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Control of the surface charge density of colloidal silica by sodium hydroxide in salt-free and low-salt dispersions

Junpei Yamanaka,[1,*] Yoshihiro Hayashi,[1] Norio Ise,[2] and Takuji Yamaguchi[1]
[1]*Department of Materials Science and Engineering, Fukui University, Fukui 910, Japan*
[2]*Central Laboratory, Rengo Co. Ltd., 186-1-4, Ohhiraki, Fukushima, Osaka 553, Japan*

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Electrical conductivity measurements and conductometric titrations were performed on dilute salt-free aqueous dispersion of a colloidal silica (diameter: $0.11 \pm 0.01 \times 10^{-6}$ m) whose charge number can be varied with the quantity of coexisting sodium hydroxide. In the absence of sodium hydroxide, the silica particle had an effective (net) surface charge density σ_e of 8×10^{-8} C cm^{-2}. Titrations by hydrochloric acid were performed in the presence of sodium hydroxide. When the NaOH concentration was sufficiently high, the titration curve could be divided into three regions with regard to slope values. These regions could be ascribed to titrations of excess sodium hydroxide, ionizable surface groups having Na ions as counterions, and excess hydrochloric acid. The analytical surface charge density σ_a, estimated from the titration curves, increased with increasing [NaOH]. It was found that the concentrations of Na and OH ions in excess were negligible when the [NaOH] was smaller than 2.5×10^{-4} M and the volume fraction of the silica, ϕ, was larger than 2.6×10^{-3}. The value of σ_a at this threshold was 1.8×10^{-5} C cm^{-2}. Under these conditions we could control the σ_a value by varying [NaOH]. The present system provides larger possibilities in studying the influence of charge density on the physico-chemical properties of ionic colloidal systems. Viscosity measurements were performed for salt-free and low-salt dispersions at [NaOH]'s where its excess concentration was found to be negligible. The σ_a dependence of the viscosity was in good agreement with previous results obtained from ionic latices having various σ_a's. A relationship between the effective charge density at an infinite dilution, $\sigma_{e|\phi=0}$, and σ_a was examined for latex systems. An empirical relation, $\ln\sigma_{e|\phi=0} = 0.49 \ln\sigma_a - 1.0$, was obtained by using $\sigma_{e|\phi=0}$ values determined by the conductivity for latices with various σ_a's from 0.21×10^{-6} to 5.6×10^{-6} C cm^{-2}. By assuming that this relation holds also for the silica system, viscosity data were analyzed. Satisfactory agreement was observed between the experimental value and Booth theoretical value on the first-order electroviscous effect. [S1063-651X(97)08902-2]

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I. INTRODUCTION

Dispersions of ionic colloidal particles exhibit characteristic behavior at salt-free and low-salt conditions, due to strong electrostatic interparticle interactions [1]. In spite of extensive studies of colloidal phenomena, it is noteworthy that the number of electric charges on colloidal particles has not been given due attention. This is an unfortunate situation, since the interaction in such ionic systems is expected to be largely determined by the Coulombic interaction, which is a sensitive function of the charge number. Thus it is fundamentally important to examine the influence of charge density on the behavior of colloidal properties while keeping other properties of the system constant. However, such a study has been formidable, because of experimental difficulties in preparing particles with various charge densities at a constant size. Very recently, Palberg *et al.* [2] studied polymer latex particles, whose charge density was varied by the addition of ionic surfactant.

To facilitate understanding, we would like to mention here a long-accepted practice in simple salt and polyelectrolyte solutions. Simple salts are safely assumed to dissociate completely into ions at very low concentrations. Thus, NaCl is treated to dissociate fully into Na$^+$ and Cl$^-$ in the Debye-Hückel scheme. However, even in this case, experimental data show the presence of a tiny amount of undissociated species as a result of attractive interaction between two ionic species. This problem was discussed by Bjerrum [3]. The incomplete dissociation took place even for a pair of monovalent anions and cations. On the other hand, polyelectrolytes (ionic polymers and colloidal particles) generally carry very large numbers of dissociable groups and counterions. A portion of counterions would exist as free ions contributing to electrical conductivity and the rest would be associated with ionized groups on colloidal particles; the ratio of these two kinds of counterions is considered to determine the effective (net) charge number N_e, or effective (net) charge density σ_e, while the self-dissociation of ionizable groups and the amount of added dissociating agent (such as sodium hydroxide to weak acid) determine the analytical charge number N_a, and hence analytical charge density σ_a.

There appear to exist three different attitudes regarding the colloidal charge number. In the first category, colloidal phenomena are discussed in terms of the analytical charge number N_a, which arises from the chemistry of the particle synthesis [4]. This quantity may be determined by appropri-

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[*] Author to whom correspondence should be addressed. Present address: Hashimoto Polymer Phasing Project, ERATO, Japan Science and Technology Corporation (JST), 15 Morimoto-cho, Shimogamo, Sakyo-ku, Kyoto 606, Japan.

ate experimental methods such as conductometric titration. In the second [1,4], colloidal properties are discussed in terms of a theoretical framework using N_a and then, if a disagreement with the theory is found, an effective charge number N_e is introduced to rescale N_a in such a way that reasonable agreement with observation is reached. In the third [5,6] the N_e is determined by independent experimental methods such as conductivity measurements and transference experiments. The second approach is found very often in the literature, particularly in computer-simulation studies. This would be satisfactory if the theory applied and the assumptions introduced were perfect, and if the resulting N_e could also be considered reliable, but even in this case an independent check of the N_e values is still desirable as a test of the theory discussed. Generally speaking, we have at least two factors to be critically examined in the second approach, namely, the theory (or the assumptions) and N_e. Unless either of these two is determined independently, the arguments become circular at best, and cannot be conclusive. It is impossible to obtain a correct understanding of colloidal phenomena unless the charge number of colloidal particles is experimentally determined, however tedious the experimental procedure may be.

Aqueous dispersions of colloidal silica particles as well as those of ionic polymer latices have been frequently studied. Colloidal silica has attracted attention for various reasons. Its high electron density contrast in aqueous dispersions, for example, has made detailed ultra-small-angle x-ray scattering studies possible [7]. In the present paper, we would like to demonstrate their possibility that the charge density can be conveniently adjusted at salt-free and low-salt conditions by changing the solvent compositions without rather tedious and not highly reproducible synthetic manipulation required for other colloidal systems such as latex particles.

One of the particular features of colloidal silica is that its surface charge is strongly affected by the properties of the dispersion medium [8]. A number of studies [9–18] have hitherto been made and the following characteristics are widely accepted, at least under relatively high-salt conditions: (1) The isoelectric point of silica is at a pH of about 2, (2) the surface bears negative charges at higher pH's, and (3) the analytical surface charge density σ_a increases with increasing pH and with increasing salt concentration. The previous studies, however, have chiefly been concerned with relatively high-salt conditions, and only a few studies [10,18] have been made so far under salt-free and low-salt conditions. Therefore first we studied the salt-free conditions. For this purpose, we applied electrical conductivity measurements and conductometric titrations. Potentiometry has also been employed in most of the previous studies [9–15,17], although applications of a chromatographic method [16] and electrophoresis [18] have recently been reported. Under salt-free conditions, when the conductivity of the dispersion medium was sufficiently small, the conductometric method allows a much more accurate determination of ionic concentrations than the potentiometric methods, so we were able to determine accurately σ_e of the order of 10^{-8}–10^{-5} C cm^{-2}.

Secondly, we studied control of surface charge density by adding sodium hydroxide to the dispersion. We found out conditions where NaOH added is used up to neutralize silanol groups, and concentrations of excess NaOH were negligible. At these conditions, σ_a is proportional to [NaOH] added and salt concentration is independent of [NaOH]. Thus the present system would be useful for systematic study of charge density on colloidal behaviors [19]. In the coexistence of NaOH, σ_e value could not be determined by the conductivity. Instead we examine the σ_e-σ_a relationship for latex systems. An empirical relation was derived by using σ_e values determined by the conductivity for latices with various σ_a's. By assuming that this relation holds also for the silica system, viscosity data were analyzed. Satisfactory agreement was observed between the experimental value and Booth theoretical value on the first-order electroviscous effect [20].

The surface charge of silica particles has been ascribed to two sources, namely, dissociation of weakly acidic silanol groups on the silica surface and adsorption of charge-determining ions, such as OH ions [8]. Here we follow the explanation in terms of dissociation of the silanol groups.

II. EXPERIMENTAL SECTION

A. Materials

The colloidal silica, Seahoster KE-P10W, was kindly donated by Nippon Shokubai Co. Ltd. (Osaka, Japan) in the form of an aqueous dispersion stabilized by ammonium hydroxide. The dispersion was purified by dialysis against purified water. The completion of the dialysis was judged by electrical conductivity measurements. The dispersion (about 100 ml) was then placed in an ultrasonic bath for 10 min to destroy aggregates. Next, 50 ml of a purified bed of mixed cation and anion-exchange resin beads, AG 501-X8 (D) (20–50 mesh, Bio-Rad Labs, Hercules, CA), was added to the dispersion, which was then kept standing for at least ten days. Dynamic light scattering measurements showed that the quantity of aggregates in the stock dispersion was negligible. The diameter of the particles was $(0.11\pm0.01)\times10^{-6}$ m, according to ultra-small-angle x-ray scattering measurements [7]. The colloidal silica thus purified had H^+ (H_3O^+) ions as counterions (hereafter designated as H-type). The volume fraction of the silica in the stock dispersion, determined by a drying-out method, was 2.73×10^{-2}. Polystyrene-based latex, N-100E, was purchased from Sekisui Chemical Co. (Osaka, Japan), and purified by a method described earlier [21]. The surface charge was due to strongly acidic sulfonic acid groups. Characteristics of the latex are shown in Table I. Samples for measurements were prepared by diluting the stock dispersion under a nitrogen atmosphere using polyethylene bottles as containers, as described elsewhere [21]. The water was purified as reported earlier [22], and had an electrical conductivity of $(0.4-0.6)\times10^{-6}$ S cm^{-1}.

B. Methods

The electrical conductivity measurements and the conductometric titrations were performed by using a conductivity meter, type DS-14, Horiba Co. Ltd. (Kyoto, Japan) at 25 ±0.05 °C. Glass cells with platinum electrodes having cell constants of 1.244 and 0.996 cm^{-1} were used. The viscosities were measured at 25±0.02 °C by using an Ubbelohde-type viscometer, a variable-shear viscometer described else-

TABLE I. Characteristics of latices.

No.	Latex	Diameter (10^{-6} m)	σ_a (10^{-6} C cm^{-2})	$\sigma_{e\|\phi=0}$ (10^{-6} C cm^{-2})	Reference
1	1P30A	0.11	0.21	0.13	[22]
2	1P30B	0.11	0.42	0.22	[30]
3	MS-5	0.1	0.82	0.48	[21]
4	1B76	0.11	0.88	0.33	[21]
5	N-100B	0.12	0.93	0.45	[30]
6	SS-114	0.13	0.97	0.29	[30]
7	N-100C	0.12	1.4	0.66	[32]
8	N-100D	0.12	1.6	0.48	[34]
9	MS-1	0.13	3.7	0.81	[21]
10	N-100E	0.12	4.8	0.47	this work
11	N-100A	0.12	5.3	0.74	[30]
12	N-100	0.12	5.6	1.0	[21]
13	N-601	0.60	0.70	0.32	[30]
14	N-1000	1.0	1.6	0.48	[30]
15		0.08	2	0.46	[5]
16		0.13	4.6	0.74	[6]

where [21], and another variable-shear capillary viscometer which was similar to that described previously [21] and was applicable to lower shear rates (about 5–200 s^{-1} for water). All apparatus were cleaned as described previously [22].

III. RESULTS AND DISCUSSION

A. Properties of surface charge

First, properties of the surface charges of H-type silica at salt-free conditions were studied by conductivity measurements and conductometric titrations. The silica dispersions were slightly conductive. Figure 1 shows the difference $\Delta\kappa$ between the measured conductivity of the dispersion κ and that of the water used (0.56×10^{-6} S cm^{-1}) at various colloid volume fractions ϕ. The $\Delta\kappa$'s observed here can be attributed to electrical conduction by the counterions (H ions), since the transport number of the ionic colloidal particles was found to be negligibly small for the H-type colloid [6]. The concentration of the counterions was estimated from the $\Delta\kappa$ value and the equivalent conductivity of H^+ at infinite dilution (349.8 S cm^2 mol^{-1} at 25 °C). The effective surface charge density σ_e of the H-type silica was then calculated at various ϕ's. The σ_e value thus obtained was 8×10^{-8} C cm^{-2}, which did not change significantly with ϕ under the present conditions. The σ_e value estimated by Dunstan [18] by using electrophoresis under salt-free conditions (particle diameter: 0.165×10^{-6} m) was 5×10^{-8} C cm^{-2}, which is close to the present value.

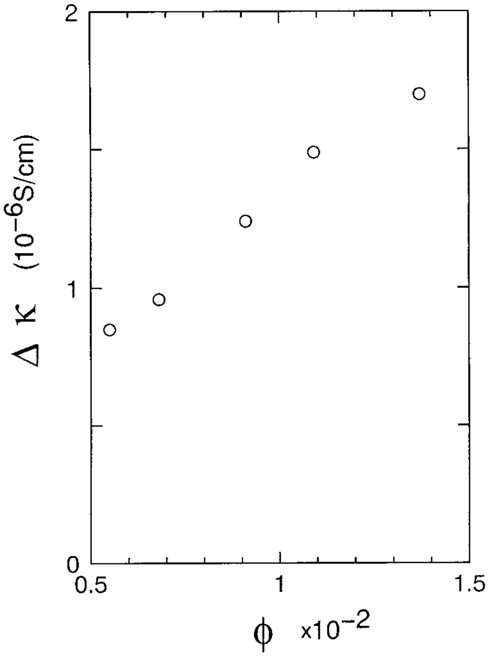

FIG. 1. Difference $\Delta\kappa$ between dispersion conductivity and that of water for salt-free dispersions of the H-type silica at various colloid volume fractions ϕ.

Furthermore, conductometric titrations were carried out by using sodium hydroxide. Figure 2 shows a plot of κ vs sodium hydroxide concentration [NaOH] at $\phi=6.8\times10^{-3}$. The value of κ first decreased with increasing [NaOH], and after passing through a minimum it increased linearly [23], with a slope of 0.077 S cm^{-1} M^{-1}. This minimum should *not* be ascribed to the neutralization point of *strong* acidic groups, since the (positive) slope value was much smaller than that due to the excess sodium hydroxide (0.248 S cm^{-1} M^{-1}), although several authors [24] have erroneously attributed the minimum in the conductometric titration plots of weakly acidic colloid to strongly acidic groups. Figure 3 shows titration curves for aqueous solutions of acids with various pK_a's calculated on the basis of the law of mass action. (The acid concentration was 10^{-5} M. The molar conductivities λ of the ions were those at infinite dilution at 25 °C. The λ value of the acid ions was taken to be zero, for convenience.) It can be clearly seen from Fig. 3 that there exists a minimum in the titration curve for a *weak* acid solution, due to exchange of H^+ and Na^+ [25], and that with increasing pK_a, the minimum shifts toward smaller [NaOH] and the (positive) slope becomes larger. Although a

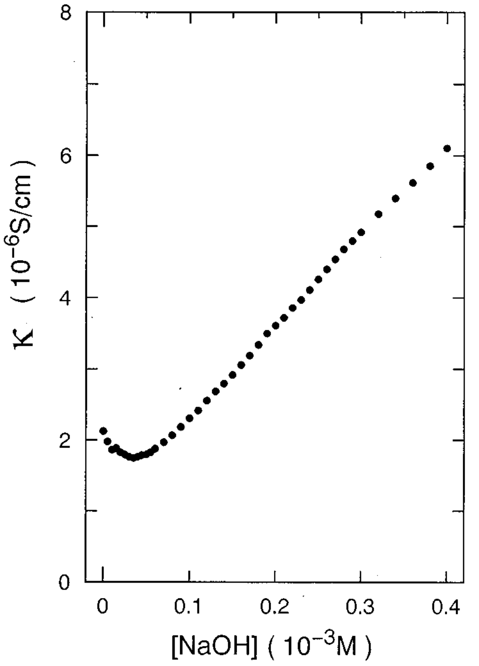

FIG. 2. Conductometric titration for a salt-free dispersion of the H-type silica by sodium hydroxide. $\phi = 6.8\times10^{-3}$.

more quantitative discussion is difficult, since the pK_a value for the present silica is not known [26], the present argument allows us to conclude that the surface ionic groups of the silica particle were weakly acidic. The present result is consistent with the view, which has been accepted at least under high-salt conditions, that the surface charges of colloidal silica are generated by dissociation of weakly acidic silanol groups.

B. Conditions where bulk NaOH concentration is negligible

In Sec. III A, it was shown that sodium hydroxide coexisting in the dispersion partially neutralizes the surface ionizable groups, at salt-free conditions. This implies that the charge number increases with increasing [NaOH], and the silica has Na ions as counterions (hereafter designated as Na-type). However, when [NaOH]'s are sufficiently large, Na and OH ions could also be present, in equilibrium with those in the Na-type silica. To evaluate the NaOH concentrations, titrations were carried out for Na-type silica dispersion using hydrochloric acid. Figure 4 shows results for the dispersion at $\phi = 9.35\times10^{-4}$ and at [NaOH]= 5×10^{-3} M. The plot could be divided into three regions with regard to the slope. The slopes in regions 1, 2, and 3 (hereafter designated as s_1, s_2, and s_3) were -0.12 (the initial slope), $+0.06$, and $+0.44$ S cm^{-1} M^{-1}, respectively. The value of s_1 was in a good agreement with that due to exchange of OH^- and Cl^- (-0.122 S cm^{-1} M^{-1}), which indicates that region 1 corresponded to the neutralization of (excess) sodium hydroxide present in the bulk. On the other hand, the boundary between regions 2 and 3 agreed with the equivalent point for the total amount of coexisting sodium hydroxide, and the s_3 value was very close to the slope due to excess hydrochloric acid (0.426 S cm^{-1} M^{-1}). This suggests that the Na-type silica was titrated in region 2.

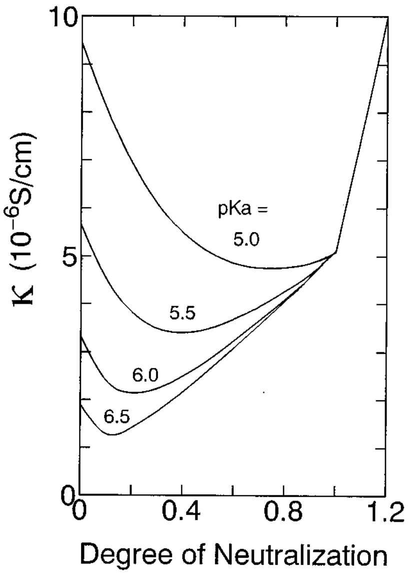

FIG. 3. Conductometric titration curve calculated for aqueous solutions of acids having various pK_a values.

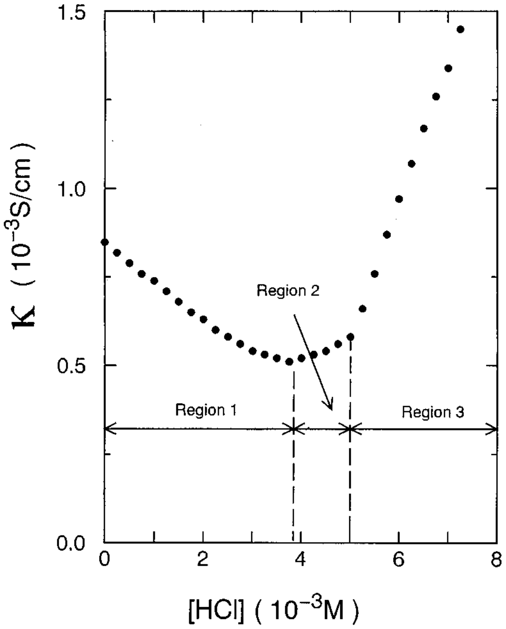

FIG. 4. Conductometric titration by hydrochloric acid for a silica dispersion ($\phi = 9.35\times10^{-4}$) in the presence of sodium hydroxide (5×10^{-3} M).

It should be noted, however, that the colloidal silica is hydrolyzed at high pH's to monosilicate. The concentration of the dissolved monosilicate was determined for a dispersion having $\phi = 8.4\times10^{-3}$ at [NaOH]=10^{-3} M, by the molybdenum blue method [27]. After having been kept at room temperature for one day, 2×10^{-4} M of monosilicate, which corresponded to 0.1 wt % of the colloidal silica particles, was present in the dispersion medium. Since the pK_a of monosilisic acid (about 9) [8] is larger than that of the H-type colloidal silica (5–7) [8], the sodium monosilicate is titrated by hydrochloric acid prior to the Na-type silica. The value of κ for a sodium monosilicate solution decreases with increasing [HCl]. Therefore the presence of the monosilicate

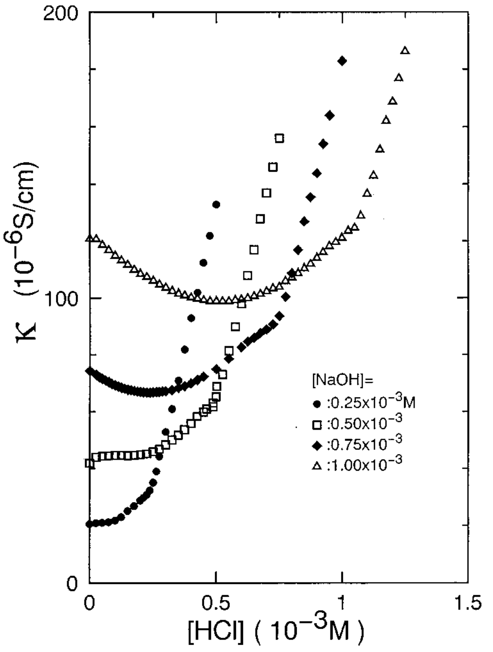

FIG. 5. Influence of the concentration of coexisting sodium hydroxide on the titration curve for a silica dispersion with $\phi=8.5\times10^{-4}$.

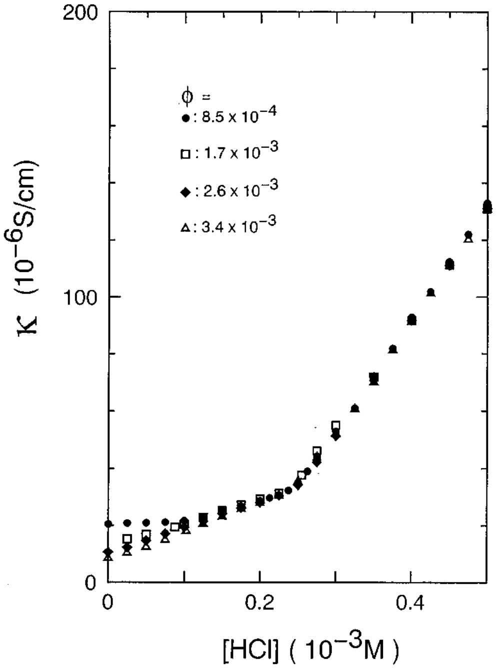

FIG. 6. Influence of colloid volume fraction on the titration curve. [NaOH]= 2.5×10^{-4} M.

would make the end point of region 1 unclear.

The influence of sodium hydroxide and silica concentrations on the titration curve were then examined to clarify the conditions when the excess concentration of Na^+ and OH^- is negligible. Heston, Iler, and Sears [10] described how the OH^- concentration in the bulk could be neglected at [NaOH]=3.34×10^{-4} M and at [silica]=0.5 g/100 ml (this corresponds to $\phi=2.3\times10^{-3}$, if the density of silica is assumed to be 2.2 g/cm^3 [28]), as determined by pH measurements. In our opinion, however, it is worthwhile to apply the conductometric method, in light of its much higher accuracy under salt-free conditions. In Fig. 5 the titration curves for a silica dispersion at $\phi=8.5\times10^{-4}$ are shown at four [NaOH]'s. In each case the bending points between regions 2 and 3, which agreed with the neutralization points for coexisting sodium hydroxide, were clearly observed. At high [NaOH]'s the boundary between regions 1 and 2 was not clear enough to determine the bending point. This might be partly due to small amounts of monosilicate dissolved from the silica. However, it was obvious that region 1 became narrower with decreasing [NaOH], and was quite small at [NaOH]=2.5×10^{-4} M. Titrations were then performed at larger ϕ's holding [NaOH] constant at 2.5×10^{-4} M. As seen in Fig. 6, region 1 was not observed when ϕ was larger than 2.6×10^{-3}. In other words, the excess concentrations of Na^+ and OH^- were found to be negligible at $\phi=2.6\times10^{-3}$ and at [NaOH]= 2.5×10^{-4} M. With respect to the present finding, it is noteworthy that the fraction of bulk sodium ions markedly decreases with decreasing [NaOH] for aqueous solutions of polyacrylic acid, which is a linear weak polyelectrolyte [29].

Under conditions where the concentration of excess NaOH is negligible, the analytical surface charge density σ_a is proportional to [NaOH]/A, where A is the total surface area of the silica particles in a unit volume of the dispersion. When expressed by silica volume fraction ϕ,

$$\sigma_a=(10^{-3}/3)N_A ea[\mathrm{NaOH}]/\phi \quad (\mathrm{C\,cm^{-2}}), \qquad (1)$$

where N_A is Avogadro's number, e the elementary charge (in C), a the particle radius (cm). The largest value of σ_a obtained under conditions where the excess concentration of NaOH is negligible was 1.8×10^{-5} C cm^{-2}, as calculated by using ϕ and [NaOH] values at the boundary shown above.

C. Relationship between analytical and effective (net) charge densities

For the Na-type silica, σ_e could not be estimated from the conductivity of the dispersion, because the equivalent conductivity of the Na ion is so small that conduction due to the silica particle itself is not negligible [6]. On the other hand, for H-type latex particles, we can evaluate both the σ_e and σ_a values by the conductivity measurements and the conductometric titrations, respectively. Here we derive an empirical relationship between σ_e and σ_a for the H-type latex system, from experimental results in the present and previous works. In Sec. III D, we will analyze the viscosity data for Na-silica, assuming that the same σ_e-σ_a relation holds for the silica system.

In Table I, σ_e values at infinite dilution, $\sigma_{e|\phi=0}$, for latices with various σ_a's are compiled. The values of $\sigma_{e|\phi=0}$ were determined by applying the first-order least-squares method for σ_e-ϕ plots at salt-free conditions. The plot for N-100E latex is shown in Fig. 7. Previous data by Ito, Ise, and Okubo [6], which were obtained from the transport number measurements, and by Schaefer [5] from the conductivity are also shown in Table I, for comparison. The surface charges are due to dissociation of strong acidic sul-

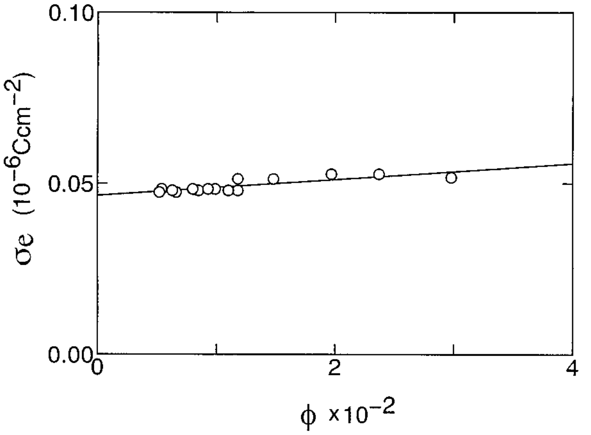

FIG. 7. The effective charge density σ_e vs ϕ plot for N-100E latex at salt-free condition.

fonate and sulfate groups in all cases. The diameters of the latices were about 0.1×10^{-6} m, except sample nos. 13 and 14. It seems that the particle diameter has little influence on the relation between $\sigma_{e|\phi=0}$ and σ_a. As demonstrated in Fig. 8, a double-logarithmic plot for $\sigma_{e|\phi=0}$ and σ_a shows good linearity. By using the first-order least-squares method through all the data points, we obtain an empirical relation,

$$\ln\sigma_{e|\phi=0}=0.49\ \ln\sigma_a-1.0, \tag{2}$$

for σ_a values from 0.21×10^{-6} to 5.6×10^{-6} C/cm^{-2}. Hereafter we use Eq. (2) in calculating $\sigma_{e|\phi=0}$ values at given σ_a's [31].

Furthermore, we examine the influence of salt concentration on the relation between σ_e and σ_a. Hydrochloric acid was used as a salt to avoid an exchange of counterions with added cations. Figure 9 shows a σ_e-[HCl] plot for N-100E latex at $\phi=1.48\times10^{-2}$. It is clearly seen that the σ_e value does not appreciably change with salt concentration. In addition, it should be noted that σ_e did not remarkably vary with ϕ, as seen in Fig. 7. These findings imply that the empirical relations obtained above can be reasonably applied even in the presence of extraneous salts and for finite latex concentrations.

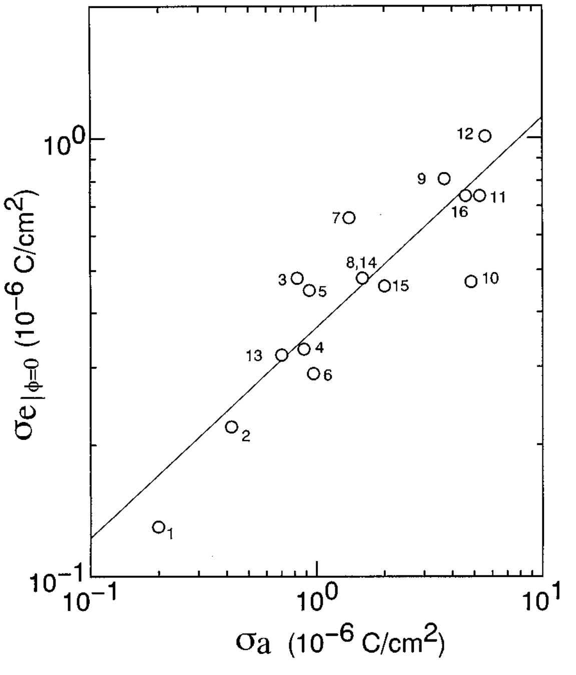

FIG. 8. Relationship between the effective charge density at $\phi=0$, $\sigma_{e|\phi=0}$, and the analytical charge density σ_a for H-type latices. Figures by the data points are sample nos. given in Table I. The line was drawn by the first-order least-squares method.

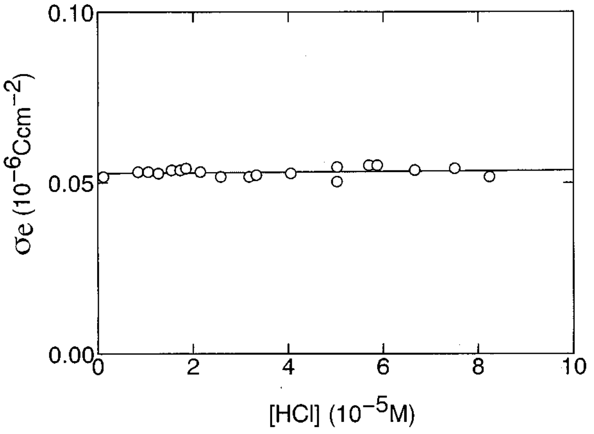

FIG. 9. Influence of HCl concentration on σ_e for N-100E latex. $\phi=1.48\times10^{-2}$.

D. Comparison of dispersion viscosities for silica and latex systems

In Sec. III A, it was demonstrated that we could control the surface charge density of the colloidal silica when [NaOH] was sufficiently low and ϕ was sufficiently large. Thus the present system could be useful for studying the effect of charge density of various colloidal phenomena. Finally we investigated the influence of the surface charge density on the viscosity of the colloidal silica dispersions, and compared it with data of ionic polymer latex system. Furthermore, the validity of the $\sigma_{e|\phi=0}$-σ_a relation obtained in Sec III C was examined by comparing with the Booth theory on the first-order electroviscous effect [20].

As reported previously [21,22,32–34], dispersions of ionic colloids have a much larger viscosity than those of nonionic colloids, due to electroviscous effects [35]. We have already studied this effect using ionic polymer latices with various σ_a's. Since the electroviscous effect depends strongly on the σ_e value and on the salt concentration in the bulk, examining the effect in the colloidal silica system is useful for judging the validity of the conclusions drawn in the previous sections.

The viscosities of the silica dispersions were measured at $\phi=3.4\times10^{-3}$ and at [NaOH]'s smaller than 10^{-4} M, when the excess concentrations of Na$^+$ and OH$^-$ were known to be negligible. Figures 10(a) and 10(b) show the plot of the reduced viscosity, η_{sp}/ϕ [$\eta_{sp}\equiv(\eta-\eta_0)/\eta_0$, where η and η_0 are the viscosities of the dispersion and the medium, respectively], vs σ_a under salt-free conditions and at [NaCl]= 5×10^{-5} M, respectively. The viscosity was measured with the Ubbelohde-type viscometer, at shear rates of about 800 s^{-1} [36]. The data reported for the latex dispersions at the

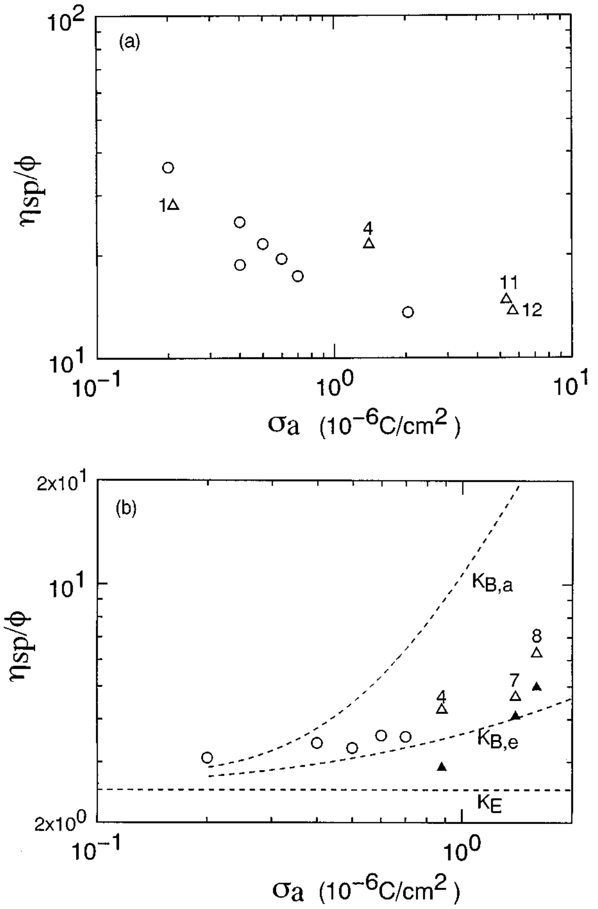

FIG. 10. The reduced viscosity η_{sp}/ϕ vs σ_a plot for dispersions of the Na-type colloidal silica and those of the ionic latices at (a) salt-free condition, and at (b) $[\mathrm{NaCl}]=5\times10^{-5}$ M. Circles, silica; triangle, latex. Open symbols, $\phi=3.4\times10^{-3}$; filled symbols, extrapolated values to $\phi\rightarrow0$. Sample nos. (same as in Table I) are given by symbols. Curves $K_{B,a}$ and $K_{B,e}$, Booth theory for σ_e and σ_a; K_E, Einstein theory.

same ϕ are also shown in Figs. 10(a) and 10(b) for comparison. In Fig. 10(b) we also show the data for latex extrapolated to $\phi\rightarrow0$ using the least-squares method for the $\eta_{sp}/\phi-\phi$ plot. As reported earlier [21], η_{sp}/ϕ decreased with increasing σ_a under salt-free conditions, whereas η_{sp}/ϕ increased with increasing σ_a at $[\mathrm{NaCl}]=5\times10^{-5}$ M. It is clear from Figs. 10(a) and 10(b) that for both the latex and silica systems the viscosity behavior as a function of σ_a shows good correspondence both in the presence and in the absence of salt. This finding supports the conclusion derived above from the conductivity study that we can control the surface charge and the particle size of a silica colloid without affecting the salt concentration in the dispersion.

Furthermore, viscosity data in the presence of salt were compared with theoretical study on the first-order (primary) electroviscous effect developed by Booth [20]. The first-order effect arises from a deformation of counterion atmosphere under shear. Booth calculated the viscosity for dispersions of a charged sphere as a power series in the ζ potential, or the effective charge number N_e to the second-order term. The first-order term was found to be zero. When expressed in terms of N_e, η_{sp}/ϕ at $\phi=0$ (hereafter designated by K_B) is given by

$$K_B=(5/2)[1+q^*(N_e e^2/\epsilon akT)^2 Z(\kappa a)], \tag{3}$$

with

$$q^*=(\epsilon kT/\eta_0 e^2)\left(\sum_{i=1}^{N} n_i Z_i^2 w_i^{-1} \Big/ \sum_{i=1}^{N} n_i Z_i^2\right) \tag{4}$$

and

$$\kappa^2=(4\pi e^2/\epsilon kT)\sum_{i=1}^{N} n_i Z_i^2, \tag{5}$$

where e is the elementary charge, ϵ is the dielectric constant of the dispersion medium, k is the Boltzmann constant, T is the temperature, a is the particle radius, N is the number of ionic species, and n_i, Z_i, and w_i are the number concentration, valency, and mobility of the ion species i, respectively. The first term in Eq. (3) corresponds to the contribution from the hydrodynamic effect, formulated by Einstein [37]. The deformability of the counterion atmosphere is expressed by the function $Z(\kappa a)$. Satisfactory agreements between Booth theory and experiment have been reported [21,22,32,33,38,39], especially at small N_e and at large κa.

By using Eq. (2) and a relation

$$N_e=(4\pi a^2/e)\sigma_{e|\phi=0}, \tag{6}$$

Booth theoretical value (hereafter designated by $K_{B,e}$) was calculated for various N_e's at $[\mathrm{NaCl}]=5\times10^{-5}$ M, as a function of σ_a. The theoretical value was calculated also for the analytical charge number N_a for comparison ($K_{B,a}$). Values of $K_{B,a}$, $K_{B,e}$, and Einstein theoretical value, $K_E=\frac{5}{2}$, are also shown in Fig. 10(b). It can be seen from Fig. 10(b) that $K_{B,e}$ values are in fairly good agreement with the experimental ones for silica, while $K_{B,a}$ values are much larger than the observed values especially at high σ_a's. The difference between $K_{B,e}$ and experimental value is partly due to use of viscosity data at finite concentration. In fact, experimental values from latex at $\phi=0$ show satisfactory agreement with $K_{B,e}$. Thus the viscosity data were reasonably explained by Booth theory, when the empirical relation between the effective and analytical charge densities, Eq. (2), was used for the Na-silica system.

IV. CONCLUDING REMARKS

In the present paper, we have examined the surface charge of colloidal silica under salt-free conditions by means of electrical conductivity measurements and conductometric titrations. The ionizable group on the surface was weakly acidic and the effective charge density σ_e for the H-type silica was 8×10^{-8} C cm^{-2}. The analytical surface charge density σ_a increased with increasing concentrations of added NaOH. It was found that the concentration of Na and OH ions in the bulk were negligible when [NaOH] was smaller than 2.5×10^{-4} M and the volume fraction of the silica was larger than 2.6×10^{-3}. In other words, it was revealed that under these conditions we could control the σ_a value by varying [NaOH]. The value of σ_a at this threshold was 1.8×10^{-5} C cm^{-2}. An empirical relation between the effective and analytical charge densities, $\ln\sigma_{e|\phi=0}=0.49 \ln\sigma_a-1.0$, was derived for H-type latex system for $\sigma_a=(0.21-5.6) \times 10^{-6}$ C cm^{-2}. Viscosity measurements were performed for salt-free and low-salt dispersions at [NaOH]'s where the bulk ion concentrations were negligible. The σ_a dependence of the viscosity agreed well with the previous results obtained for ionic latices having various σ_a's. Satisfactory agreement was also obtained for the silica system between the experiment and Booth theory on the first-order electroviscous effect, when σ_e was calculated from σ_a by applying the empirical relation obtained above.

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