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Which Controls Conductivity of Sulfonic Latex Suspension, Hydrogen Ion or Latex Core?

*Xiaoyu Zhao, Koichi Jeremiah Aoki**, *Jingyuan Chen, Toyohiko Nishiumi*

Department of Applied Physics, University of Fukui, 3-9-1 Bunkyo, Fukui, 910-0017 Japan
*E-mail: kaoki@u-fukui.ac.jp

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The answer of the title by conductometry of the deionized suspension is that the latex core controls, although a major charge carrier in the suspension seems intuitively to be hydrogen ion. Our experimental result is supported partially by the thermodynamic theory that the conductivity should be proportional to squares of the charge number, z, per ion, where the net charge number of the sulfonate latex is of order of 10^5. In contrast, the ionic conductivity of the latex seems to be rather small because the diffusion coefficient, D, of the latex core is much smaller than D of hydrogen ion. In order to respond to this competition between z and D, we synthesized four kinds of polystyrene sulfonic latex, ranging from 1 to 3 μm in diameter. Conductivity of the deionized suspensions was evaluated from the dependence of an in-phase component of ac-impedance on inter-distances of two parallel wire electrodes. Then it did not include contribution of electric double layers or adsorption of latex. The values of z determined from the conductivity were 1 % of the loaded amounts of sulfonate moieties. They were proportional to a cube of the particle diameter. The relation of the ionic molar conductivity, $\lambda = Dz^2F^2/RT$, was confirmed by the proportionality of λ/D to z^2 for four latexes, and mono-ions. The conductivity was mainly provided by the latex anions rather than hydrogen ion.

Keywords: suspensions of latex particles; polystyrene-polystyrenesulfonic acid; ionic conductivity; ac impedance

1. INTRODUCTION

We review here the dependence of ionic conductivity on the charge number, z, [1] in order to understand the physical meaning of the dependence. The expression for the Ionic conductivity has been derived from the relation between the current and applied voltage, ϕ. The velocity, u, is caused by the balance of the electric force, $ze(\mathrm{d}\phi/\mathrm{d}x)$, in the electric field, $\mathrm{d}\phi/\mathrm{d}x$, and the Stokes' friction, $6\pi\eta r_o u$, for a spherical ion r_o in radius in the solution of viscosity, η. Then the velocity is expressed by $u = (Dze/k_BT)(\mathrm{d}\phi/\mathrm{d}x)$, where D is the diffusion coefficient given by $k_BT/6\pi\eta r_o$. On the other hands, the electric current density is given by $j = zeu$. Since u is proportional to ze as above, the current density is expressed by $j = (Dz^2e^2/k_BT)(d\phi/dx)$. Rewriting $e/k_B = F/R$, and defining the molar ionic conductivity $\lambda = jN_A/(d\phi/dx)$ for Avogadro constant N_A, we obtain

$$\lambda = Dz^2F^2/RT \qquad (1)$$

The square of z in Eq. (1) comes from the multiplication of the Coulomb's force by the external electric field and the charge amount transferred. The former is important in conductometry and electrophoresis, but is not often discussed in voltammetry.

Polyions such as SO_4^{2-} and PO_4^{3-} exhibit higher conductivity than mono-ions [1], according to Eq. (1). Polyoxometalates, of which stoichiometic charge numbers, n, are more than 7, are predicted to show high conductivity in voltammetry [2-6], as well as in solids [5-8]. However, conductivity larger than 49 ($=7^2$) times has not been obtained [2.3.8], because the charge number, z, effective to the conductivity is less than n. Polyelectrolyte has more charge in a molecule than polyoxometalates, and hence is expected to show high conductivity. However, the conductivity has been considered to be provided by counterions [7], because the charge is distributed widely in the polymer chains. An example of the role in the counterions is high permeation of hydrogen ion in Nafion or related films [7-12]. In contrast, ionic polymer microspheres, called latex, in solutions provide huge values of the loaded charge n per particle because their ions are localized on and /or in a sphere. Values of the net charge z are also huge if foreign ions are removed from the latex suspension sufficiently [11]. Then, the charge-charge interaction sometimes forms colloidal crystals with well-ordered structure [11]. The large values of z may generate high conductivity, according to Eq. (1).

Latex particles with redox sites are an electrochemical tool of finding properties of colloidal dispersion. They include polystyrenesulfonic acid [11-16], polyallyamine [15,16], ferrocenyl derivatives [15-19], polyacrylic acid [18,19], and polyaniline [18-21]. These redox reactions may be supported by conduction of not only of counterions but also charged latex particles. A determination of a role in the ionic conduction may be useful for evaluating voltammetric rate determining steps.

This report deals with a question about whether the conductivity of latex suspensions of polystyrenesulfonic acid varies with z or z^2 in the absence of foreign electrolyte. We synthesize four sizes of the latex in order to vary z. Conductivity of the deionized suspensions is evaluated from the dependence of an in-phase component of ac-impedance on inter-distances of two parallel wire electrodes in order to prevent contribution of electric double layers or adsorption of latex. The conductometric results will support the validity of Eq. (1), which leads to the conclusion that the latex particle be a predominant charge carrier rather than hydrogen ion. The conductivity of the deionized suspension can be applied to salt-free voltammetry of hydrogen gas.

2. EXPERIMENTAL

2.1. Chemicals

Water used was ion-exchanged at first, distilled and then ion-exchanged again by a ultrapure water system, CPW-100 (Advantec, Tokyo). The resistivity immediately after the ion-exchange was 18

MΩ cm. Styrene was distilled before the polymerization, according to ref. **Error! Bookmark not defined.**. Other chemicals were of analytical grade, and were used as received.

2.2.Synthesis of polystyrenesulfonate latex suspensions

A typical synthetic process was presented in our last paper [20]. The size of polystyrene particles was empirically controlled with concentrations of styrene, of the radical initiator (azobisisobutyronitrile) and of the stabilizer (polyvinylpyrrolidone), and with stirring speeds.

Purification was carried out by addition of pure water to the suspension, by centrifugation, and by decantation. The centrifugation was made at 4600 *g* with a refrigerated centrifuge, SRX-201 (Tomy, Tokyo) for 50 min. This process was repeated three times. Sodium ion in the suspension was replaced by hydrogen ion by adding 1 mol dm^{-3} HCl to the suspension, by being stirred gently for 14 h by centrifugation. In order to remove residual H^{+} and Cl^{-} thoroughly, the purification was repeated more than 5 times until the pH value of supernatant reached 7.

2.3. Measurements and instrumentation

Two platinum wires 0.1 mm in diameter were inserted into a suspension in parallel. The insertion length was 4 mm. Ac impedance between the two electrodes was obtained by varying the distance, according to the previous method [39,20]. This technique allowed us to eliminate capacitive component from the ac impedance data.

Hydrogen gas was bubbled in the suspension for 15 minutes. Voltammetry of hydrogen gas or latex suspension was observed at the Pt disk electrode 1.6 mm in diameter. A Pt coil was used commonly as a reference electrode and a counter electrode.

3. RESULTS AND DISCUSSION

3.1 Amount of sulfonate in latex particles

Aqueous suspensions of the latex particles were kept for one day without sedimentation. Shaking the vessel retrieved readily the dispersion. Figure 1 shows photographs of four kinds of latex suspensions by an optical microscope. The particles were uniform in size. The particles were arranged spontaneously in a crystal form. The smaller the particles, the faster the arrangement occurred.

Diameters of the latex particles were evaluated by means of the linear least square [20] for 10 points on a circular boundary of a spherical particle on the photograph. Their values were the average of 12 sampled particles in the wet state. The number concentration of particles in the suspension was determined by drying and weighing a sample volume of the suspension. The weight was converted into the volume by use of the density of polystyrene (1.05 g cm^{-3}) on the assumption that the density of the polystyrene sulfonate was the same as that of polystyrene. Then number concentration of a stock suspension was calculated.

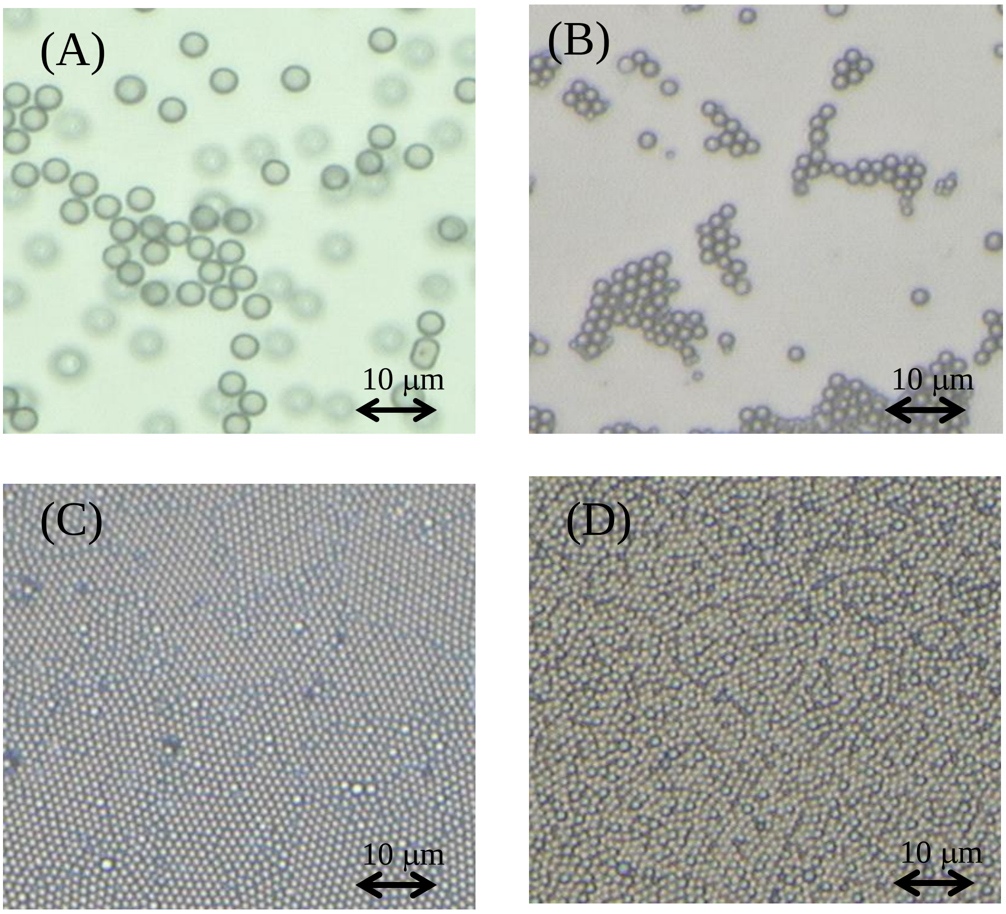

Figure 1. Photographs of suspensions of polystyrene-polystyrenesulfonic acid latex particles by the optical microscope. (A)-(D), corresponding to PSS1-PSS4.

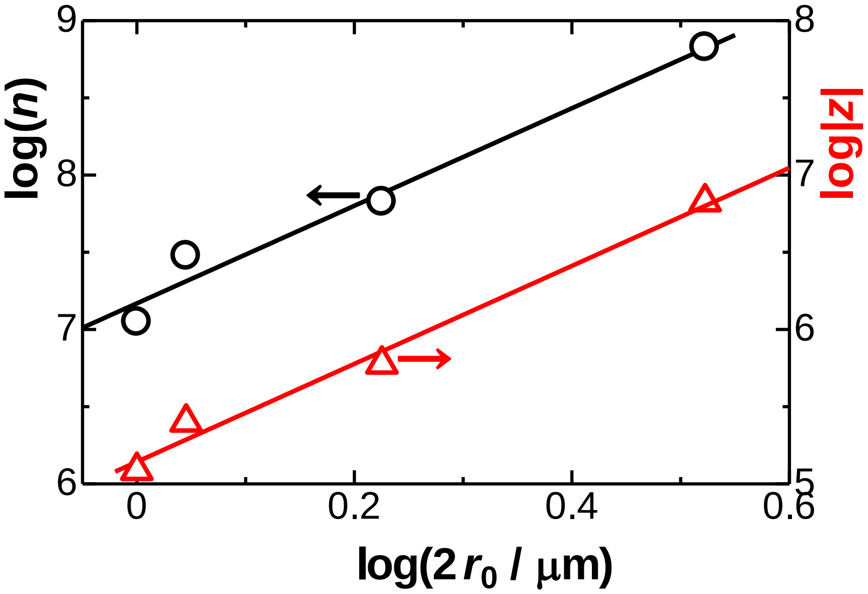

Figure 2. Logarithmic plots of n (circles: the number of the loaded sulfonate moiety per particle) and z (triangles: the number of fixed charge on the particle) against diameters of the latex particles, $2r_0$.

The amount of hydrogen ion on the latex particle was determined by titration with NaOH under monitoring of the conductivity of the suspension, as was made previously [39]. From the turning point of the titration curve, we determined number concentration of the sulfonate moiety per particle, n, and are listed in Table 1. Figure 2 shows logarithmic variation of n against the diameters. The plot has a linear relation with the slope of 3.1, indicating that the sulfonate moiety would be distributed uniformly in the spherical volume. The geometric structure predicted from the polymerization of styrene sulfonate on the polystyrene latex is of a core-shell form, which should exhibit the slope 2. Since a water drop located on powder of dried polystyrene latex penetrated readily into the powder, the synthesized polystyrene was hydrophilic owing to the added surfactant. The average molar concentration, c_{av}, of sulfonate moiety in the particle is shown in Table 1, together with the volume fraction of the particles at the synthesis. Sulfonate concentrations less than 10 mM suggest negligible interaction of sulfonate moiety. It varied complicatedly with diameters, volume fractions and n.

Table 1. Properties of four latex suspensions

	$2r_0$ 1)/ μm	volume fraction	n 2)	c_{av} 3)/ mM	Λ 4)/ S m^2 mol^{-1}	z 5)
PSS1	1.0_0	0.183_3	$1.1_2\times10^7$	4.4	$3.1_7\times10^{10}$	1.2×10^5
PSS2	1.1_1	0.057_5	$3.0_0\times10^7$	8.7	$1.1_4\times10^{11}$	2.5×10^5
PSS3	1.6_8	0.024_5	$6.7_2\times10^7$	5.6	$4.1_0\times10^{11}$	6.0×10^5
PSS4	3.3_3	0.017_3	$6.7_3\times10^8$	7.2	$2.5_1\times10^{13}$	6.7×10^6

1) r_0: radii
2) n: number concentration of the sulfonate moiety per particle
3) average molar concentration of sulfonate moiety per particle
4) "molar conductivity" of the suspensions
5) z: the number of dissociated hydrogen ions per particle

3.2 Effective charge of latex

Ac impedance of the well-deionized suspension between the two wire electrodes was obtained at zero dc voltage at the two-electrode system for the ac-voltage, 10 mV. The solution resistance between parallel two cylindrical wires a in diameter L in length separated by distance d is expressed by the following approximation [40]:

$$R_s = 0.916\frac{\log(d/a-1)}{Lc\Lambda} \qquad (3)$$

where Λ is the molar conductivity of the ion with concentration c. Figure 3 shows variations of the real part of the ac-impedance, Z_1, with log(*d/a*-1) for several frequencies. Values of Z_1 had a linear relationship with log(*d/a* -1), being supported partially by Eq. (3). The linear plot, however, does not satisfy the proportionality of Eq. (3) in the appearance positive intercepts at log(*d/a* -1) = 0 or $d = 2a$. The intercept may be ascribed to the capacitive properties at the electrode|solution interface [**Error! Bookmark not defined.**]. Our concern is not to the capacitance but to the resistance. The slope corresponds be $0.916/c\Lambda$, of which values were independent of frequency, as predicted for the property of solution resistance. We determined values of conductivity, $\kappa = c\Lambda$, averaged over frequencies more than 50 Hz from the slope, and listed them in Table 1. In order to compare these conductivity values with molar conductivities of ordinary ions, we divided the number concentration of particles by the Avogadro constant.

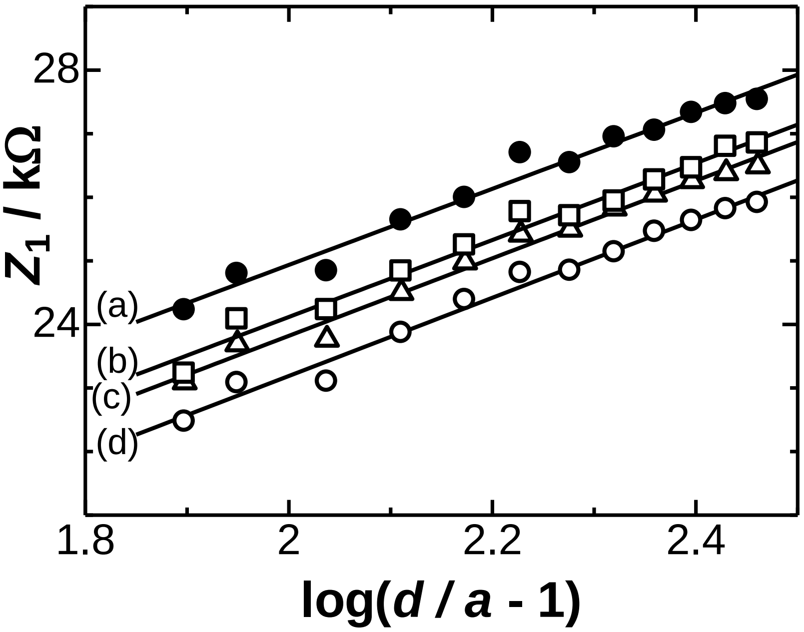

Figure 3. Variations of real part of the ac-impedance of the latex suspension (PSS3) with log(*d/a* - 1) for frequency *f* = (a) 200, (b) 500, (c) 1000 and (d) 4000 Hz, obtained at two wire platinum electrodes.

The concentration were to be equivalent to molar concentration if a latex particle could be regarded as a molecule. Then the "molar conductivity" calculated are listed in Table 1.

The values of the "molar conductivity" are extremely larger than those of ordinary ions (0.015 S m^2 mol^{-1} for KCl). This is because one particle occupies the huge number of negative charge of sulfonic acid. Figure 4 shows logarithmic plot of Λ against the diameters, r_o, lying on a straight line. The slope is 5.1, suggesting $\Lambda = kr_o^5$. This fact implies that larger particles should enhance extremely "molar conductivity".

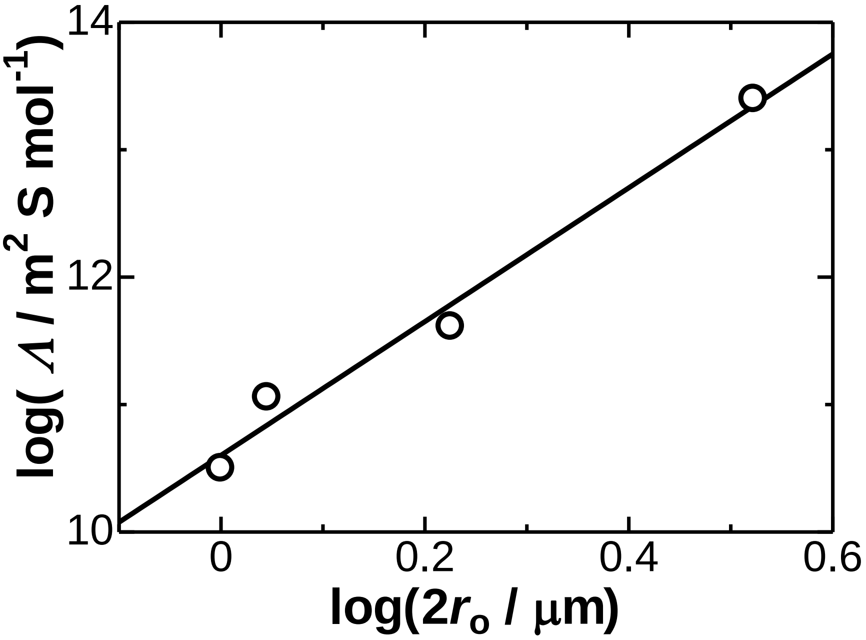

Figure 4. Logarithmic variation of "molar conductivity" of the suspensions with the diameters.

We define the molar conductivity of the latex suspension per N_A (Avogadro's number) latex particles as the sum of the molar conductivity of z free hydrogen ions, $z\lambda_H$, and the conductivity of N_A sulfonic latex particles, λ_L:

$$\Lambda_L = |z|\lambda_H + \lambda_L \qquad (4)$$

Ionic conductivity is generally represented in terms of the diffusion coefficient of the ion, D, through Eq. (1) [20]. Inserting $\lambda_H = F^2D_H/RT$ and $\lambda_L = F^2z^2D_L/RT$ into Eq. (4) yields

$$\Lambda_L = (F^2/RT)(zD_H + z^2D_L) \qquad (5)$$

where D_H and D_L are the diffusion coefficients of hydrogen ion and the latex particle, respectively. Applying the Stokes-Einstein equation for D_L, we estimated D_L for each latex sphere in water from the diameter. From the values of D_L, D_H and the experimental value of Λ_L, we evaluated z by solving the quadratic equation for z. The values are listed in Table 1 and plotted against the diameters on the right axis in Fig. 2. The slope of the line is 3.1, the same as for log(n) vs. log ($2r_0$). The ratio of z to n was 0.01, which can represent the dissociation of the sulfonic acid in a particle as

$(\text{-SO}_3\text{H})_n \leftrightarrow (\text{-SO}_3\text{H})_{n-z}\,(\text{-SO}_3^-)_z + z\text{H}^+$ (100 ↔ 99 : 1 : 1) (6A)

The ratio is invariant to the volume of the particle although the volume varies thirty times. By inserting $z = 0.01n$ in Eq. (6A), reaction (6A) is reduced to

$(\text{AH})_{100} \leftrightarrow (\text{AH})_{99}\text{A}^- + \text{H}^+$ (6B)

where A stands for -SO_3. The reaction (6B) suggests the law of mass action:

$K = [(AH)_{99}A^-][H^+] / [(AH)_{100}]$ (7)

for the equilibrium constant, *K*. $[H^+]$ is approximately proportional to the loaded concentration of the latex.

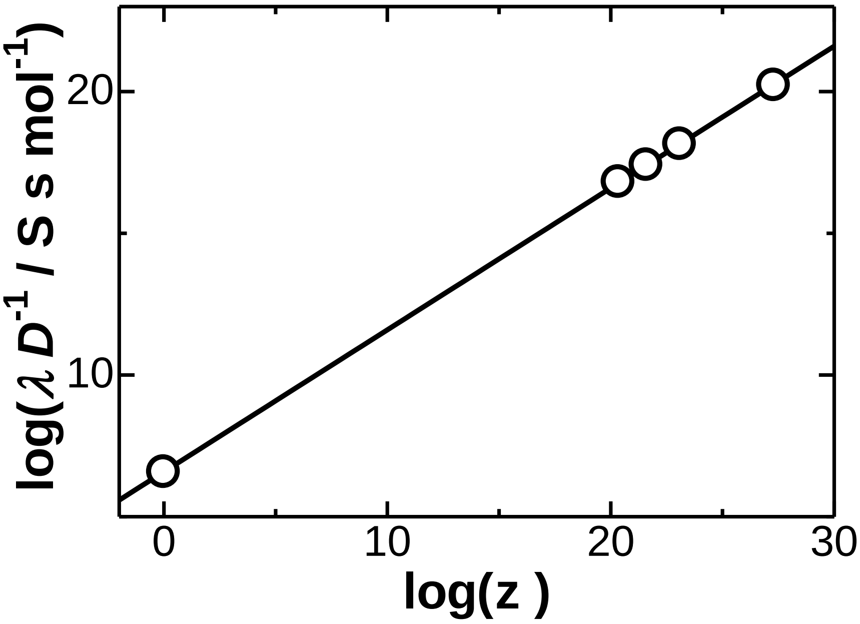

Figure 5. Logarithmic plot of λ/D against *z* for the four latex suspensions and halide ions.

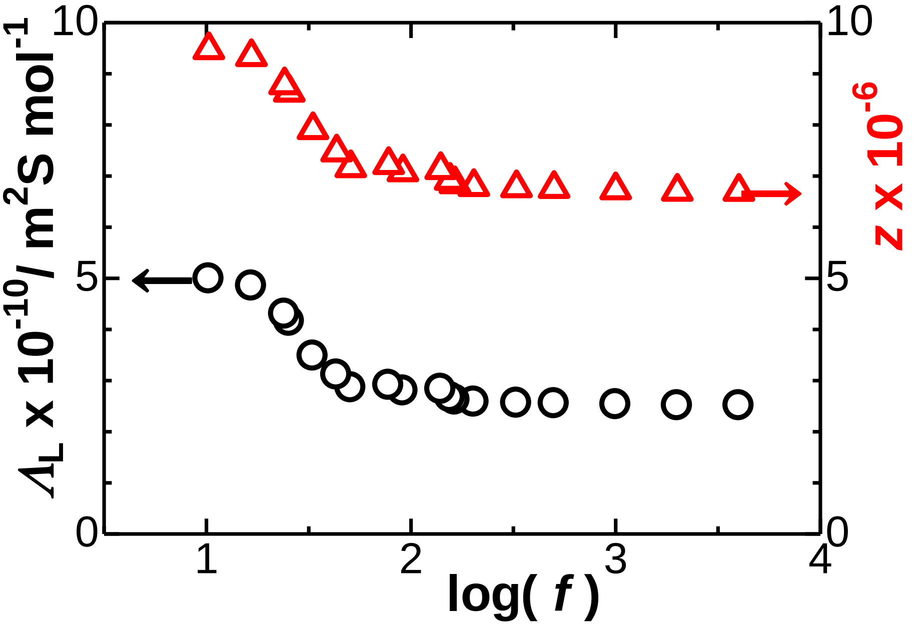

Figure 6. Variations of Λ_L and *z* of PSS4 with ac-frequency.

Known values of *z*, D_H and D_L allows us to separate Λ_L numerically into λ_H and λ_L in Eq. (5). According to Eq. (1), values of λ/Dz^2 ($= F^2/RT$) should be independent of diameters or other properties of particles. We plot the calculated values of λ_L/D against z for the four latex particles on the logarithmic scale in Fig. 5. They fell on a line with slope 0.5. The line passed through values of λ/D of F^-, Cl^-, Br^-, I^- and OH^- (for $z = 1$). Therefore Eq. (1) can be proved to hold even for huge values of z.

Values of Λ_L and z increase with a decrease in frequency for $f < 40$ Hz only for the largest latex, as is shown in Fig. 6. The conductance is mainly caused by formation of $(AH)_{100}A^-$ and H^+ through reaction (6B). If the formation period is longer than the measurement time, the conductance may be determined to be smaller values. The diffusion thickness of H^+ for 40 Hz or $t_1 = 0.025$ s is approximately $(D_H t_1)^{1/2} = 15$ μm, which is close to the average distance between two neighboring latex particles in the suspension. Longer measurement time lets reaction (6B) reach the equilibrium state. Since distances of the other three latex suspensions are less than 4 μm, no frequency-dependence was observed for the other three suspensions.

Dukhin and Goetz have discussed enhancement of conductivity by adding non-ionic surfactants with a help of dispersed alumina particles 1 μm diameter [20]. The charge number around the alumina particle is only 100, the enhancement is not due to the effect of z^2 but due to generation of protective solvating shells by non-ionic surfactants, as they insisted on. Dispersed particles, which are charged by ionic adsorbed species, shows high conductivity [20,21,22]. The conductivity is attributed to the alteration of molecular by the external ac field [**Error! Bookmark not defined.**]. The well-utilized models of conduction on ionic latex is the surface conduction by ionic motion on particles [20,21] and the hairy layer model [20]. They are still under debate, because experimental data include ambiguity, especially of discriminating the conductance from the capacitance [39,40].

3.3 Applications to voltammetry

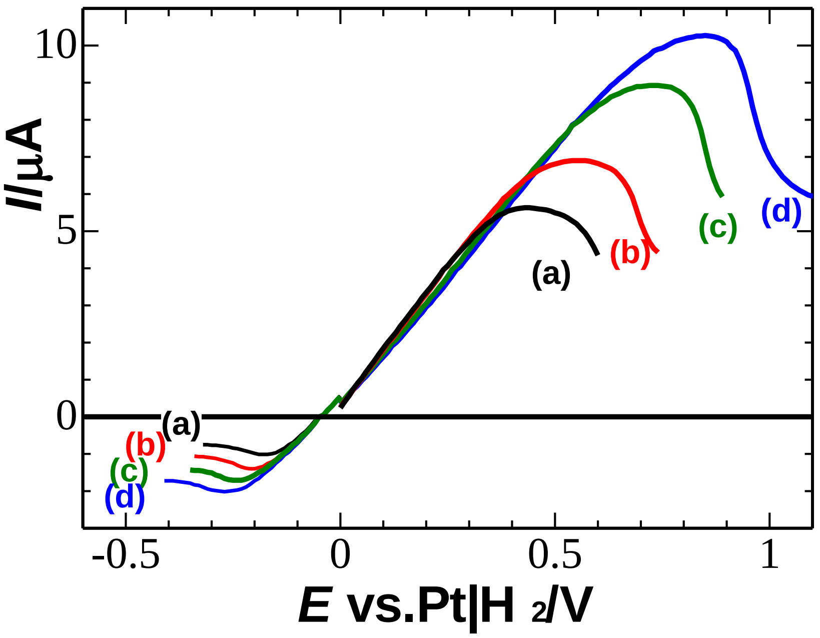

Figure 7. Voltammograms in the deionized suspension of PSS1 including saturated hydrogen gas at the platinum disk electrode for v = (a) 40, (b) 60 (c) 80 and (d) 100 mV s^{-1}.

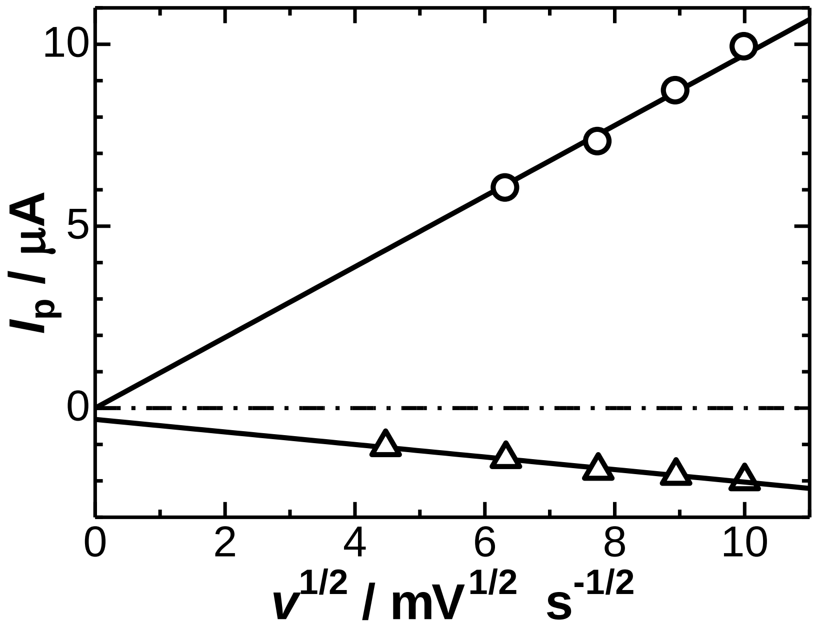

Figure 8. Dependence of peak currents for (circles) the oxidation of H_2 and (triangles) the reduction of H^+ on square-roots of the scan rates in the deionized suspension of PSS1 including saturated hydrogen gas at the platinum disk electrode.

It is predicted that the high conductivity of latex suspensions is useful for voltammetry without deliberate addition of supporting electrolyte. We selected hydrogen gas as a non-charged redox species. Linear sweep voltammograms in the latex suspension (PSS2) including hydrogen gas are shown in Fig.7, where the positive and the negative currents were scanned in the positive and the negative directions, respectively. The potential shift at the high scan rates may be caused by solution resistance. Although the concentration of H^+ was as low as 10^{-5} M, the voltammograms were obtained. Voltammograms in solutions of [HCl] = 10^{-5} M + saturated H_2 gas got an ohmic line. It is the latex particle that supports the appearance of the voltammetric peaks.

Figure 8 shows variations of the peak currents with the square-roots of the scan rates, v. The oxidation peak current was proportional to $v^{1/2}$, the suggesting diffusion-controlled current. The values of the oxidation peak currents were closed to those calculated from the diffusion-controlled equation of H_2 [41] for [H_2] = 0.5 mM at all the scan rates. In contrast, the reduction peak currents were not proportional to $v^{1/2}$ (with a non-zero intercept). Other steps than diffusion should control the peak current. A possible step is the dissociation kinetics in reaction (6B), which may be related with the delay of the conductivity, as shown in Fig. 6.

Figure 9 shows plot of the peak currents against the peak potentials for various scan rates. The points for each latex suspension fell on a given line. The slope should stand for the solution resistance [20,21]. The inverse slope of the line (c) gives the solution resistance, 85 kΩ, which is 2/3 of the solution resistance obtained by the ac-impedance at the voltammetric disk electrode, as shown in the inset of Fig. 9. The smaller values by the ac-impedance may be ascribed to the inclusion of the double layer capacitance in Z_1 [40] because the resistance was determined by the extrapolation of Z_1 to the infinite frequency in the Nyquist plot. Since the reduction peak current is not controlled by simply diffusion, as can be seen from the appearance of the intercept in Fig. 7, the slopes of the plots do not represent the resistance.

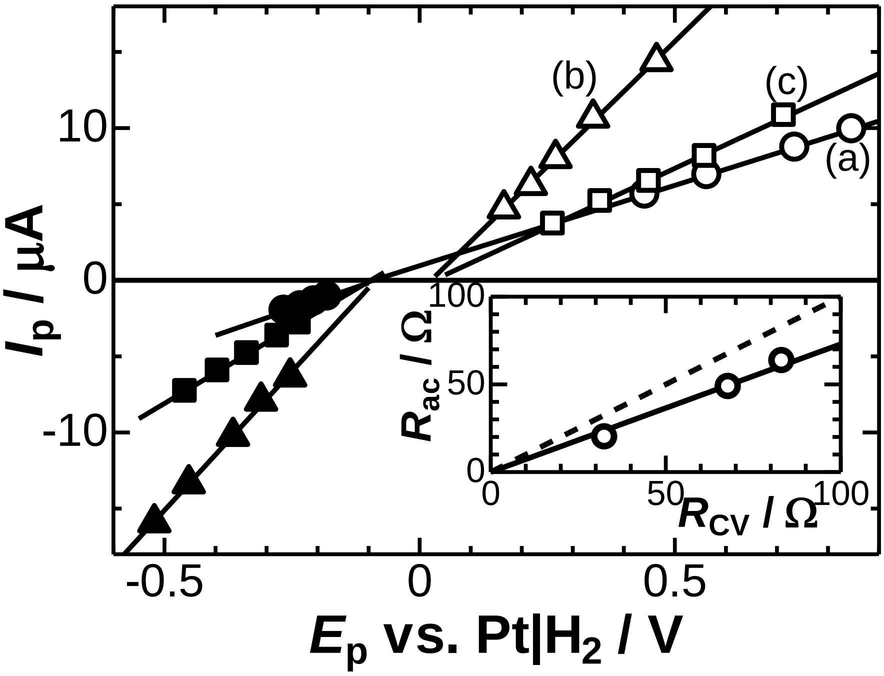

Figure 9. Plots of peak currents against peak potentials of voltammograms in the deionized suspension of (a) PSS1, (b) PSS3 and (c) PSS4 including saturated hydrogen gas at the platinum disk electrode for various scan rates. The inset is the plot of the resistance by ac-impedance against that by slope of I_p vs. E_p in CV.

4. CONCLUSIONS

Conductivity of deionized sulfonate latex suspension is mainly provided by the negative charge of the latex sphere. Although hydrogen ion can move much faster than the latex particle and its population is ca. 10^6 times larger than the latex particle, the hydrogen ion does not contribute to the conductivity. The reason is the proportionality of the conductivity to z^2, or in detail the relation $D_H/D_L < z$. Eq. (1) can be demonstrated by the proportionality in Fig. 5 for $1 \leq z \leq 7\times10^6$. The proportionality for this wide domain of z is ascribed to accurate measurements of the conductivity by changing distances between two wire electrodes. The value of z is 1 % of the amount (n) of the loaded sulfonate ion. Since it is proportional to the volume of the latex particle, the dissociation must occur within the particle volumetrically rather than on the particle surface.

The conductivity of the deionized latex suspension can support electrochemical reactions of hydrogen gas in water under the deionized conditions. Although the voltammograms are deformed by the solution resistance, the anodic peak current is controlled by diffusion.

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