dispersed at pH 5, as seen in Figs.-1 and 2. Figures 3~5 show turbidity of $TiO_2-C_nE_7-NaCl$ suspensions as a func-

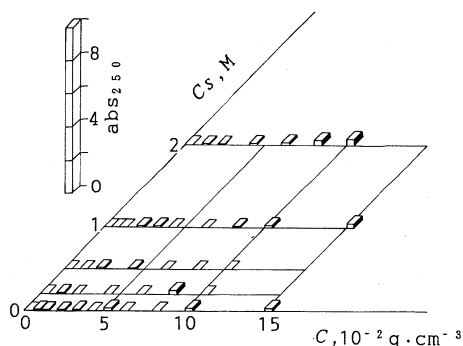
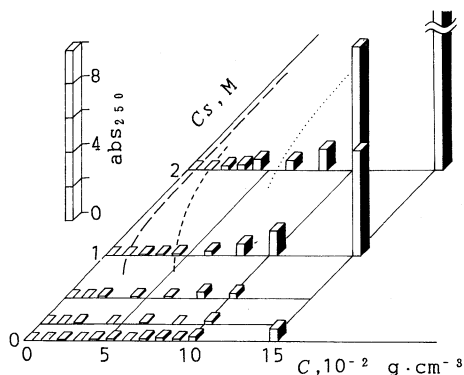
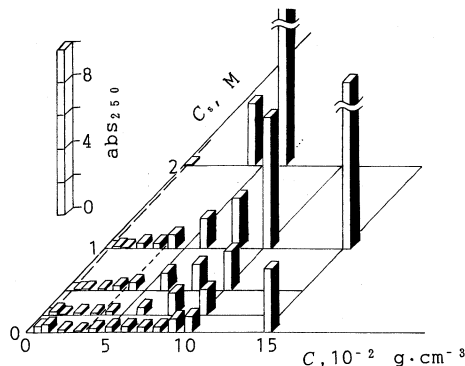


Fig.-3 Turbidity of $TiO_2-C_{12}E_7-NaCl$ suspensions as a function of $C_{12}E_7$ and NaCl concentrations.



---, $(c-c_0)^*$; ---, $(c-c_0)_{\eta}^*$; , $(c-c_0)^{**}$.

Fig.-4 Turbidity of $TiO_2-C_{14}E_7-NaCl$ suspensions as a function of $C_{14}E_7$ and NaCl concentrations.



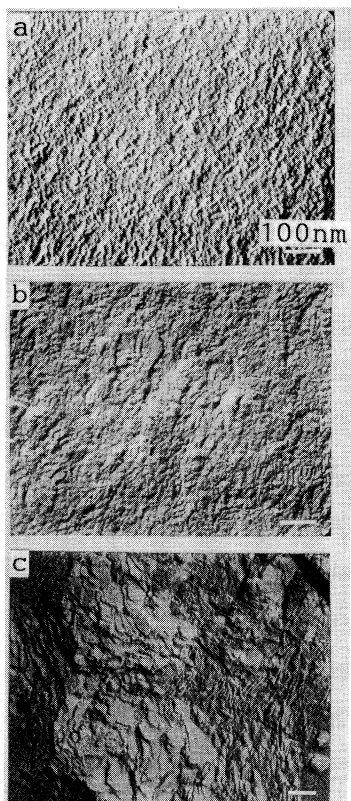
---, $(c-c_0)^*$; ---, $(c-c_0)_{\eta}^*$; , $(c-c_0)^{**}$.

Fig.-5 Turbidity of $TiO_2-C_{16}E_7-NaCl$ suspensions as a function of $C_{16}E_7$ and NaCl concentrations.

tion of C_nE_7 and NaCl concentrations (c, C_s). While turbidity of $TiO_2-C_{12}E_7-NaCl$ system is rather low even at high concentrations of $C_{12}E_7$ and NaCl, that of $TiO_2-C_{14}E_7-NaCl$ system increases at high $C_{14}E_7$ concentrations. The increase is remarkable at high NaCl concentrations. Turbidity of $TiO_2-C_{16}E_7-NaCl$ system is more remarkable than that of $TiO_2-C_{14}E_7-NaCl$ system. Suspensions disperse even at low concentrations of $C_{16}E_7$ and NaCl.

Transmission electron micrographs of TiO_2 suspensions with C_nE_7 of $10^{-2} \text{ g} \cdot \text{cm}^{-3}$ and NaCl of 0.5 M are shown in Fig.-6. Photograph of $TiO_2-C_{12}E_7-NaCl$ system displays homogeneous texture of micelles, indicating less dispersion stability of TiO_2 particles. Since the texture of micelles is heterogeneous for $TiO_2-C_{14}E_7-NaCl$ and $TiO_2-C_{16}E_7-NaCl$ systems, it is obvious that TiO_2 particles are dispersed in the suspensions. Moreover, photograph of a suspension with $C_{16}E_7$ suggests that size of particles is larger than that of primary TiO_2 particles. This displays the existence of secondary particles which are formed by the flocculation of primary particles. The formation of flocs was already clarified on a transmission electron micrograph for TiO_2-SDS suspension²⁾.

The optical microscopic observation supports the electron microscopic results : while there are no visual particles in a sus-



a), $C_{12}E_7$ (0.20 M) ; b), $C_{14}E_7$ (0.19 M) ;
c), $C_{16}E_7$ (0.18 M).

Fig.-6 Transmission electron micrographs of $TiO_2-C_nE_7$ ($10^{-2} g \cdot cm^{-3}$)-NaCl (0.5 M) suspensions.

pension with $C_{12}E_7$, particles with diameters less than 3 and 20 μm are observed on an optical microscope for suspensions with $C_{14}E_7$ and $C_{16}E_7$, respectively. This is consistent with that dispersion stability increases for the suspension of C_nE_7 with longer alkyl chain.

4 Discussion

TiO_2 particles charge positively at lower pH and negatively at higher pH than the isoelectric point. Dispersion stability of TiO_2 in water increases by the electrostatic repulsion between particles with increasing charge density at acidic and alkaline pH. In 0.2 M NaCl, Na^+ or Cl^- ions adsorb abundantly on TiO_2 particle surface, and electric double layer becomes thin, inducing the less electrostatic repulsion. As a result, disper-

sion stability decreases at whole pH region. Specific adsorption of Na^+ may be dominant to that of Cl^- , since stable dispersion of TiO_2 in 0.2 M NaCl is not observed at alkaline pH.

Critical micelle concentration (cmc) of aqueous $C_{12}DAO$ solutions is $0.03 \times 10^{-2} g \cdot cm^{-3}$, and $C_{12}DAO$ molecules in water are associated into spherical micelles at concentrations above cmc⁷⁾. On the other hand, $C_{14}DAO$ molecules in 0.2 M NaCl form rodlike micelles at surfactant concentrations examined in this work, since the cmc is very low⁸⁾. Dispersion stability of TiO_2 increases at pH 3~7 for both micellar systems, independent of the micellar shape, if dispersion stability is compared with that of TiO_2 or TiO_2-NaCl suspensions. In this pH region, C_nDAO molecules may be adsorbed as hemimicelles, giving rise to dispersion stability of particles, as previously estimated²⁾. Dispersion stability of TiO_2 at pH 3~7 in 0.2 M NaCl increases with $C_{14}DAO$ concentration. This seems to imply the significant affection of surfactant concentration on dispersion stability of TiO_2 . However, it is not evident that whether the increase in dispersion stability is due to the adsorption of surfactant or the coexistence of micelles.

The dispersion stability was not remarkably improved by the addition of $C_{12}E_7$ in a TiO_2 suspension, even if $C_{12}E_7$ molecules were adsorbed on a TiO_2 surface²⁾. Therefore, C_nE_7 is an appropriate surfactant to examine the effect of coexisting micelles. Fortunately, at pH 5 where the effect of C_nE_7 micelles was examined, dispersion stability of TiO_2 itself is also negligibly low, as seen in Fig.-1.

The formation of C_nE_7 micelles has been investigated by light scattering and viscosity measurements^{9),10)}. Cmc of aqueous C_nE_7 ($n=12, 14, 16$) solutions is less than $10^{-5} g \cdot cm^{-3}$ in 0~2 M NaCl. $C_{12}E_7$ forms spherical micelles in 0~1 M NaCl and short rodlike micelles in 2 M NaCl. $C_{14}E_7$ micelles are small or ellipsoidal in water but rodlike in NaCl solutions. $C_{16}E_7$ is always associated into rodlike micelles in water and NaCl solutions.

Rodlike micelles increase in number density and in size with increasing surfactant and NaCl concentrations. Therefore, above a certain micellar concentration, rodlike micelles overlap each other. This concentration is the crossover point $(c-c_0)^*$ from dilute to semidilute regime. Rodlike micelles entangle each other at high concentrations above $(c-c_0)_\eta^*$. At further high concentration $(c-c_0)^{**}$, semidilute concentration regime transfers to concentrated regime. The schematic representation of characteristics of rodlike micelles in aqueous solutions is illustrated in Fig.-7, and the corresponding crossover concentrations for aqueous NaCl solutions of C_nE_7 ^(9),10) are listed in Table-1 and drawn in Figs.-4 and 5.

Dispersion stability of TiO_2 particles at pH 5 is always very low in aqueous NaCl solutions of $C_{12}E_7$ where spherical micelles or short rodlike micelles are formed. Disper-

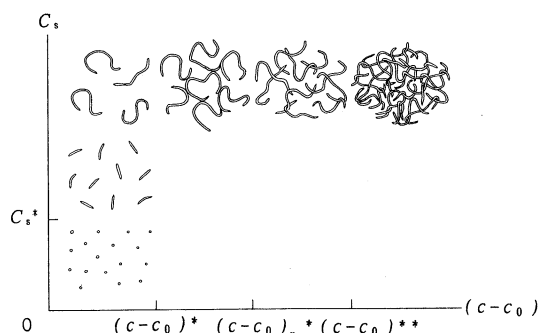


Fig.-7 Schematic representation of characteristics of rodlike micelles in aqueous solutions.

Table-1 Crossover concentrations for aqueous NaCl solutions of C_nE_7 ^(9),10).

	C_s (M)	$(c-c_0)^*$	$(c-c_0)_\eta^*$ ($10^{-2} \text{ g}\cdot\text{cm}^{-3}$)	$(c-c_0)^{**}$
$C_{12}E_7$	4	0.80		
$C_{14}E_7$	1	1.26	4.3	
	2	0.40	1~1.5	5.6
$C_{16}E_7$	3	0.42		4.3
	0	0.79	3.5	
	0.1	0.60		
	1	0.20	3.8	
	2	0.21		6.1

sion stability is also low for solutions at low $C_{14}E_7$ concentrations, despite that rodlike micelles are formed. However, it increases at high $C_{14}E_7$ concentrations, if $C_{14}E_7$ concentration is in region above $(c-c_0)_\eta^*$. The increase is especially remarkable for solutions at concentrations above $(c-c_0)^{**}$. The situation for $C_{16}E_7$ is very similar to that for $C_{14}E_7$: in aqueous solutions of $C_{16}E_7$, dispersion stability increases at surfactant concentrations above $(c-c_0)_\eta^*$ and is remarkable above $(c-c_0)^{**}$.

It can be concluded that high dispersion stability of TiO_2 is affected by coexisting C_nE_7 micelles: dispersion stability of TiO_2 in aqueous solutions of C_nE_7 does not depend on micellar shape, that is, whether micelles are spherical or rodlike. It depends on concentration region, that is, where rodlike micelles are in nonentangled, entangled, and concentrated regimes.

It is possible as a dispersion mechanism that TiO_2 particles are mechanically captured in compact networks which rodlike micelles construct. It can not be decided in this work that this is originated by the bridging of rodlike micelles between TiO_2 particles as well as that of polymer chains. The finding of large flocs in TiO_2 - $C_{16}E_7$ -NaCl suspension may result from the formation of more compact networks by $C_{16}E_7$ micelles to capture large particles.

Acknowledgment

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界面活性剤水溶液中での TiO₂ 粒子の分散性

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球状、棒状ミセルの水溶液中で、TiO₂ 粒子の分散性が調べられた。アルキルヘプタ(オキシエチレン)エーテル(C_nE₇, n=12, 14, 16)のpH 5での水溶液中では、TiO₂ 粒子の分散性は、共存するミセルの形、すなわち、球状であるか棒状であるかには影響されなかった。分散性は、棒状ミセルがからまりのない領域、からまりのある領域、濃厚な領域のうちのどこに属するかに依存した。TiO₂ 粒子は、棒状ミセルが構築する密な網目内に機械的に捕獲されているようだ。

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本書は、現在、第一線で活躍されている 155 名の研究者によって執筆された 1,069 頁におよぶ膨大な範囲の内容を網羅した表面改質の入門書であり、応用例の解説書でもある。第一編は改質の基礎になる総論、第二編は金属、木材、セラミックス、粉体、膜のコロイド処理、含浸による処理等の各種材料の表面改質について、第三編は電子顕微鏡、走査型プローブ顕微鏡、表面の組成と分析、表面特性等の材料表面の評価について、第四編は前処理、めっき、塗装、溶射、ドライプロセス、粉体の表面改質等に関わる装置及び周辺機器について、第五編は実用例について、第六編に物性特性表が掲載されており、最終編は資料編となっている。どの章を取って見ても、現在著者自身が研究している専門分野の極意が紹介されている。従って、引用文献も極最近のものが多く、最新の情報が取り上げられていることを示している。本書は、当研究会で材料に関する基礎的問題、材料改質面の評価方法、改質面の実用上の効果等についての研究会、講演会、討論会を数多くこなして得た他に類を見ない貴重な成果の総集編であり、基礎研究や実学の分野は云うにおよばず、学際領域にも欠くことの出来ない貴重な著書である。

(上野 實)