**Effect of anionic surfactants on the stability ratio and
electrophoretic mobility of colloidal hematite particles**

Motoyoshi Kobayashi^{1,*}, Shunzo Yuki², Yasuhisa Adachi¹

¹*Faculty and* ²*Graduate School of Life and Environmental Sciences, University of Tsukuba,
Tennodai 1-1-1, Tsukuba, Ibaraki 305-8572, Japan*

*: Corresponding author: kobayashi.moto.fp@u.tsukuba.ac.jp

Tel.: +81 29 853 5721; Fax: +81 29 853 4861.

1. Introduction

Surfactants are amphiphilic molecules having a hydrophobic tail and a hydrophilic head [1,2]. They are widely used in many industrial processes, because their adsorption on the solid-liquid interface of colloidal particles modifies the interfacial properties such as surface charging and wetting phenomena [1-7]. Such modifications affect surface interactions, and thus colloid stability and rheological behaviors of colloidal dispersions are controlled by the addition of surfactants. Therefore, detailed studies on surfactant adsorption, resulting change in surface charge, and colloid stability were carried out [6-14].

The addition of ionic-surfactants into a suspension containing oppositely charged particles causes changes in zeta potential and aggregation-dispersion of the particles [6-11]. In general, as the adsorbed amount of ionic surfactants to oppositely charged particles increases, the magnitude of zeta potential of the particle decreases and reaches zero at the isoelectric point, and the sign of zeta potential reverses [6-11]. The length of hydrophobic chain of surfactants is one of the key factors for determining the isoelectric point. The required surfactant concentration leading to the isoelectric point decreases with increasing the chain length [5-9]. Simple theoretical models were proposed to describe the dependence of isoelectric points on the chain length of surfactants [5, 7]. From the analysis, it is suggested that the chemical/hydrophobic energy of adsorption per a carbon atom is close to the hydrophobic energy obtained from the analysis of critical micelle concentration [1, 5, 6]. However, theoretical models have not yet been sufficiently examined for the description of the zeta potential and stability ratio as a function of the concentration of surfactant.

Colloidal particles are destabilized by the addition of optimum dosage of oppositely charged surfactants [4, 6-11]. The range of the optimum aggregation concentration is around the isoelectric point, meaning that the colloid is destabilized by charge neutralization. Most of the studies on surfactant-induced aggregation were carried out by simple aggregation-sedimentation experiments. On the one hand, measurements of stability ratio W , which is the relative rate of aggregation, of well-characterized particles with ionic-surfactants are scarce [6-8,10]. It is difficult from the aggregation-sedimentation experiment to unveil the existence of additional inter-particle interaction such as steric repulsion and charge-patch attraction, which are found from the stability ratio in the presence of polymers [8, 15-18]. As for the surfactant-induced aggregation, Liang and Morgan [6] showed the stability ratio of positively

charged hematite as a function of the concentration of fatty acids. Their data demonstrated that the minimum value of stability ratio increases with increasing the chain length of fatty acids, implying the development of steric repulsion by the surfactants with longer hydrophobic chain [8]. On the one hand, the values of the minimum stability ratio of positively charged AgI particles with sodium alkyl sulfates were almost unity irrespective of the chain length [7], indicating that there is neither additional attraction nor repulsion at the optimum aggregation concentration. Leong et al. [12] claimed the appearance of additional hydrophobic attraction from the measurement of shear yield stress of concentrated ZrO_2 suspension with surfactants. Sakamoto et al. [14] suggested that the origin of hydrophobic attraction is due to the bridge formed by microscopic bubbles. These previous studies reported different effects of ionic-surfactants on the surface interactions and the behavior of colloidal suspensions.

While the minimum stability ratio W of hematite around isoelectric point increased with increasing the chain length of fatty acids and became larger than unity ($W > 1$) [6], the minimum stability ratio of positively charged AgI particles with sodium alkyl sulfates were almost unity ($W=1$) irrespective of the chain length [7]. These two results are different in terms of the dependence of the minimum stability ratio reflecting the existence of steric repulsion on the chain length, and one may explain that this inconsistency is because they used different particles and surfactants. In addition, the detailed comparison of theoretical model with experimental stability ratio has not yet fully been carried out for the ionic-surfactant-induced aggregation. To better understand the surfactant-induced aggregation, we need systematic measurements and analysis of stability ratios that examine the effect of type of oppositely charged surfactants on the stability ratio by using an identical colloidal suspension. By such systematic experiments with theoretical analysis, we can unveil the role of ionic surfactant on the aggregation–dispersion of oppositely charged particles in detail.

In this context, our goal was set to clarify the effect of both fatty acids and sodium alkyl sulfates on the stability ratio and electrophoresis of hematite particles, which were chosen since the minimum stability ratio larger than unity was reported for hematite with fatty acids [6]. Measured data were analyzed using theoretical models. From the comparison of the experiment and theory for the stability ratio and electrophoretic mobility, possible mechanisms are delineated.

65

66 2. Experiments

67 2.1. Materials

68 We used hematite particles, which were obtained from Chemirite Kogyo Industry, Japan. The
69 hematite particles have 141 ± 35 nm in a number averaged diameter $2a$ determined from transmission
70 electron microscopy (Fig. 1) and the specific surface area of $26.3 \text{ m}^2/\text{g}$ from N_2 -BET measurement. The
71 density of hematite particles is 5.24 g/cm^3 [19]. The hematite particles were purified as follows: the
72 particles were dispersed in 1 M NaCl with pH 4, then after sedimentation and decantation, the solution
73 condition of hematite suspension was adjusted to 1 M NaCl with pH 10. These procedures were
74 performed for the saturation of surface with Na^+ and Cl^- ions and for washing by acid and base. Finally,
75 the suspension was extensively dialyzed in a Visking tube against pure water to remove excess ions.
76 The purified hematite particles were freeze-dried and stored in a polystyrene vial. In the following
77 experiment, hematite suspension was prepared by dispersing the dried powder in pure water. The
78 prepared suspensions were used within two weeks after preparation to avoid the change of surface
79 properties after the contact with water. Intensity-weighted average hydrodynamic diameters d_h of
80 hematite are around 170 nm. The size is close to the corresponding size from TEM, $d_{h,\text{TEM}} = \langle d^6 \rangle / \langle d^5 \rangle$
81 $= 174$ nm, where d is the diameter from TEM and $\langle \dots \rangle$ stands for averaging.

82 Six anionic surfactants with different lengths of hydrophobic chain and different charged groups
83 were used as received. Three of these were sodium alkyl sulfates: sodium dodecyl sulfate with 12 C
84 atoms (Wako Pure Chemical Industries) referred as SDS, sodium decyl sulfate with 10 C atoms (Wako
85 Pure Chemical Industries) referred as SDeS, and sodium octyl sulfate with 8 C atoms (Kanto Chemical)
86 referred as SOS. The others were fatty acids from Sigma-Aldrich, sodium dodecanoate with 12 C atoms
87 referred as C12, sodium decanoate with 10 C atoms referred as C10, and sodium octanoate with 8 C
88 atoms referred as C8. Ionic strength and pH were adjusted by the addition of NaCl (Wako Pure Chemical
89 Industries), HCl and NaOH (Wako Pure Chemical Industries). Pure water from Elix Advantage 5
90 (Millipore) was used for the preparation of all the solutions and suspensions in this work.

91

92 2.2. Electrophoretic mobility

93 Electrophoretic mobility of hematite particles was measured as a function of the surfactant dosage.
 94 Samples were prepared by mixing appropriate volumes of hematite suspension, water, surfactant
 95 solution, NaCl and HCl solutions. The total volume of the sample was set 10 mL. Most of experiments
 96 were carried out at the particle concentration of 25 mg/L, 10 mM NaCl, and pH 4. A portion of the
 97 prepared sample was injected into a capillary cell, and then the cell was placed in Zeta Sizer Nano ZS
 98 (Malvern). With the Zeta Sizer, we measured the electrophoretic mobility of hematite particles at 20°C.
 99 The pH of the rest of the sample was measured with a combination electrode (6.0234.100, Metrohm).

100

101 2.3. Stability ratio

102 The stability ratio of hematite suspension was obtained at 20°C from the temporal variation in
 103 turbidity due to aggregation. The suspension of hematite with a volume of 2 mL was prepared in a
 104 polystyrene disposable cuvette by mixing appropriate volumes of the stock hematite suspension, water,
 105 NaCl solution, HCl solution, and surfactant solution using pipettes. The prepared suspension was shaken
 106 and immediately put in a spectrophotometer (U-1800, Hitachi). Then, the temporal change in the
 107 absorbance, which is proportional to turbidity, at the wavelength of light of 450 nm was recorded.
 108 Turbidity measurements were mostly carried out at the particle concentration of 25 mg/L, 10 mM NaCl,
 109 and pH 4. Before use, all the cuvettes were cleaned by the sequential soak of the cuvettes in 0.1 M NaOH,
 110 0.1 M HCl, and pure water for over two hours, respectively. Then, after rinsing the cuvettes with pure
 111 water, they were air-dried and stored in a covered container to avoid dust.

112 In the early stage of aggregation, the initial slope of temporal change in turbidity $(d\tau/dt)_0$ is related
 113 to the aggregation rate coefficient k_{11} [20,21]

$$114 \quad \frac{1}{\tau_0} \left(\frac{d\tau}{dt} \right)_0 = k_{11} n_0 \left(\frac{C_2}{2C_1} - 1 \right) \quad (1)$$

where $k_{11} = \alpha_B 8k_B T / (3\mu)$ for Brownian aggregation with α_B the capture efficiency of Brownian aggregation, k_B is the Boltzmann constant, T is absolute temperature, μ is the viscosity of the solution, τ_0 is the initial turbidity, n_0 is the number concentration of particles, C_1 and C_2 are the extinction cross sections of a singlet and a doublet. In a simple electrolyte solution, the rate of aggregation increases with increasing the electrolyte concentration, and the rate reaches a plateau at a so-called critical coagulation concentration, CCC. The regime at the concentration above CCC is called a fast aggregation regime, where the fastest rate k_{11}^f and $(d\tau/dt)_0^f$ is obtained. With the fastest rate, the stability ratio W is defined as [8,22]

$$W = \frac{k_{11}^f}{k_{11}} = \frac{\left(\frac{d\tau}{dt}\right)_0^f}{\left(\frac{d\tau}{dt}\right)_0}. \quad (2)$$

with Eq. (1). In this study, the CCC was 30 mM in NaCl at pH 4 and the fastest slopes were obtained from the data taken within the aggregation-half time, $2/(n_0 k_{11}^f)$ with $\alpha_B \sim 0.5$ [19,23] ~ 120 s. All the stability ratios in this paper are given using Eq. (2) with an average value of $(d\tau/dt)_0^f$ obtained at NaCl concentrations above 30 mM. Therefore, $W=1$ means that the aggregation rate is the same as the fastest rate induced by simple salt, $W > 1$ corresponds to the situation where repulsive forces reduce the aggregation rate, and $W < 1$ indicates the existence of additional attractive force. Liang and Morgan [6] showed that the minimum W of hematite, which was found around the isoelectric point, increased with increasing the chain length of fatty acids and became $W > 1$; their results implied the development of steric repulsion around the isoelectric point. On the one hand, values of the minimum W of positively charged AgI particles with sodium alkyl sulfates were almost unity irrespective of the chain length [7]. These two results do not agree, and one possible reason of this inconsistency is because they used different particles and surfactants. However, systematic measurements clarifying the effect of oppositely charged surfactants on the stability ratio of colloidal particle are lacking. In this context, we decided to examine the effect of fatty acids and sodium alkyl sulfates on the stability ratio of positively charged hematite.

3. Theory and Modeling

3.1. Simple surfactant adsorption model

Let us consider the adsorption of monovalent anionic surfactants onto positively charged surfaces using the concept of Stern-Gouy-Chapman double layer [3,5]. The adsorption amount of anionic surfactants in the Stern layer Γ_s is given by

$$\Gamma_s = 2r_s C_s \exp\left(-\frac{e\psi_d - \Phi}{k_B T}\right) \quad (3)$$

$$\Phi = N\phi \quad (4)$$

where r_s is the radius of adsorbed ion, C_s is the bulk concentration of surfactants, ψ_d is diffuse layer potential, Φ is the chemical/intrinsic adsorption energy per a surfactant, N is the number of carbons in a surfactant, ϕ is the chemical/intrinsic adsorption energy per a carbon atom. Equation (3) considers that the surfactant adsorption is induced by both charged head $e\psi_d$ and hydrophobic tail $\Phi = N\phi$. The charge density of the Stern layer σ_s is thus

$$\sigma_s = -eN_A \Gamma_s \quad (5)$$

where e is the elementary charge and N_A is the Avogadro number. The diffuse layer charge σ_d in an 1:1 electrolyte solution with a concentration of n is given by the Grahm equation [1,5,19]

$$\sigma_d = -\frac{2\varepsilon_r \varepsilon_0 \kappa k_B T}{e} \sinh\left(\frac{e\psi_d}{2k_B T}\right) \quad (6)$$

$$\kappa = \sqrt{\frac{2e^2 n}{\varepsilon_r \varepsilon_0 k_B T}} \quad (7)$$

based on the Gouy-Chapman theory, where ε_r is the relative permittivity and ε_0 is the dielectric constant of vacuum. Values of κa are ~ 7 , ~ 23 , and ~ 70 for 1, 10, and 100 mM NaCl in this study. Electro-neutrality including surface charge density σ_0 is expressed by

$$\sigma_d = -(\sigma_s + \sigma_0). \quad (8)$$

In the present study, we use $r_s \sim 0.2$ nm, because it is comparable to the hydrodynamic sizes of sulfate and acetate ions and the radius of alkane [1, 24]. From Eqs. (3)-(8) with assumed values of ϕ , we can evaluate the diffuse layer potential ψ_d as a function of the concentration of surfactant with N carbon atoms. With the assumption that the diffuse layer potential is the same as the zeta potential ζ , one can calculate the electrophoretic mobility μ_m by using appropriate electrokinetic theories as described in the next section. The diffuse layer potential is also used when computing stability ratios based on the Derjaguin, Landau, Verwey, Overbeek (DLVO) theory [1, 19, 22, 25] described below.

3.2. Electrophoretic mobility including double layer relaxation

We use the Ohshima equation evaluating the electrophoretic mobility of a sphere with a radius of a in an 1:1 electrolyte solution [26]. The Ohshima equation for electrophoretic mobility μ_m in an 1:1 symmetrical electrolyte solution such as NaCl is given by

$$\begin{aligned} \mu_m = & \text{sgn}(\zeta) \frac{\varepsilon_r \varepsilon_0}{\mu} \left\{ |\zeta| - \frac{2F}{1+F} \left(\frac{k_B T}{e} \right) H \right\} \\ & + \text{sgn}(\zeta) \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\mu e} \left[\frac{1}{\kappa a} \left\{ -18 \left(t_m + \frac{t_m^3}{9} \right) K \right. \right. \\ & + \frac{15F}{1+F} \left(t_m + \frac{7t_m^2}{20} + \frac{t_m^3}{9} \right) - 6(1+3\bar{m}) \left(1 - \exp(-\bar{\zeta}/2) \right) G + \frac{12F}{(1+F)^2} K \\ & \left. \left. + \frac{9\bar{\zeta}}{1+F} (\bar{m}G + mH) - \frac{36F}{1+F} \left(\bar{m}G^2 + \frac{m}{1+F} H^2 \right) \right\} \right] \end{aligned} \quad (9)$$

with

$$\bar{\zeta} = \frac{e\zeta}{k_B T} \quad (10)$$

$$F = \frac{2}{\kappa a} (1+3m) \left\{ \exp(|\bar{\zeta}|/2) - 1 \right\} \quad (11)$$

$$H = \ln \left[\frac{1 + \exp(|\bar{\zeta}|/2)}{2} \right] \quad (12)$$

$$G = \ln \left[\frac{1 + \exp(-|\bar{\zeta}|/2)}{2} \right] \quad (13)$$

$$K = 1 - \frac{25}{3(\kappa a + 10)} \exp \left(-\frac{\kappa a}{6(\kappa a - 6)} |\bar{\zeta}| \right) \quad (14)$$

$$t_m = \tanh(\bar{\zeta}/4) \quad (15)$$

$$m = \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\mu e^2} \lambda, \quad \bar{m} = \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\mu e^2} \bar{\lambda} \quad (16)$$

$$\lambda_i = \frac{N_A e^2}{A_i^0} \quad (17)$$

In the above equations, the function $\text{sgn}(x)$ is 1 when $x > 0$ or -1 when $x < 0$, m and $\bar{m}$ are the scaled drag coefficients of counter ions and coions, respectively, A_i^0 the limiting conductance of i th ion specie. The Ohshima equation is available when $\kappa a \geq 10$, and the equation successfully describes the mobility of latex particles [27, 28]. This condition is satisfied for our hematite particles in 10 mM NaCl. We also assume $\bar{\zeta} = \psi_d$.

3.3. Stability ratio with DLVO theory

Stability ratio W with the DLVO interaction potential between identical spheres with a radius of a and a diffuse layer potential ψ_d in an 1:1 electrolyte solution, whose concentration is n , is expressed as

$$W = \frac{\int_0^\infty \frac{B(h)}{(2a+h)^2} \exp \left(\frac{V_R(h) + V_A(h)}{k_B T} \right) dh}{\int_0^\infty \frac{B(h)}{(2a+h)^2} \exp \left(\frac{V_A(h)}{k_B T} \right) dh} \quad (18)$$

$$B(h) = \frac{6(h/a)^2 + 13(h/a) + 2}{6(h/a)^2 + 4(h/a)} \quad (19)$$

where h is the separation distance between particles' surfaces and $B(h)$ takes account of the hydrodynamic interaction [22, 29]. Electric double layer potential V_R and van der Waals' potential V_A are given by [1, 22]

$$V_R(h) = \frac{64\pi a n k_B T}{\kappa^2} \gamma^2 \exp(-\kappa h) \quad (20)$$

$$\gamma = \tanh\left(\frac{e\psi_d}{4k_B T}\right) \quad (21)$$

$$V_A(h) = -\frac{Aa}{12h} \quad (22)$$

where A is the Hamaker constant, and we use $A = 6 \times 10^{-20}$ J for hematite in water [19].

Recently, Ohshima [22] proposed an analytical approximate expression of the stability ratio W given by Eq. (18) as follows:

$$W = 1 + \frac{1}{2q^0} \sum_{m=1}^{\infty} \frac{1}{m!} \left(\frac{G_W \kappa a}{12} \right)^m K_0 \left(\sqrt{\frac{A \kappa a m}{3k_B T}} \right) \quad (23)$$

with

$$q^0 = \frac{11}{8} \exp\left(\frac{A}{24k_B T}\right) E_1\left(\frac{A}{24k_B T}\right) - \frac{9}{8} \exp\left(\frac{A}{8k_B T}\right) E_1\left(\frac{A}{8k_B T}\right) \quad (24)$$

$$G_W = \frac{384\pi\gamma^2 \varepsilon_r \varepsilon_0 k_B T}{e^2 \kappa} \quad (25)$$

where $E_1(x)$ is 1st order exponential integral and $K_0(x)$ is the modified Bessel function of the second kind of order 0. In this study, we computed stability ratios by using Eq. (23) with diffuse layer potentials calculated by the method described above.

4. Results and Discussion

4.1. Aggregation and charging of bare hematite

Figure 2 shows the electrophoretic mobility of hematite particles as a function of pH measured in NaCl solution without surfactants. The value of mobility is positive at pH below 7 and is negative at higher pH. The isoelectric point is around pH 7. The isoelectric point of the hematite used in the present work is in the range of reported values, pH 7-9 [19, 30]. In this study, we focused on the effect of anionic surfactants onto positively charged hematite. Therefore, the relationship between stability ratios and NaCl concentrations was measured at lower pH. Figure 3 shows the stability ratio of hematite against the NaCl concentration at pH 4, 5, and 6. The stability ratio decreases with increasing NaCl concentration and reaches unity at a critical concentration, CCC. The stability ratios at different pH are kept unity at higher NaCl concentrations, while Penners and Koopal [31] reported the dependence of the fast aggregation rate on pH. Our stability ratio shows typical behaviors expected from the DLVO theory [8]. That is, we confirm that our hematite particles behave normally, while some colloids behave anomaly [25, 32]. From Fig. 3, the CCC can be determined around 30 mM, which is close to previously published values [19, 31].

4.2. Electrophoretic mobility in the presence of anionic surfactants

Experimental and theoretical values of electrophoretic mobility are plotted against the surfactant dosage in Fig. 4 (a), in which the symbols are experimental data and the lines are theoretically calculated. The mobility was insensitive to the concentration of hematite, indicating the reversibility of the adsorption (Fig. S1 in Supplementary). Figure 4 (a) shows that the hematite particles are positively charged at low surfactant dosage and low pH. With increasing the added amount of surfactants, the mobility decreases, goes through zero, and reverses; charge reversals occur due to the adsorption of oppositely charged surfactants. These trends are seen at 1 and 100 mM and at pH 5 and 6 (Figs. S2 and S3 in Supplementary). The isoelectric point, which is the surfactant concentration where the mobility is zero, shifts to lower concentrations as the number of carbon atoms increases. Similar trends were found

in previous researches [5-7, 9]. The shift of the isoelectric point means that surfactants with longer hydrocarbon chains are effectively adsorbed on the hematite-water interface; hydrophobic chains of surfactant are apt to escape from water, hydrophobic effect, and to be adsorbed on the interface. This tendency of surfactant escaping from water is significant for the surfactant with longer chains as expected from Eq. (4) and the data of critical micelle concentration, CMC; CMC usually increases with decreasing the length of chain [1,14]. This study used surfactants with two different charged head groups; sodium alkyl sulfates, SAS, are strong electrolytes, and fatty acids are weak electrolytes and are partly uncharged in bulk solution at lower pH. Nevertheless, the type of charged groups does not significantly affect mobility data at the same number of carbon atoms, while we see the difference in isoelectric point for SDeS and C10. We consider that this is due to charge adjustment [33-36]. That is, pH-dependent charging groups such as oxides and COOH of fatty acids are protonated/deprotonated upon the adsorption of surfactants at the charged interface. As a result, deprotonated fatty acids give rise to mobility values close to those with SAS at the same carbon number.

The dotted, solid, and dashed lines in Fig. 4 (a) are theoretical curves calculated by the method described above for the number of carbon atoms $N = 8, 10$, and 12 , respectively. In the calculation, we assume that the charge density of hematite σ_0 is 20 mC/m^2 at pH 4 in 10 mM NaCl solution to obtain the good agreement between theory and experiment at low surfactant concentration, and the chemical/intrinsic adsorption energy per a carbon atom ϕ is $0.8 k_B T$ for the agreement between theoretical isoelectric points and experimental ones. The magnitude of mobility calculated with the Ohshima equation is 10-30% smaller than that by the Henry equation when the magnitude of the mobility exceeds $3 \text{ } \mu\text{mcm}/(\text{Vs})$ at low and high surfactant concentrations. The difference in mobility is due to the effect of double layer relaxation which is taken into account by the Ohshima equation used in this study. While the theoretical model in this study is quite simple, the model reasonably describes the experimental behavior of the mobility. Somasundaran et al. [6] showed that $\phi = 0.97 k_B T$ for the adsorption of alkyl-ammonium on quartz sand. Liang and Morgan [6] suggested that $\phi = 1.2 k_B T$ for the fatty acids on the surface of hematite. Both of the groups obtained the value of ϕ from the dependence of the isoelectric point on N and claimed that the value of ϕ agrees with the hydrophobic energy from

studies on micelle formation. Israelachvili [1] listed $0.68 k_B T$ (1.7 kJ/mol) for the transfer energy of the SAS from water into micelle per $-\text{CH}_2-$ unit. Compared to these values deduced from the previous studies, we consider that the assumed value $\phi = 0.8 k_B T$ in this study is reasonable. The consistency on the energy suggests that the interaction between hydrophobic chains is crucial in surfactant adsorption on the water-hematite interface. We can demonstrate, as a first approximation, that the simple theoretical model captures the dependence of the electrophoretic mobility on the surfactant concentration. If we look closely the data around the isoelectric point, the mobility changes rapider than theoretical predictions. This is probably related to the self-assembly of surfactants on the surface [3, 37], because such a cooperative effect is not explicitly included in the model used here. Also, the charge adjustment is neglected in the present model. Focusing on such effects, we need to improve the theoretical model in future studies.

4.3. Stability ratio of hematite in the presence of anionic surfactants

The experimental and theoretical values of stability ratio W of the hematite are plotted in Fig. 4 (b, c). The symbols and the lines have the same meaning as in Fig. 4 (a). The theoretical curves are drawn by Eq. (23) with the parameters describing the electrophoretic mobility as discussed above. The stability ratio is close to that without surfactants at low surfactant concentration. With increasing the surfactant concentration, the stability ratio W gradually declines, reaches the minimum value of unity, and sharply increases; there exist a slow aggregation regime at low surfactant concentrations, a fast aggregation regime around the optimum aggregation concentration, and a slow aggregation regime at higher surfactant concentrations. The minimum of the stability ratio emerges around the optimum aggregation concentrations, which are close to the isoelectric points shown in Fig. 4 (a). That is, charge neutralization is a dominant mechanism for the aggregation by oppositely charged surfactants. These trends are observable at 1 and 100 mM and at pH 5 and 6 (Figs. S2 and S3 in Supplementary).

The optimum aggregation concentration decreases with increasing the number of carbons N of the surfactant, because surfactants with larger N are effectively adsorbed by the hydrophobic interaction as

discussed in the previous section. The shift of the optimum aggregation concentration to lower surfactant concentrations was reported by several researchers [6-9]. This study was able to reproduce the lowering of the optimum aggregation concentration with increasing N .

The minimum values of W at the optimum aggregation concentration are unity irrespective of N , meaning that the fastest aggregation rate with the surfactants is identical to the fast aggregation rate induced by the charge-screening with sufficiently higher concentrations of NaCl without surfactants. The present data do not clearly show the dependence of the minimum value of W on N . This result is the same as in the study by Watanabe [7]. In contrast, Liang and Morgan [6] showed that the minimum stability ratio increased with N , and the minimum W was larger than unity. Behrens and Borkovec [8] speculated that there is an additional stabilization mechanism through steric repulsion in the system studied by Liang and Morgan. It is shown that the steric repulsion by non-ionic surfactants works as a stabilization mechanism at the minimum stability ratio from the fact that the fastest rate is slower than the fastest rate induced by salt [8, 38]. The hydrophilic part of non-ionic surfactants may not be strongly attracted to the solid-water interface, but may be extended to the water phase. The existence of the layer of protruding hydrophilic chains is deduced from the shift of slipping plane detected from the reduction of electrophoretic mobility with non-ionic surfactants [2, 39]. In this case, the layer of protruding hydrophilic chains can induce steric repulsion. On the one hand, charged groups of ionic surfactants are expected to be attached on the surface. Thus, in the present study, we could not observe strong steric repulsion due to the lack of thick adsorbed layers.

Additives like polymers and surfactants give rise to additional non-DLVO attractive forces in some cases [1,12,14,16]. From the measurements of the shear yield stress of zirconia suspension with surfactants, Leong et al. [12] demonstrated that the hydrophobic attraction lead to the increase in the yield stress six times. However, the minimum W of the present study is unity, and thus the additional attraction does not appear. This is because the yield stress reflects rupturing force, while the stability ratio reflects the approaching process. Studies on the stability ratio in the presence of ionic-surfactant in well-defined systems are scarce, and thus we will need detailed studies clarifying the quantitative effect of additional forces in surfactant induced aggregation-dispersion.

The theoretical model based on the DLVO theory qualitatively describes the behavior of W . With increasing the concentration of surfactant, the theoretical W sharply decreases, make a flat bottom at $W=1$ through the charge neutralization, and again sharply increases by the charge reversal. While the theoretical relationships of W vs. surfactant concentration C_s are almost symmetrical below and beyond the minimum bottom, the experimental ones are asymmetrical. The magnitude of experimental slopes $d\log W/d\log C_s$ at higher C_s is larger than that of lower C_s . The theoretical slopes $d\log W/d\log C_s$ are rather close to those at higher C_s . Similar trends were reported for the stability ratio of colloidal particles in the presence of oppositely charged polyelectrolytes [16, 17, 40, 41]. At lower C_s , the surface is partially covered with oppositely charged surfactants and probably shows heterogeneous charge-patch structure. By which, an additional attractive force could develop and destabilize the hematite suspension. Also, Hiemstra and Van Riemsdijk [42] suggested that the surface of bare hematite at low pH has different crystalline faces producing surface heterogeneity. On the one hand, at higher C_s , the surface is fully covered with surfactants and thus is homogeneously charged. This situation would be rather ideal as assumed in the theory. As a consequence, the slope $d\log W/d\log C_s$ becomes close to the theoretical one.

It should be noted that a narrower range of the minimum W for fatty acids is found compared to those for the theory and SAS, while the electrophoretic mobility does not clearly show the systematic difference between fatty acids and SAS at each N . This fact indicates that the suspension with fatty acids is more stable through additional repulsive forces or the prevention of a closer approach between the surfaces. The additional repulsive force is not so strong that it appears at the optimum aggregation concentration. Nevertheless, to explain the difference in the range of the minimum W between fatty acids and SAS, we should assume a kind of electro-steric additional force in the slow aggregation regime. At this moment, the expression of the electro-steric effect is unclear, but it may be related to the self-assembled structures of adsorbed surfactants.

5. Conclusions

The charging and aggregation of hematite particles in the presence of anionic surfactants were investigated. The effect of types of charged groups, surfactant dosage, and surfactant chain length was

examined. At pH 4, the electrophoretic mobility of bare hematite was positive. With increasing the surfactant dosage, the electrophoretic mobility went down to zero and became negative. The required surfactant concentration reaching the isoelectric point decreased as the chain length of surfactant increased. The stability ratios (W) showed the minimum around the isoelectric point, indicating that the destabilization is induced by charge neutralization due to the adsorption of oppositely surfactants onto the hematite. The values of minimum stability were almost unity ($W=1$) irrespective of the chain length; the fastest aggregation rate with surfactants equals the salt-induced fast rate. Therefore, in the case with ionic-surfactant, additional non-DLVO interactions like charge-patch attraction and steric hindrance do not significantly work around isoelectric point. This finding differs from the previous result ($W>1$) [6]. In the slow aggregation regime, however, our detailed comparison of theoretical model and experimental stability ratios with different surfactants for the identical particles demonstrated that there would be non-DLVO forces in the presence of surfactants: charge patch attraction at low surfactant dosage and steric-like repulsion for fatty acids.

Acknowledgments

The authors are grateful for the financial support from JSPS KAKENHI (15H04563).

Conflict of interest

The authors declare that they have no conflict of interest associated with this article.

References

- [1] J. N. Israelachvili, Intermolecular and surface forces: revised third edition. Academic press, 2011.
- [2] B. Kronberg, K. Holmberg, B. Lindman, Surface chemistry of surfactants and polymers, John Wiley & Sons, 2014.

366 [3] D. W. Fuerstenau, Equilibrium and nonequilibrium phenomena associated with the adsorption of
 367 ionic surfactants at solid–water interfaces, *Journal of colloid and interface science*, 256 (1) (2002), 79-
 368 90.

369 [4] L. K. Koopal, T. Goloub, A. de Keizer, M. P. Sidorova, The effect of cationic surfactants on wetting,
 370 colloid stability and flotation of silica. *Colloids and Surfaces A: Physicochemical and Engineering*
 371 *Aspects*, 151 (1) (1999), 15-25.

372 [5] P. Somasundaran, T.W. Healy, D.W. Fuerstenau, Surfactant adsorption at the solid—liquid
 373 interface—dependence of mechanism on chain length. *The Journal of Physical Chemistry*, 68 (12)
 374 (1964), 3562-3566.

375 [6] L. Liang, J.J. Morgan, Coagulation of iron oxide particles in the presence of organic materials:
 376 application of surface chemical model. In: D. C. Melchior, R. L. Bassett (Eds.), *Chemical Modeling of*
 377 *Aqueous Systems II*, ACS symposium series (Vol. 416). Oxford University Press, 1990, pp. 293-308.

378 [7] A. Watanabe, Physico-chemical Studies on Surface Active Agents. (II) : The Coagulation of Positive
 379 Silver Iodide Sols by Anionic Surface Active Agents, *Bulletin of the Institute for Chemical Research*,
 380 *Kyoto University*, 38 (1960), 179-215.

381 [8] M. Borkovec, S.H. Behrens, Stabilization of aqueous colloidal dispersions: electrostatic and steric
 382 forces, In: A. T. Hubbard (Ed.), *Encyclopedia of colloid and surface science*, CRC press, 2002, pp. 4795-
 383 4806.

384 [9] D. W. Fuerstenau, M. Colic, Self-association and reverse hemimicelle formation at solid–water
 385 interfaces in dilute surfactant solutions. *Colloids and Surfaces A: Physicochemical and Engineering*
 386 *Aspects*, 146 (1) (1999), 33-47.

387 [10] P. Somasundaran, T. W. Healy, D. W. Fuerstenau. The aggregation of colloidal alumina dispersions
 388 by adsorbed surfactant ions, *Journal of Colloid and Interface Science* 22 (1966), 599-605.

389 [11] T. Imae, K. Muto, S. Ikeda, The pH dependence of dispersion of TiO₂ particles in aqueous
 390 surfactant solutions. *Colloid and polymer science*, 269 (1) (1991), 43-48.

391 [12] Y. K. Leong, P. J. Scales, T. W. Healy, D. V. Boger, Interparticle forces arising from adsorbed
 392 polyelectrolytes in colloidal suspensions. *Colloids and Surfaces A: Physicochemical and Engineering*
 393 *Aspects*, 95 (1) (1995), 43-52.

394 [13] A. Satoh, Brownian dynamics simulation of a dispersion composed of disk-like hematite particles
 395 regarding aggregation phenomena, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*
 396 483 (2015), 328-340.

397 [14] M. Sakamoto, Y. Kanda, M. Miyahara, K. Higashitani, Origin of long-range attractive force
 398 between surfaces hydrophobized by surfactant adsorption. *Langmuir*, 18 (15) (2002), 5713-5719.

399 [15] J. Gregory, Rates of flocculation of latex particles by cationic polymers. *Journal of Colloid and*
 400 *Interface Science*, 42 (2) (1973), 448-456.

401 [16] I. Szilagyi, G. Trefalt, A. Tiraferri, P. Maroni, M. Borkovec, Polyelectrolyte adsorption,
 402 interparticle forces, and colloidal aggregation. *Soft Matter*, 10 (15) (2014), 2479-2502.

403 [17] W. Lin, P. Galletto, M. Borkovec, Charging and aggregation of latex particles by oppositely
 404 charged dendrimers. *Langmuir*, 20 (18) (2004), 7465-7473.

405 [18] L. Feng, Y. Adachi, Brownian flocculation of negatively charged latex particles with low charge
 406 density polycation at various ionic strengths. *Colloids and Surfaces A: Physicochemical and*
 407 *Engineering Aspects*, 454 (2014), 128-134.

408 [19] M. Schudel, S. H. Behrens, H. Holthoff, R. Kretzschmar, M. Borkovec, Absolute aggregation rate
 409 constants of hematite particles in aqueous suspensions: a comparison of two different surface
 410 morphologies. *Journal of colloid and interface science*, 196 (2) (1997), 241-253.

411 [20] M. Kobayashi, D. Ishibashi, Absolute rate of turbulent coagulation from turbidity measurement.
 412 *Colloid and Polymer Science*, 289 (7) (2011), 831-836.

413 [21] Z. Sun, J. Liu, S. Xu, Study on improving the turbidity measurement of the absolute coagulation
 414 rate constant. *Langmuir*, 22 (11) (2006), 4946-4951.

415 [22] H. Ohshima, Approximate analytic expression for the stability ratio of colloidal dispersions. *Colloid*
 416 *and Polymer Science*, 292 (9) (2014), 2269-2274.

417 [23] Y. Adachi, Dynamic aspects of coagulation and flocculation. *Advances in colloid and interface*
 418 *science*, 56 (1995), 1-31.

419 [24] D. R. Lide, ed., *CRC Handbook of Chemistry and Physics*, 82nd Ed., David, CRC Press, Boca
 420 Raton, FL, 2001–2002.

421 [25] M. Kobayashi, F. Juillerat, P. Galletto, P. Bowen, M. Borkovec, Aggregation and charging of
 422 colloidal silica particles: effect of particle size. *Langmuir*, 21 (13) (2005), 5761-5769.

423 [26] H. Ohshima, T. W. Healy, L. R. White, Approximate analytic expressions for the electrophoretic
 424 mobility of spherical colloidal particles and the conductivity of their dilute suspensions. *Journal of the*
 425 *Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, 79 (11) (1983), 1613-1628.

426 [27] M. Kobayashi, Electrophoretic mobility of latex spheres in the presence of divalent ions:
 427 experiments and modeling. *Colloid and polymer science*, 286(8-9) (2008), 935-940.

428 [28] T. Sugimoto, M. Kobayashi, Y. Adachi, The effect of double layer repulsion on the rate of turbulent
 429 and Brownian aggregation: experimental consideration. *Colloids and Surfaces A: Physicochemical and*
 430 *Engineering Aspects*, 443 (2014), 418-424.

431 [29] M. Kobayashi, M. Skarba, P. Galletto, D. Cakara, M. Borkovec, Effects of heat treatment on the
 432 aggregation and charging of Stöber-type silica. *Journal of colloid and interface science*, 292 (1) (2005),
 433 139-147.

434 [30] M. Kosmulski, The pH dependent surface charging and points of zero charge. VI. Update, *Journal*
 435 *of colloid and interface science* 426 (2014), 209-212.

436 [31] N. H. G. Penners and L. K. Koopal, The effect of particle size on the stability of haematite (α -Fe₂
 437 O₃) hydrosols, *Colloids and surfaces* 28 (1987), 67-83.

438 [32] M. Kobayashi, M. Nitnai, N. Satta, Y. Adachi, Coagulation and charging of latex particles in the
 439 presence of imogolite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 435 (2013),
 440 139-146.

441 [33] D. Čakara, M. Kobayashi, M. Skarba, M. Borkovec, Protonation of silica particles in the presence
 442 of a strong cationic polyelectrolyte. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*,
 443 339 (1) (2009), 20-25.

444 [34] E. M. Lee, L. K. Koopal, Adsorption of cationic and anionic surfactants on metal oxide surfaces:
 445 surface charge adjustment and competition effects. *Journal of colloid and interface science*, 177 (2)
 446 (1996), 478-489.

447 [35] T. D. Pham, M. Kobayashi, Y. Adachi, Adsorption of anionic surfactant sodium dodecyl sulfate
 448 onto alpha alumina with small surface area. *Colloid and Polymer Science*, 293 (1) (2015), 217-227.

- [36] A. W. Vermeer, L. K. Koopal, Charge adjustments upon adsorption of a weak polyelectrolyte to a mineral oxide: the hematite–humic acid system. *Journal of colloid and interface science*, 212 (1) (1999), 176-185.
- [37] S. Nishimura, P. J. Scales, S. R. Biggs, T. W. Healy, AFM studies of amine surfactant hemimicelle structures at the mica-water interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 103 (3) (1995), 289-298.
- [38] K. G. Mathai, R. H. Ottewill, Stability of hydrophobic sols in the presence of non-ionic surface-active agents. Part 2.—Stability of silver iodide sols in the presence of non-ionic surface-active agents. *Transactions of the Faraday Society*, 62 (1966), 759-769.
- [39] Y. M. Glazman, Effect of surface-active agents on stability of hydrophobic sols. *Discussions of the Faraday Society*, 42 (1966), 255-266.
- [40] R. Ferretti, J. Zhang, J. Buffle, Kinetics of hematite aggregation by polyacrylic acid: effect of polymer molecular weights. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 121(2) (1997), 203-215.
- [41] T. Szabo, V. Tóth, E. Horváth, L. Forró, I. Szilagyi, Tuning the aggregation of titanate nanowires in aqueous dispersions. *Langmuir*, 31(1) (2015), 42-49.
- [42] T. Hiemstra, and W. H. Van Riemsdijk, Effect of different crystal faces on experimental interaction force and aggregation of hematite, *Langmuir*, 15(23) (1999), 8045-8051.

468

469

470

471 **Figure captions**

472 **Fig. 1** Transmission electron microscope (TEM) picture of used hematite particles.

473 **Fig. 2** Electrophoretic mobility of bare hematite as a function of pH at different NaCl
474 concentrations. 25 mg/L hematite concentration.

475 **Fig. 3** Stability ratio (W) of bare hematite as a function of NaCl concentration at different pH.
476 25 mg/L hematite.

477 **Fig. 4** (a) Electrophoretic mobility and (b, c) stability ratio (W) of hematite as a function of
478 surfactant concentration for 6 different surfactants. pH 4, 25 mg/L hematite and 10 mM NaCl.
479 The behaviors are insensitive to pH. The dotted, solid, and dashed lines are theoretical curves
480 calculated for the number of carbon atoms $N = 8, 10,$ and $12,$ respectively.

481

482

483

484

Fig. 1 Transmission electron microscope (TEM) picture of used hematite particles.

Fig. 2 Electrophoretic mobility of bare hematite as a function of pH at different NaCl concentrations. 25 mg/L hematite concentration.

Fig. 3 Stability ratio (W) of bare hematite as a function of NaCl concentration at different pH. 25 mg/L hematite.

Fig. 4 (a) Electrophoretic mobility and (b, c) stability ratio (W) of hematite as a function of surfactant concentration for 6 different surfactants. pH 4, 25 mg/L hematite and 10 mM NaCl. The dotted, solid, and dashed lines are theoretical curves calculated for the number of carbon atoms $N = 8, 10$, and 12 , respectively.

Supplementary

Effect of anionic surfactants on the stability ratio and electrophoretic mobility of colloidal hematite particles

Motoyoshi Kobayashi^{1,*}, Shunzo Yuki², Yasuhisa Adachi¹

*¹Faculty and ²Graduate School of Life and Environmental Sciences, University of Tsukuba,
Tennodai 1-1-1, Tsukuba-shi, Ibaraki 305-8572, Japan*

*: Corresponding author: kobayashi.moto.fp@u.tsukuba.ac.jp

Tel.: +81 29 853 5721; Fax: +81 29 853 4861.

Fig. S1 Electrophoretic mobility of hematite at different hematite (Hm) concentrations (2.5, 25, and 250 mg/L at pH 4 in 10 mM NaCl. Data are plotted against (a) SDS concentration and (b) normalized SDS/Hm concentration ratio. This figure indicates reversible adsorption of SDS to hematite.

Fig. S2 (a) Stability ratio (W) and (b) electrophoretic mobility of hematite as a function of SDS concentration at different NaCl concentrations (1, 10, and 100 mM). 25 mg/L hematite concentration and pH 4. The optimum aggregation concentration and isoelectric point are insensitive to NaCl concentration.

Fig. S3 (a, c) Stability ratio (W) and (b, d) electrophoretic mobility of hematite as a function of (a, b) SDS or (c, d) C12 concentration at different pH. 25 mg/L hematite and 10 mM NaCl. The behaviors are insensitive to pH.