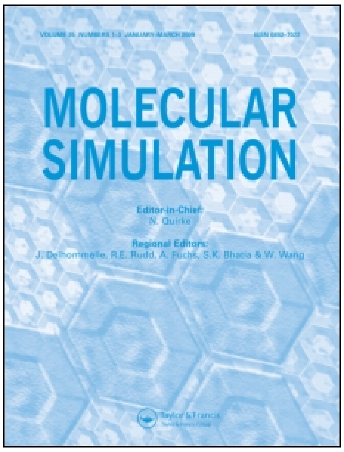

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Particle Size Dependence for Effective Charge Density of Ionic Colloids

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Particle size dependence of the effective surface charge density, σ_e, of colloidal silica particles, having radius a ranging from 16 to 60 nm, was examined by applying electrical conductivity measurements. σ_e markedly increased with decreasing a, and approached to the case for small ions, namely, σ_e = analytical (net) charge density, σ_a. σ_e was roughly proportional to $1/a$, as expected from the mean field theories. However, leveling off of σ_e at high σ_a, which was expected from charge renormalization approach, was not observed.

Keywords: Surface charge density; Electrical conductivity; Ionic polymer latex; Colloidal silica

INTRODUCTION

Ionic colloidal particles, such as ionic polymer latex and colloidal silica, have ionizable groups on their surfaces, which dissociate into counterions and surface charges, when dispersed in polar medium. Due to the resulting long-range electrostatic interparticle interaction, ionic colloids are stabilized against aggregation. As is well known, the counterions are partly condensed near the particle surface due to a strong electrostatic field, and reduce the surface charge of the particles [1,2]. Therefore, the effective surface charge density of the particle, σ_e, is largely different from the analytical charge density, σ_a. Since the interparticle interaction, and consequently the state of the dispersion, is determined by σ_e, not by σ_a, experimental examination of the relationship between σ_e and σ_a is quite important.

In our previous studies [3–5], we have determined σ_e for polymer latex and silica particles by applying electrical conductivity measurements. For latex, which had strongly acidic ionizable groups, we examined samples having various σ_a's, whose radius, a, ranged from 40 to 500 nm [3]. For the case of colloidal silica ($a = 60\,\text{nm}$), we could tune the σ_a value by changing pH of the dispersion [4,5], as will be described later. In both cases, σ_e values were much smaller than σ_a, and we found an empirical relationship,

$$\ln \sigma_e = C_1 \ln \sigma_a - C_2 \qquad (1)$$

where C_1 and C_2 are constants ($(C_1, C_2) = (0.49, 1.0)$ for latex; (0.51,1.0) for the silica).

The influence of a on the $\sigma_e - \sigma_a$ relation was very small, under the a region examined in our previous studies. However, if one considers the limit of $a \rightarrow 0$, the $\sigma_e - \sigma_a$ relation should be that for small strong electrolyte (such as NaCl), namely $\sigma_e = \sigma_a$. Here we examine the particle size dependence of σ_e for colloidal silica particles, whose radius a ranges from 16 to 60 nm.

The surface of silica is covered by weakly acidic silanol groups (Si-OH), whose isoelectric point is at a pH of about 2 [6]. At higher pH's, the surface bears negative charges because the silanol groups partly dissociate. Thus, the charge density of silica increases with pH, which enables one to tune the charge density continuously. Here we demonstrate that the silica particle takes more highly charged states with decreasing particle size. The observed $\sigma_e - \sigma_a$ relation is compared with charge renormalization model proposed by Alexander *et al* [7].

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EXPERIMENTAL SECTION

The colloidal silica particles, Seahoster KE-P10W and Cataloid SI-80P, were purchased from Nippon Shokubai Co., Ltd. (Osaka, Japan) and Catalyst & Chemicals Co., Ltd. (Kanagawa, Japan), in the form of aqueous dispersions stabilized under alkaline conditions. KE-W06 was kindly gifted from Nippon Shokubai Co., Ltd. Four kinds of silica particles, HYS-3, 5, 6 and 7 were prepared according the to sol–gel method by Stöber *et al.* [8]. An aqueous solution of 10^{-4} M NaOH was then added to the resulted silica/ethanol dispersion (1:1 by volume), and ethanol was distilled out under reduced pressure. The sample thus obtained was purified by dialysis against Milli-Q water for about 30 days, and further deionized by ion-exchange method, as described elsewhere [5]. The specific gravity of the silica, estimated by picnometry was $2.24\,\mathrm{g/cm^3}$ [3]. The particle concentrations in the dispersions were determined by a drying-out method.

The average radius of the particles used were determined by DLS measurements (model DLS-7000, Otsuka Electronics Co., Ltd., Tokyo) to measure autocorrelation functions of sufficiently dilute dispersions at particle volume fraction $\Phi = 1 \times 10^{-4}$. The particle radii determined by cumulant method were 60 nm (KE-P10W), 55 nm (SI-80P), 33 nm (KE-W06), 40, 33, 21 and 16 nm (HYS-3, 5, 6 and 7).

The water used was purified by Milli-Q Simpli-Lab. system (Millipore, Bedford, MA), and had a conductivity of 0.4–0.6 μS/cm. The concentration of ionic impurities in the water was estimated to be 2 μM.

The electrical conductivity was measured by employing a conductivity meter (DS-12, Horiba, Kyoto, Japan) and two kinds of conductance cells, each of them having a pair of parallel platinum electrodes (cell constants: 1.00 and $1.28\,\mathrm{cm^{-1}}$). The temperature was controlled at 25.00 ± 0.05°C. The titration was repeated at least three times and the averaged value was adopted. pH measurements were performed by using a Horiba F-13 *p*H meter at room temperature, and the observed *p*H values were corrected to those at 25°C. In order to avoid ionic impurities from glass wall, Teflon and polystyrene bottles and apparatuses were used for all the measurements.

RESULTS AND DISCUSSION

Potentiometric and Conductometric Titrations

Figure 1a shows potentiometric titration curves for salt-free aqueous dispersions of two kinds of silica (KE-W06 and HYS-3) by NaOH at $\Phi = 0.01$. In the absence of NaOH, the dispersions were weakly acidic, due to dissociation of the silanol groups. We note that under this condition, the counterions of the silica particles are hydronium (H_3O^+) ions (hereafter designated simply as H^+) and that by addition of NaOH, they are gradually replaced by Na^+. At pH = 6, for example, the [NaOH] for the HYS-3 was 5.0×10^{-5} M, while [H^+] was 1 μM, as estimated from the pH value. Thus, under this condition, most of the counterions were Na^+. At large [NaOH]s, added NaOH might partly exist in the dispersion medium in excess. However, even at pH = 8 ([NaOH] = 3.4×10^{-4} M for the HYS-3) the concentration of excess NaOH is 1 μM, which is comparable to ionic impurity level of the water used. Thus at pH < 8, added NaOH was almost completely used up in neutralizing the silanol groups.

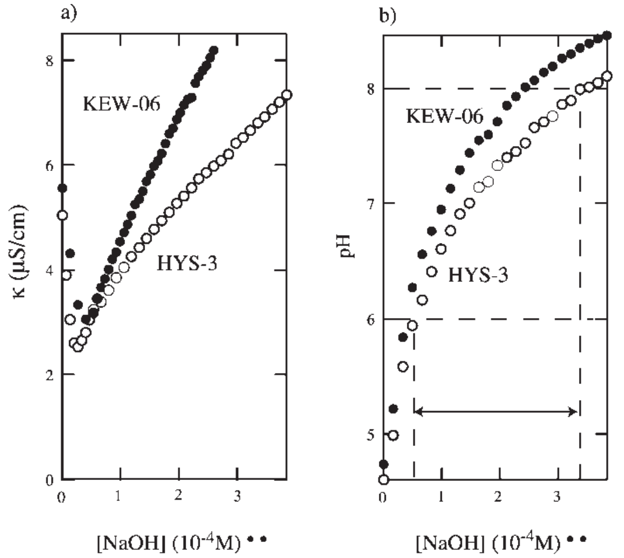

FIGURE 1 (a) Potentiometric titration curves for salt-free aqueous dispersions of KE-W06 (filled circles) and HYS-3 (open circles) silica at $\Phi = 0.01$. The [NaOH] regions indicated by an arrow corresponds to 6 < pH < 8 for HYS-3. (b) Conductometric titration curves for the two silica dispersions.

From the considerations mentioned above, we can conclude that in the pH range of 6 < pH < 8, most of the counterions are Na^+ ions, and the concentration of excess NaOH is negligibly small. Thus in this pH region (shown by an arrow in Fig. 1a for HYS-3), we can safely assume that σ_a is simply determined by the ratio of [NaOH] to Φ, which leads a to a linear relationship between σ_a and [NaOH] as

$$\sigma_{\mathrm{a}} = (10^{-3}/3) N_{\mathrm{A}} e_0 a\,[\mathrm{NaOH}]/\Phi \qquad (2)$$

where N_A is Avogadro's number, and e_0 the elementary charge.

Effective Charge Density

The electrical conductivity of the silica dispersion, κ, is given by

$$\kappa = 10^{-3}(\lambda_{\mathrm{c}C_{\mathrm{c}}} + \lambda_{\mathrm{p}}\Phi) + \kappa_{\mathrm{b}} \qquad (3)$$

where λ_c and λ_p are the equivalent conductivities of the counterions (349.82 and 50.10 S cm/mol for $H^+$and Na^+, at 25°C in water) and the particles [3–5]. κ_b is the background conductivity due to the water and a small amount of excess NaOH. κ_b was calculated as a sum of the conductivities of the ionic impurities in the water and the excess NaOH estimated from the pH values. C_c is the concentration of counterions, which is related to σ_e [3] by

$$\sigma_e = (10^{-3}/3)N_A\, e_0\, aC_c/\Phi \tag{4}$$

Figure 1b shows conductometoric titration curves for the two silica dispersions at $\Phi = 0.01$. Both curves show minima at small [NaOH]s. As we have reported before [3] the presence of the minimum can be reasonably explained in terms of (1) occurrence of counterion exchange between $H^+$and Na^+ which reduces the (averaged) value of λ_c, and (2) an increase in the degree of dissociation, with which C_c and λ_p increase. After passing through a minimum, κ increased with increasing [NaOH]. For $6 < \mathrm{pH} < 8$, the plots were slightly concave upward. As will be described below, this behavior is attributable to counterion condensation.

The transport number of the particles, $t_p(\equiv \lambda_p\phi/(\lambda_c C_c + \lambda_p\Phi))$ did not vary significantly with Φ in the region of $\Phi = 0.01–0.03$, and was 0.50 ± 0.02 for the Na-type silica [5]. We assumed that the t_p value is independent of σ_a.

In Fig. 2, the σ_es for various silica samples are plotted against the σ_a calculated from [NaOH] using Eq. (2). Φ was 0.01 for all the cases. σ_e was always smaller than σ_a, and more significantly different from σ_a at larger σ_as. This trend is reasonably attributable to counterion condensation, which is expected to be more pronounced at higher surface potentials. It is clearly seen that the σ_e increased with decreasing a as compared at $\sigma_a = \text{constant}$, and approached to the case of simple salt, $\sigma_{e=}\sigma_a$. The particle size dependence of σ_e observed here is explainable in terms of decrease of particle surface potential with a. Though we compared at constant σ_a, the analytical charge *number* of the particle $(= 4\pi a^2\, \sigma_a/e_0)$ becomes smaller with decreasing a, and give smaller surface potential.

We compared the observed data with charge renormization model proposed by Alexander *et al* [7]. The concept of the renormalized charge was introduced to extend applicability of Yukawa-type interaction pair potential $U_Y(r)$ to strongly interacting charged colloidal system. $U_Y(r)$ was derived under Debye–Hückel (D–H) approximation, which holds under low surface potential. In order to apply the $U_Y(r)$ to large potential case, they proposed to alter the particle charge density as follows: The electrostatic potential around the particle $\phi(r)$ (r: the distance from the center of particle) is detremined by solving Poisson–Boltzmann (P–B) equation for spherical symmetry

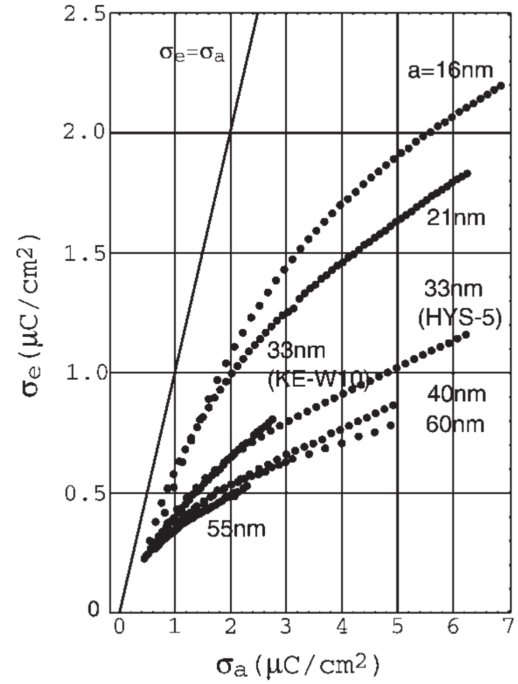

FIGURE 2 Relationship between the effective (σ_e) and analytical (σ_a) surface charge densities for salt-free dispersions of various silica particles, having a radius ranging from 16 to 60 nm. $\Phi = 0.01$. Solid line represents $\sigma_e = \sigma_a$.

$$\frac{d^2\phi}{dr^2} + \frac{2}{r}\frac{d\phi}{dr} = -\frac{\beta e_0^2}{\varepsilon\varepsilon_0}\rho_D^{(+)}\exp(-\phi) \tag{5}$$

(β: Bjerum length, ϵ: the specific dielectric constant, ϵ_0: the dielectric constant of vacuum, $\rho_D^{(+)}$: counterion concentration). By linearlizing the P–B equation, D–H equation

$$\frac{d^2\phi^*}{dr^2} + \frac{2}{r}\frac{d\phi^*}{dr} = -\frac{\beta e_0^2}{\varepsilon\varepsilon_0}\rho_D^{(+)}(1 - \phi^*) \tag{6}$$

is obtained. Here we denote the potential as $\phi^*(r)$, to distinguish from the solution of P-B equation. Equation (5) can be solved numerically, while Eq. (6) has an analytical solution. By solving them in spherical Wigner-Seitz cell of radius $= D$ under boundary conditions $\phi(D) = \phi^*(D) = 0$ and $d\phi(r)/dr = d\phi^*(r)/dr = 0$ at $r = D$, one can obtain two kinds of surface charge densities

$$\sigma = -\left[\varepsilon\varepsilon_0/(\beta e_0)\right] d\phi/dr|_{r=a} \tag{7}$$

$$\sigma^* = -\left[\varepsilon\varepsilon_0/(\beta e_0)\right] d\phi^*/dr|_{r=a} \tag{8}$$

The σ correspond to the analytical charge density σ_a, while the charge density derived by D–H equation, σ^*, is called renormalized charge density. Several authors have reported that order–disorder transition of charge colloids were successfully

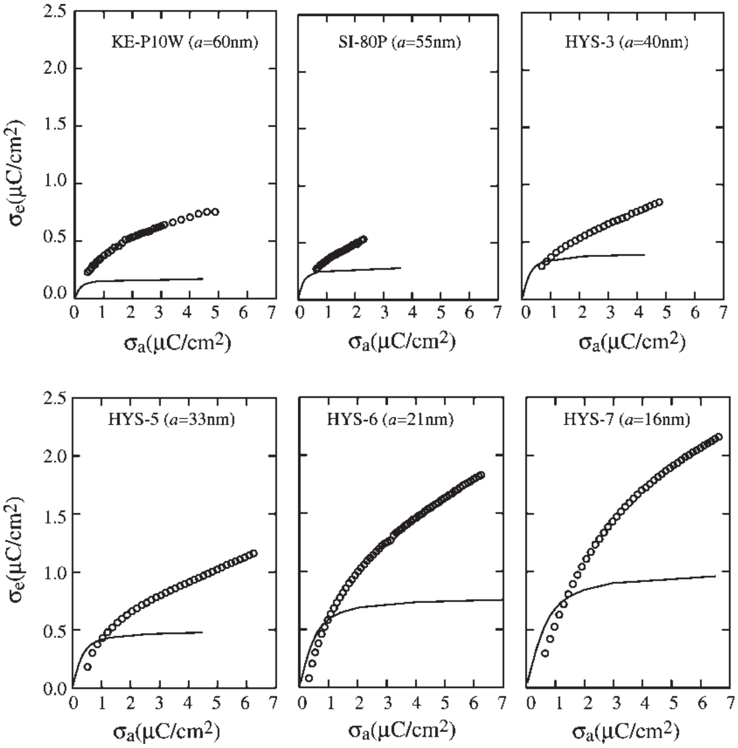

FIGURE 3 Comparison between σ_e (open circles) and renormalized charge density, σ^*(full lines), for various silica particles.

explained for in terms of $U_Y(r)$, by using σ^* instead of σ_a [9]. Furthermore, it has been reported that the σ^* is close to the σ_e determined by conductometry [10]. However, it should be noted that these conclusions were drawn from the experimental results under relatively low charge densities.

Figure 3 shows comparison between σ_e and σ^* for various particle sizes. σ^* increased with decreasing a, which reproduced the size dependence observed for σ_e. In fact, observed σ_e was roughly proportional to $1/a$, which is expected from the mean field theories. At small σ_a, σ^* shows close agreement with σ_e in all the cases, as reported previously. However, under high σ_a conditions, σ^* leveled off, and did not reproduce the observed monotonous increase of σ_e.

CONCLUSIONS

In the present paper, we examined particle size dependence of the effective surface charge density of colloids, by applying electrical conductometry, for colloidal silica whose radius a ranging from 16 to 60 nm. It was clearly demonstrated that the effective charge density increases with decreasing particle radius, a, and approached to the case for small salt. This trend was explained by charge renormalization model; however, leveling off of the effective charge at high charge condition, which was expected from the theory, was not observed in all the cases.

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