Concentration-dependence of faradaic currents and conductivity in a polystyrene sulfonic latex suspension

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Abstract

The conductivity, κ, in a suspension of polystyrene sulfonic latex without supporting electrolyte showed a linear dependence on the volume fraction, v_f, of the latex for v_f < 0.03 with a finite intercept. In contrast, this deviated upward from the linear line for v_f > 0.03. These variations were qualitatively consistent with the dependence of the voltammetric reduction current of H⁺ on v_f without supporting electrolyte. The current values were only a few percent of the theoretical diffusion-controlled current that could be observed in the suspension with supporting electrolyte. This fact indicates the electrostatic immobilization of the hydrogen ions by sulfonic latex particles. A plot of the current against κ at common v_f values of v_f showed that the current for v_f > 0.07 was smaller than the value predicted from the conductivity. This can be explained in terms of a combination of the increase in electrostatically unbounded H⁺ estimated by conductance measurements and electric migration in which the electrochemical depletion of [H⁺] also causes the depletion of the latex.

Keywords: Polystyrene latex; Colloidal suspensions; Electrostatic immobilization; Conductance; Voltammetry; Reduction of hydrogen ion

1. Introduction

A physicochemical field of interest for polyelectrolytes is the electrostatic interactions [1,2] between polymer and polymer as well as those between polymer and counterion. This is conspicuous especially for suspensions of mono-dispersed microparticles when the foreign electrolyte is removed sufficiently from the suspensions. Then, the particles are well-ordered even in the solution phase [3–8], and are known as colloidal crystals. The ordering is provided by electrostatic interaction between neighboring charged particles. They exhibit a striking iridescence similar to precious opals [9] when the inter-distance between closest neighboring particles is of the order of the wavelength of visible light [10,11]. The iridescence is caused by optical interference of the diffraction from the ordered lattice, and has been analyzed quantitatively by diffraction theory [12], similarly to the method used with X-rays for molecular crystals. The formation of the crystalline structure indicates that counterions are immobilized around latex particles [13,14]. The immobilization of counterions obviously leads to a decrease in ionic mobility. This decrease has been observed as a decrease in the conductivity of the latex suspensions. The decrease is more remarkable with a decrease in concentration of supporting electrolyte, because the local ionic atmosphere near the latex particle is more structured against a uniform ionic distribution caused by supporting electrolyte [15,16]. The conductivity of the suspensions shows a linear relation to the molar fraction of the microparticles, and its slope, corresponding to the molar conductivity, decreases with the concentration of foreign electrolyte [17,18].

The faradaic current of a counterion is also a good measure of ion mobility [16,23] if the counterion is electroactive. The current is often measured at microelectrodes [19–26] because the microelectrode technique provides a well-defined current–potential curve without the use of deliberately added supporting electrolyte [27]. The reduction current of hydrogen ion in a polystyrene latex suspension decreased with a decrease in concentration of supporting electrolyte [23–25]. This observation

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can be explained as being due to either a very small diffusion coefficient of the large latex particle on which most of counterions are immobilized [23], or a very low concentration of the counterions which are not immobilized by the latex owing to local electric non-neutrality or trace amounts of foreign ions [26]. When the polystyrene sulfonic latex suspension is electrochemically reduced without supporting electrolyte, a red-shift of the interference light is observed [28]. In contrast, oxidation produces a blue-shifted iridescent light [28]. Furthermore, the current includes an activation process investigated by means of temperature-dependent measurements [25]. Therefore, features of the suspension determined by the current-probe are not exactly equivalent to those determined from the conductance. This report is devoted to comparison of the reduction current of hydrogen ion in the polystyrene latex suspension with the conductance under common experimental conditions when the suspension is completely deionized.

2. Experimental

2.1. Chemicals and synthesis of latex

The styrene monomer was distilled before polymerization. Water used was ion-exchanged in advance, distilled and then ion-exchanged again by CPW-100, Advantec (nominal resistivity 18 MΩ cm). Other chemicals were of analytical grade and were used as received.

The polystyrene sulfonate latex was synthesized as follows [25]: we mixed styrene (21.6 g), p-styrenesulfonate (0.225 g), K₂S₂O₈ (0.09 g), KH₂PO₄ (0.9 mg), KOH (0.284 g), NaCl (0.04 g) with water (128 g) in a N₂-purged vessel at 70 °C for 1 day. The coagulum was filtered from the mixture. The emulsion was kept for 1 day at 65–70 °C to hydrolyze the residual sulfate groups. The latex suspension included 9.3% of solid. The concentration of hydrogen ion included in the latex particle was determined by titration with NaOH under monitoring by a conductometer, HEC-110 (DKK, Tokyo). The diameter was evaluated with a dynamic light scattering (DLS) instrument, DLS-7000 (Otsuka Electronics, Osaka) to be 155±0.002 nm. The uniformity ratio [10] was 1.004. The TEM image of the particles showed full circles in the projected shape, of which the diameter agreed with the value by DLS.

Ionic exchange resins, Dowex 50W-X4 (H⁺ form) and Dowex 1-X4 (Cl⁻ form), were used for cationic and anionic exchange, respectively. Each resin was rinsed successively with water at 85 °C, 3 M NaOH aqueous solution, hot water, MeOH, cold water, 3 M HCl solution, hot water, MeOH, and cold water. Volumes of the NaOH solution, hot water, MeOH, cold water and the HCl solution were three times the volume of the resin. This cycle was repeated three times. In order to convert Dowex 50W-X4 into a H⁺ type, 3 M HCl was added to the thus prepared Dowex 50W-X4. In contrast, Dowex 1-X4 was converted into an OH⁻ form by addition of 3 M NaOH. The latex suspension to which the equivalent amount of both resins was added was stirred for 24 h and filtered. This process was repeated three times. Then we obtained a brilliantly iridescent suspension.

2.2. Conductometry

The conductometry was carried out in an optical cell (10 × 10 × 42 mm³), onto the opposite sides of which two Pt plates (0.5 × 10 × 40 mm³) were glued with epoxy resin. The relationship between the given volume, the electrode distance and height of solution level was calibrated with various water volumes. The cell was mounted in a glass flask filled with nitrogen gas. All the measurements were made at room temperature (r.t.).

Ac impedance was recorded with a combination of a home-made potentiostat and a lock-in amplifier (5210, EG&G). The equivalent circuit used was a series connection of a resistance, R, and a capacitance, C, of which impedance, Z, at angular velocity, ω, is expressed by

\[ |Z|^2 = R^2 + (\omega C)^{-2} \]  

(1)

The resistance and the capacitance were evaluated from plots of \(|Z|^2\) against \(1/\omega^2\). The plot did not show a straight line in the following cases: poor approximation of the series combination, frequency-dependent capacitance and a delay of the potentiostat. In order to examine the possibility of the delay of the potentiostat, impedance values were obtained for a dummy cell composed of a series combination of 100 kΩ and 39.5 nF at 10 mV amplitude in the frequency range from 50 to 600 Hz. The variation of \(|Z|^2\) with \(\omega^2\) showed an excellent line, implying negligible delay of the potentiostat.

Ac currents of the sample cell were measured at frequencies which were increased and then decreased between 50 and 600 Hz. In the case where hysteresis of the capacitance for the frequency variations occurred, we did not use these data. A main source of the hysteresis was the inclusion of air in the cell.

The conductance of KCl solutions with several concentrations (<0.05 M) was obtained in order to calibrate the cell and to justify the method. A linear variation of \(|Z|^2\) with \(\omega^{-2}\) was obtained. Values of the molar conductance of KCl for [KCl] < 0.02 M were in good agreement with the literature value [29].
2.3. Voltammetry

The working electrodes (WEs) were Pt microdisks commercially available (BAS, Tokyo). The reference electrode (RE) was a Pt coil. A saturated calomel electrode was used only to confirm the reproducibility of potentials at the Pt RE. The potentiostat used was an Autolab µStat.

Before voltammetric measurements, the WE was polished with alumina powder. Diameters of the WE were 10, 15 and 100 mm. The anionic and the cationic exchange resins were added to the suspension in a glass cell 10 mm in diameter and 40 mm in height in order to protect the deionized conditions from ionic contamination by air and leak of ions from the latex particles throughout the experiments.

3. Results and discussion

3.1. Conductometry

The latex suspension was titrated with standardized NaOH solution during measurements of its conductance, i.e. conductometric titration for evaluating the total amount of the bound surface charge [30,31]. Fig. 1 shows the variation of the conductance with amount of NaOH. The variation shows two clear lines except near the end point, indicating the strongly acidic behavior of the suspension. This is in contrast with conductivity and voltammetric currents in the deionized suspension, described later. From the end point, we estimated the total number of H⁺ per particle to be \( z = 6.64 \times 10^4 \) using the density of polystyrene, 1.05 g cm⁻³ [32]. We do not know whether the value of \( z \) is only at the surface of the particle or includes the inner charge of the particle. If all the sulfonic groups are exposed on a microscopically smooth surface of a spherical particle, one group occupies the average area, \( 4\pi r_o^2/z = 1.14 \text{ nm}^2 \), where \( r_o \) is the average radius of the latex particle (155 nm). This is 4.5 times larger than those of alkanethiol self-assembled films on a (111) gold surface, indicating a much smaller contribution of the van der Waals interaction between neighboring sulfonic groups than for self-assembled films.

Fig. 2 shows variations of \(|Z|^2\) with \( \omega^{-2} \) for two volume fractions, \( v_f \), of the suspension. Although, the variations are slightly convex, the intercept can be determined without ambiguity. Values of \( R \) and then conductivity, \( \kappa \), were obtained from the intercepts at various volume fractions.

Fig. 3A shows the dependence of the conductivity on the volume fraction in small values of \( v_f \), exhibiting good linearity. The intercept was identical with the value of \( \kappa \) only for the ion-exchanged water we used. This is 10 times larger than values of the ion-exchanged water conventionally available (\(<10 \mu \text{S cm}^{-1}\)). Our aim is not to evaluate accurately the conductivity of the suspension under strictly deionized conditions but to obtain a relationship between the conductivity and reduction currents of hydrogen ion under the common conditions. Therefore, we did not pursue the further purification of the suspension. The linearity in Fig. 3A shows the behavior of a strong acid [33]. The slope of the line gives a value corresponding to the molar conductivity except for a coefficient, according to the definition [29]. Obviously, the hydrogen ion contributes to the ionic conduction rather than the latex particle in the colloidal crystal. Thus the slope seems to be close to the ionic conductivity of hydrogen ion (34.96 mS m⁻¹) if the abscissa is replaced by \([\text{H}^+]\) via \( z = 6.64 \times 10^4 \). However, it is only 2% of the molar conductivity of \( \text{H}^+ \). Most (98%) of hydrogen ions may be immobilized electrostatically by latex particles so that they do not contribute to the conductance. This is the behavior of weak acids.

When the volume fraction was over 0.03, the conductivity deviated upwards from the line, as is shown in Fig. 3B. This tendency is opposite to Kohlrausch’s law [33]. There are two possible reasons to explain the upward deviation: leakage of ions latent in a latex sphere into the suspension [34], and destruction of the ionic atmosphere of \( \text{H}^+ \) in terms of stronger latex–latex interactions as if salts had been added to the suspension. No time-variation of the conductance was found, as is
described in Section 2. Thus, the former reason is not acceptable. As a further confirmation, the suspension at \( v_\ell = 0.025 \), which was prepared from dilution of the suspension at \( v_\ell = 0.1 \), showed the same conductance as plotted in Fig. 3B. The degree of the dilution should be proportional to the variation of the conductance. Therefore, the leaked ions make a negligible contribution to the increase in the conductivity. The predicted relation between the diameter (155 nm) and interdistance (250 nm) of particles at \( v_\ell = 0.1 \) is illustrated in the inset of Fig. 3B. The value \( v_\ell = 0.1 \) corresponds to 0.1 mM [H\(^+\)] if only 2% of the total H\(^+\) is dispersed freely in the suspension. Then the Debye length is 30 nm on the assumption of a 1:1 electrolyte. The ionic atmosphere with the Debye length is also shown in Fig. 3B (gray rings). The ionic atmospheres do not overlap, but are so close to each other that the edge of the exponentially decayed atmosphere can overlap. Then, a hydrogen ion in the partially overlapping domain is controlled electrostatically by some neighboring latex particles as if it were in the ionized solution.

3.2. Voltammetry

Voltammograms in the quiescent deionized latex suspension at microelectrodes are shown in Fig. 4. The reduction waves rise at \(-0.85 \) V and reaches a limiting current at \(-0.95 \) V at an electrode of 100 \( \mu \)m diameter. The half-wave potential shifted in the positive direction slightly with a decrease in the diameter or the current, probably because of lower \( IR \)-drop effects. The voltammograms at the 10 \( \mu \)m electrode were independent of potential sweep rate at sweep rates less than 100 mV s\(^{-1}\). Therefore, there is no \textit{convection} by electrophoresis on this time-scale. We attempted to use electrodes with different diameters (10 \( \leq a \leq 100 \) nm) at various potential sweep rates (5 \( \leq v \leq 300 \) mV s\(^{-1}\)) in order to find the best conditions to obtain well-defined steady-state voltammograms. We found that the best conditions in terms of reproducibility as well as appearance of a plateau of the limiting current were to use a larger electrode at a lower potential sweep rate. These conditions are understandable because a smaller electrode provides a higher current density or a higher density of the adsorbed hydrogen [25], which blocks the reduction of H\(^+\). Indeed, the limiting currents at smaller electrodes were underestimated. The underestimation was also found at higher volume fractions [25]. The use of larger electrodes did not guarantee a steady-state voltammogram. In order to confirm the validity of the steady-state currents, we measured the limiting currents, \( I_{\text{L}} \), at various sweep rates. The variations with \( v/2 \) are shown in Fig. 5, suggesting a slight dependence of \( I_{\text{L}} \) on \( v \) for any volume fraction. According to the theory of linear sweep voltammetry at microdisk electrodes [35], the condition, \((Fv/RTD)^{1/2} a < 0.2\), ensures steady-state currents with a 3% error. This corresponds to \( v < 5 \) mV s\(^{-1}\) for \( D = 9.3 \times 10^{-5} \) cm\(^2\) s\(^{-1}\) [29]. Therefore, voltammograms at \( v < 5 \) mV s\(^{-1}\) can be regarded as steady-state.

In order to confirm further the sweep rate dependence, current values calculated from Eq. (10) of Ref. [35] were plotted in Fig. 5 for data (c) by use of an adjustable parameter for the bulk concentration. Agreement is found. We used a 100 \( \mu \)m electrode at 5 mV s\(^{-1}\) for the experimental conditions.

Values of the limiting current at \( v = 5 \) mV s\(^{-1}\) are plotted against volume fractions in Fig. 6. The currents for \( v_\ell < 0.02 \) are proportional to the volume fraction whereas those for \( v_\ell > 0.03 \) deviate upward from the

![Fig. 3](image-url)  
Variation of conductivity with the volume fraction of the suspension for: (A) \( v_\ell < 0.0015 \); and (B) \( v_\ell < 0.10 \). The line in (B) is the regression line obtained for (A). The inset of (B) is an illustration of the predicted arrangement of particles (black circles) with ionic atmospheres (gray rings) at \( v_\ell = 0.1 \) on the assumption that particles are ordered in a close-packed structure. The relation between the particle distance: \( b \), and the radius: \( r_\ell \), of the particle in the inset of (B) was obtained from \((4\pi r_\ell^2/3) = 0.1(2^{1/2}/12)b^3 \) or \( r_\ell/db = 0.369 \).

![Fig. 4](image-url)  
Voltammograms of the deionized latex suspension with \( v_\ell = 0.042 \) at Pt disk electrodes: (a) 100; (b) 15; and (c) 10 \( \mu \)m in diameter. The potential sweep rate was 5 mV s\(^{-1}\).
proportionality. These variations are similar to those for the conductivity (Fig. 3B).

Next we compared the limiting current values with the theoretical equation for a conventional steady-state current at a microdisk electrode. If a fraction, \( f \), of all the hydrogen ions that might be released from the latex particle participates in the electrode reduction, the steady-state current without electric migration is expressed by

\[
I_L = -4FcfDa \tag{2}
\]

where \( c \) is the concentration of hydrogen ion obtained from the titration. However, the electrode reaction in the deionized suspension necessarily includes migration effects, and hence the current value should be larger than that found from Eq. (2) [36]. For example, four in Eq. (2) should be replaced by eight [37,38] when the redox couple is a 1:1 strong electrolyte without deliberately added supporting electrolyte. Therefore, Eq. (2) underestimates the current. Although, Eq. (2) includes this ambiguity, we used Eq. (2) for evaluating \( f \) from known values of \( I_L \), \( c \), \( D \) and \( a \), and plotted \( f \) against \( \nu_f \) also in Fig. 6. The values of \( f \) increased slightly from 0.015 and then reached 0.03 for \( \nu_f > 0.05 \). Those for \( \nu_f < 0.03 \) are close to the fraction of the conductivity (0.02) for the linear domain in Fig. 3. Consequently, the limiting current is apparently given by Eq. (2) as if the migration effect might be cancelled out with the immobilization effect.

In order to understand the relationship between the current and the conductivity, we plotted the limiting currents against the conductivities at a common value of \( \nu_f \) in Fig. 7. A good proportionality was found for \( \nu_f < 0.07 \), whereas the contribution of \( \nu_f \) to the conductivity for \( \nu_f > 0.08 \) was larger than that to the current. We can write this phenomenon as

\[
\Delta I(\nu_f > 0.08)/\Delta I(\nu_f < 0.08) < \Delta \kappa(\nu_f > 0.08)/\Delta \kappa(\nu_f < 0.08) \tag{3}
\]

The dynamic properties of the conductivity are similar to those of the steady-state voltammetric current in that both include ionic mobility or diffusion coefficients. In contrast, the voltammetric current is different from the conductivity in that it is associated with macroscopic mass transport. We might intuitively explain Eq. (3) in terms of mass transport of hydrogen ion, as follows: the electrode reduction depletes the concentration of hydrogen ion near the electrode. The depletion requires also a decrease in concentration of anions in order to retain the electrically neutral condition. Since the suspension has no supporting electrolyte, the only anion present is in the sulfonic latex. Then the volume fraction is decreased by making the distance between latex particles greater, as has been demonstrated by the optical interference [28]. However, this explanation is essentially the same as the conventional migration effect, and hence the limiting current should be proportional to the bulk concentration or \( \nu_f \). Therefore, considering only a migration effect fails to explain the variation of Eq. (3) satisfactorily.

If we accept the non-linear relation between \( \kappa \) and \( \nu_f \) (Fig. 3B) as a experimental fact, we can explain the variation in Fig. 7, as follows: we draw in Fig. 8 the illustrative dependence of both the conductance (solid curve) and the limiting current (dashed curve) on the volume fraction on such a scale that both values for \( \nu_f < 0.05 \) overlap on the basis of the experimental results. For a given volume fraction (0.096, arrow in Fig. 8), the concentration of \( H^+ \) participating in the conductivity is represented by point (A). The electrochemical reduction decreases the local volume fraction near the electrode.

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Fig. 5. Variation of the limiting current with square root of potential sweep rates in the deionized suspension for: (a) \( \nu_f = 0.012 \); (b) \( 0.034 \); (c) \( 0.051 \); (d) \( 0.068 \); (e) \( 0.085 \); and (f) \( 0.104 \), observed at the 100 \( \mu \text{m} \) electrode. The dotted curve was calculated from Eq. (10) of Ref. [35] for \( D = 9.3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \) and \( a = 0.05 \text{ mm} \).

Fig. 6. Dependence of the limiting currents (full circles) and ratios (open circles) of the currents to the theoretical values on volume fractions. The solid line was drawn by regression for \( \nu_f < 0.02 \).

Fig. 7. Relationship between the conductivity and the limiting current at common values of volume fractions. The numbers denote values of volume fractions.
owing to the depletion of [H\(^+\)] and the electric neutrality condition. Then the effective volume fraction decreases to point (B), and hence the concentration of H\(^+\) actually participating in the limiting current decreases to point (C) as a measure of the conductance. This concentration provides the net limiting current (D). Consequently, the current is lower than the value corresponding to [H\(^+\)] for the conductivity.

4. Conclusion

We found an upward deviation of the conductivity from the conventional proportionality between \(\kappa\) and \(v_f\) when \(v_f > 0.03\). This may be caused by destruction of the colloidal crystal due to the close approach of neighboring ionic atmospheres.

More reliable voltammetric currents of H\(^+\) were observed at a larger microelectrode, because the smaller current density decreases the surface density of adsorption species (H). Attention should be paid to using slow enough potential sweep rates to satisfy the steady-state condition. The limiting current was proportional to the volume fraction for \(v_f < 0.03\) (Fig. 6), where Eq. (2) is valid. In contrast, it showed an upward deviation from the proportionality for \(v_f > 0.03\). The upward deviation can be explained in terms of a combination of an increase in electrostatically unbound H\(^+\) estimated by the conductance measurement and the electric migration in which the electrochemical depletion of [H\(^+\)] also causes the depletion of the latex.

References