Electrostatic Immobilization of Hydrogen Ion on Latex

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When alkali metal counterions of sulfonated polystyrene latex particles (spheres with radius a) were replaced by hydrogen ion, the voltammetric current for reduction of the hydrogen ion without supporting electrolyte was only a few percent of the bulk-diffusion current of the equivalent concentration of hydrogen ion. The steady-state current at microelectrodes is much smaller than the diffusion current of completely dissociated hydrogen ion (property of a weak acid) and is much larger than the current by diffusion of the latex (property of a weak acid). The Debye–Hückel theory applied to the latex system predicts only the voltammetric property of a weak acid. We propose a model of a rigid spherical unit cell, in which a latex particle is surrounded with 2 hydrogen ions that obey the Poisson–Boltzmann (PB) equation without the electrostatic effect from the other latex particles. Linearization of the PB equation does not give satisfactory solutions, whereas numerical calculation without the linearization provides reasonable potential and polarization variations. The condition under which the reaction order of the dissociation of the hydrogen ion is unity is that the hydrogen ion in the segment r > 4.2a participates in the electrode reaction and that the ions in the segment a < r < 4.2a are bounded to the latex particle.

Introduction

Development of synthetic monodisperse polymeric latex particles has played a vital role in exploring various properties of colloidal dispersions, such as the phase transition between crystal and melt, the interaction between particles, and the establishment of a specific phase by shear stress. Sulfonated polystyrene latex has been synthesized with a uniformity of 1.01 in diameter, which corresponds to a uniformity of 1.02 in surface charge. The ordered structure of particles in latex dispersions has played a vital role in exploring various properties of colloidal dispersions, such as the phase transition between particles, and the establishment of a specific phase by shear stress. Sulfonated polystyrene latex has been used to evaluate the diffusion coefficient, Video-supported observation of the displacement of particles can be observed readily with a microscope. Observation of trajectories of particles demonstrates the coexistence of ordered and disordered states as well as the interaction of neighboring particles. These findings support the introduction of an attractive force between identically charged particles. Highly quantitative data for investigating the attractive force have been acquired using dynamic light scattering, which can determine the central positions of the particles. Since the ordered distribution of the latex particles is claimed to arise from the cooperation of the particles with the counterions, investigating a measurable property of the counterions may provide information on the latex structure. When counterions of charge-stabilized colloidal particles or polyelectrolytes are replaced by hydrogen ion using exchange, the hydrogen ion can be monitored by electrochemical techniques, not only under equilibrium conditions as in potentiometry but also under dynamic conditions as in voltammetry. When the solution does not contain supporting electrolyte, the voltammetric current for the reduction of the hydrogen ion as a counterion to a polyelectrolyte anion is smaller than the current in the polyelectrolyte-free solution with the

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equivalent concentration of hydrogen ion. The decrease in the current has been ascribed to electrostatic immobilization of hydrogen ion to the macroion. This immobilization is relaxed with the addition of supporting electrolytes because of replacement of the hydrogen ion by the supporting cation. A monodisperse latex with well-defined crystal structure may immobilize hydrogen ion to a greater extent due to long range order in the suspension, and hence should decrease the current. The sulfonated polystyrene spherical latex in the deionized suspension shows only a few percent of the bulk-diffusion current of the equivalent concentration of hydrogen ion, whereas the linear polystyrene sulfonic acid shows 35% of the current. Thus, the rigidity of the spherical particle is also important in suppressing the current. Observed ionic properties in the monodisperse latex studied are as follows:

(a) Each particle had a charge of $-7.73 \mu C \text{cm}^{-2}$, corresponding to $1.17 \times 10^{10}$ ($=Z$) electrons per particle, which was electrically neutralized by the same amount of hydrogen ion.

(b) The steady-state current for the reduction of hydrogen ion was observed.

(c) Current values in the deionized suspension, where iridescent appearance, ranged from 2.4% to 4.6% of the bulk-diffusion-controlled current value.

(d) Current values increase linearly with the molar fraction of supporting electrolyte. We suggest that the electrostatic interaction between hydrogen ion and the latex is responsible for the suppression of the current (c). This idea explains consistently all of the electrochemical behavior. It is the basis for a model that predicts how much the current is suppressed by the electrostatic force and under which conditions. In this work, we develop a model that describes the electrostatic interactions responsible for suppression of the current drawn at the microelectrode.

Experimental Section

Synthesis and characterization of the latex have been described in detail previously. Briefly, the latex is a suspension of monodisperse (44 nm radius) polystyrene particles in water. The surface of the particles is covered with sulfonic acid groups, which dissociate to give polystyrene ions in the water phase and a negatively charged part with a surface charge density of $-7.73 \mu C \text{cm}^{-2}$ (11 700 electrons/particle). Suspensions containing only the latex particles and hydrogen counterions, without deliberately added electrolyte, are referred to as deionized. All water used for rinsing glassware and preparing solutions had a resistivity of 18 M\(\Omega\)cm (Millipore, Bedford, MA). Platinum disk microelectrodes with radii, \(r_p\), of 5.5 and 10.5 \(\mu m\) were polished to a smooth finish with a 0.25 \(\mu m\) diamond suspension (Buehler, Lake Bluff, IL) immediately before use. The electrodes were inspected with an inverted metallurgical microscope (Leitz, Diavert) to ensure the surface was free of debris. A Pt wire served as both the counter and quasi-reference electrode. The latex suspension and \(\text{HClO}_4\) solution volumes were 5 cm\(^3\). To assess the diffusion behavior of hydrogen ion in the latex suspension, \(\text{HClO}_4\) solution was used as a reference system. Parallel experiments were carried out in each system, neither of which contained deliberately added electrolyte. Voltammetric and chronoamperometric experiments were carried out using a PAR 273 potentiostat, controlled with in-house software on a PC computer. The measured current was amplified by means of a Keithley 427 current amplifier. For chronoamperometric experiments, a current amplifier with a rise time of less than 0.3 ms caused no delay in the current response at times longer than 20 ms in the \(\text{HClO}_4\) reference system. The rise time of 0.3 ms was selected; a shorter rise time lowered the ratio of signal to noise. With this arrangement the sampled current flowing through a dummy cell was quantitatively that expected for the RC combination employed. Steady-state staircase voltammograms for the reduction of hydrogen ion in the latex suspension, and in \(\text{HClO}_4\), were carried out before chronoamperometric experiments in order to find the mass-transport-limited region of the voltammogram. A staircase amplitude of 5 mV and a sampling frequency of 1 Hz were employed. For the chronoamperometric experiments, the potential was stepped from a region in which no Faradaic reaction occurred to a potential in the limiting current plateau of the voltammogram. Stepping the potential to more negative potentials showed a slightly steeper current response at short times (less than 0.5 s). This suggests involvement of a capacitive component. At longer times, the current converged with current values measured at less negative potentials. Thus the ohmic drop was not significant on the time scale of the experiment. Measurements of particle electrophotometric mobility were carried out using a Malvern ZetaMaster IV. The z-potential corresponding to the measured mobility was estimated from the theory of O'Brien and White (Figures 3 and 4 of ref 22).

Results and Discussion

Voltammetric Behavior. The latex with negative charge is neutralized by cations in spatial average. If the neutralization occurs locally on a molecular scale and the counterions are immobilized, the behavior with respect to the hydrogen ion resembles that of a weak acid. In contrast, if the averaged space is spread to the solvent and includes dynamic exchange between bound and unbound ions, the behavior of the hydrogen ion should be that of a strong acid. Voltammetric reduction of a strong acid shows a diffusion-controlled current for hydrogen ion in the bulk, whereas that of a weak acid shows, at sufficiently short times, a kinetic current from the dissociation or diffusion-controlled current of the weak acid. To find which behavior the latex has, voltammetry at two microdisk electrodes of different sizes was carried out without deliberately added supporting electrolyte. Voltammograms were sigmoidal, as shown previously. The limiting current values were proportional to the diameter of the electrodes rather than the area, indicating spherical diffusion control. Staircase voltammograms at a large Pt electrode showed a peak, although their shape was not well-defined. The distortion is obviously ascribed to an ohmic drop in the absence of supporting electrolyte. The peak current was proportional approximately to the potential sweep rate for sweep rates less than 45 mV s\(^{-1}\). Therefore, the current is controlled by diffusion rather than by the kinetics of dissociation of hydrogen ion from the latex. First, we assume that the current is controlled by diffusion of the latex which releases hydrogen ions only when it arrives at the electrode. This behavior is akin to that of a weak acid. Then we estimate the diffusion coefficient by use of the expression of the steady-state current \(I = 4zF \varepsilon \rho_i D_e \rho_r\), where \(\varepsilon\) is the bulk concentration of the latex, \(D_e\) is the diffusion coefficient of the latex, and \(\rho_r\) is the radius of the microdisk electrode. From the experimental value of \(I\), we obtained \(D_e = 2.8 \times 10^{-10}\) m\(^2\) s\(^{-1}\). This corresponds to values of Keggin-type heteropolyanions of (XM\(_{12}\)O\(_{40}\))\(^{4-}\) (\(X = \text{Si and Ge}\), M = Mo and W), for which radii are approximately 1 nm. It is assumed that \(D_e\) is governed by the Stokes–Einstein relation \(D = k \rho T / 6\pi \eta a\), where \(\eta\) is the kinematic viscosity of the medium and \(a\) is the radius (44 nm) of the latex.
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Without spatial restriction. The too small value of which is only 5% of the surface of the latex area. Thus, immobilization of the hydrogen ion has been recognized by and partially free from the latex on the voltammetric time scale of these steady-state experiments. The partial acid. In other words, hydrogen ion is partially immobilized behavior between the two extremes of a weak and strong mental value. That is, the voltammetry shows the behavior between the two extremes of a weak and strong acid. In other words, hydrogen ion is partially immobilized by and partially free from the latex on the voltammetric time scale of these steady-state experiments. The partial immobilization of the hydrogen ion has been recognized and is expressed quantitatively as the fraction f of free hydrogen ion.7 The value of f of a latex similar to the present latex is 0.13, which was obtained from transference measurement.7 However, this value is much larger than the fraction (1/30) of steady-state current of the free hydrogen ion. Therefore the f value is different from the fraction of the voltammetric current.

Unsuccessful Explanation of the Voltammetric Results by Debye–Hückel Theory. As a measure of the localization of counterions, we apply the Debye–Hückel theory to the present system. According to the definition of the Debye length, 27 \( \kappa^{-1} \), it is given by

\[
\kappa^{-1} = \left( \frac{q^2 n_0 (1 + Z)}{k_B T \epsilon_r \epsilon_0} \right)^{1/2}
\]

where q is the elementary charge, \( n_0 \) is the number density of hydrogen ions at uniform distribution without an electric potential, \( \epsilon_0 \) is the vacuum permittivity, and \( \epsilon_r \) is the dielectric constant of the medium. The value of \( \kappa^{-1} \) calculated for the volume fraction 0.237%, corresponding to \( q = 0.13 \text{ mM} \) of the neutralizing hydrogen ion, is 0.35 nm at 25 °C, and \( \epsilon_r = 78.5 \). This value is comparable with the closest distance of two oxygen atoms in water (0.30 nm), according to the peak of the radial distribution function of water.28 If Z hydrogen ions are arranged on a plane, the occupied area is \( 18 n_0 A = 1.1 \times 10^{-15} \text{ m}^2 \), which is only 5% of the surface of the latex area. Thus, all of the hydrogen ions can be confined to the latex surface without spatial restriction. The too small value of \( \kappa^{-1} \) comes from the large value of Z, indicating that \( \kappa^{-1} \) has no specifically physical meaning for the present latex suspension. However this image is inconsistent with the electrochemical observation. The Debye–Hückel theory has some restrictions; two of which are pertinent to the present system: (A) except for the test (reference) ion, the medium is a continuum without ion size, and (B) the Boltzmann term is linearized. Since the latex forms a macroscopic ordered structure, assumption (A) should be modified. Also, the value of Z in the present case is extremely large, so even a small value of the potential causes a large variation in the Boltzmann factor. Thus linearization (B) is not valid. We take into account these two points and proceed by solving the PB equation.

Non-neutralized Charge Distribution Model. The Debye–Hückel theory assumes a continuum medium or an assembly of infinitely small charges except for the object particle, to which the PB equation is applied. To account for the effect of the ordered structure, the medium should be partially ordered, except for freedom of the ion distribution. We propose the model of a rigid unit cell in which a latex particle is centered, as shown in Figure 1. The latex particle is surrounded with Z hydrogen ions that obey the PB equation in the unit cell. Since the rigid cell does not share any charge of the neighboring latex particles, each cell is independent electrostatically. Therefore, the local electric potential \( \phi \) at the cell outer boundary \( r = b \) has the periodic condition

\[
\frac{d \phi}{dr} \bigg|_{r=b} = 0
\]

The spherical shell in the range \( a < r < b \) is occupied by only the hydrogen ion, which obeys the Boltzmann equation

\[
\rho = q n = q n_0 \exp(-q \phi/k_B T)
\]

where \( n \) is the spatially dependent number density of hydrogen ions. Then Poisson’s equation in spherical coordinates is given by

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d \phi}{dr} \right) = -\frac{q n_0 \exp(-q \phi/k_B T)}{\epsilon_r \epsilon_0}
\]

Although the charge within the shell \( a < r < b \) does not satisfy the electrical neutrality, the charge in a whole cell is satisfied in terms of the surface charge on the latex \(-Zq\) at \( r = a \):

\[
\frac{d \phi}{dr} \bigg|_{r=a} = \frac{Zq}{4 \pi a^2 \epsilon_r \epsilon_0}
\]
At first, the linear approximation is applied to test its validity. If the value of \(q\phi/k_B T\) in eq 4 is smaller than unity, linearization with respect to \(-q\phi/k_B T\) leads to

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\phi}{dr} \right) = \kappa^2 \phi - \frac{q n_0}{\epsilon_r \epsilon_0} \tag{6}
\]

where

\[
\kappa = \sqrt{\frac{q^2 n_0}{k_B T \epsilon_r \epsilon_0}} \tag{7}
\]

The term \(q n_0 \epsilon_r \epsilon_0\) arises from non-neutralization in \(a < r < b\), and it plays a role in screening the interactions between colloidal particles. The neutralization is completed in \(a < r < b\). The numerical value of the distance is given by \(\kappa^{-1} = 38 \text{ nm}\), being \([1/(Z + 1)]^1/2\) times \(\kappa^{-1}\) (in eq 1). In comparison with \(a = 44 \text{ nm}\), this gives the image of an extended distribution of the hydrogen ion rather than the adsorbed hydrogen ion. The solution of eq 6 has the form

\[
\phi = \frac{1}{r} \left( c_1 e^{-r/b} + c_2 e^{r/b} \right) + \frac{k_B T}{q} \tag{8}
\]

The constants \(c_1\) and \(c_2\) were determined by conditions 5 and 2 to give

\[
c_1 = \frac{Z q (b \kappa - 1)}{4 \pi \epsilon_r \epsilon_0 B}
\]

\[
c_2 = \frac{Z q (b \kappa - 1)}{4 \pi \epsilon_r \epsilon_0 B}
\]

\[
B = (a \kappa - 1)(b \kappa + 1)e^{-(b-a)} - (a \kappa + 1)(b \kappa - 1)e^{-(b-a)}
\]

Figure 2 shows the variation of \(\phi\) for experimental conditions of \(n_0 = 7.77 \times 10^{22} \text{ m}^{-3}\), corresponding to the volume fraction of 0.237%, which is equivalent to \(b = 330 \text{ nm}\). Since the boundary conditions were given by the fluxes (electric field) rather than potentials, \(\phi\) varies from negative to positive values. The potential at the latex surface approaches \(\approx 2.23 \text{ V}\), equivalent to \(q\phi/k_B T = -87\). This is in consistent with the condition of the linearization \((q\phi/k_B T < 1)\). Since the values of \(q n_0 \exp(-q\phi/k_B T)/\epsilon_r \epsilon_0\) are larger than those of \(\kappa^2 \phi\) in the linearized equation, the accurate \(\phi\) versus \(r\) curve should exhibit larger curvature than the linearized \(\phi\) versus \(r\) curve. Consequently, the potential difference across the double layer, \(\phi(b) - \phi(a)\), might be smaller than that given by the linearized form of the PB equation.

Under this prediction, eq 4 was solved numerically by combining the finite difference and Newton–Raphson methods. By change of the variables \(\xi = r/a\) and \(\psi = (q/r a k_B T)\phi\), we rewrote eq 4 as \(d^2\psi/d\xi^2 = -(a \kappa)^2 \psi \exp(-\phi/\xi)\). The N-digitized finite difference form is given by

\[
\psi_{i+1} - 2 \psi_i + \psi_{i-1} = -(\Delta \xi a \kappa)^2 \psi_i \exp(-\psi_i/\xi) \tag{9}
\]

for \(1 \leq i \leq N - 1\), where \(\Delta \xi = (b - a)/a N\). The boundary conditions were

\[
(\psi_1 - \psi_{-1})/2 \Delta \xi - \psi_0 = Z k^2/4 \pi a n_0 \text{ at } i = 0 \tag{10}
\]

and

\[
(\psi_{N+1} - \psi_{N-1})/2 \Delta \xi - (a/b) \psi_N = 0 \text{ at } i = N \tag{11}
\]

The quantities \(\psi_{i+1}\) and \(\psi_0\) were eliminated from these boundary conditions and eq 9 for \(i = 1\) and \(i = N\). Initially, \(\psi_i\) was assigned the value 0. We evaluated the unknown \(\psi_i\), on the right hand side of eq 9 for given values on the left hand side using the Newton–Raphson method. This process was iterated until errors were less than \(10^{-5}\). When \(N\) was changed from 40 to 150, only digitization errors were observed. The potential profile is shown in Figure 2 (solid curve). The curvature is larger than that obtained from the linearized PB equation, and hence the variation of \(\phi\) is smaller. The potential at \(r = a\) is \(-0.207 \text{ V}\), an acceptable value in the sense of the electrochemically controllable measurement. This may be contrasted with the physically realistic value of \(-2.23 \text{ V}\) obtained from the linearized PB equation. Note that the nonlinearized \(\phi\)-curve is close to the value of \(-0.210 \text{ V}\) for the \(\xi\)-potential, which was determined by the balance with the external electric field. The relationship between the \(\xi\)-potential and the calculated potential at \(r = a\) will be discussed in a forthcoming paper. Most of the variation of \(\phi\) occurs in the domain \(r \ll \kappa^{-1}\).

The distribution of the concentration of hydrogen ion evaluated from \(n = n_0 \exp(-q\phi/k_B T)\) is shown in Figure 3. The concentration at \(r = a\) reaches \(10^5 n_0\), equivalent to 1 M. The domain for \(n > n_0\) is \(r \ll \kappa^{-1}\), indicating that \(\kappa^{-1}\) is a reasonable measure of the thickness of the excess.
concentration. The concentration of counterions at the potential \( q_0 = k_0 T \) has often been discussed because the concentration (or the potential), which is balanced by thermal fluctuations, is a characteristic in the PB equation. This concentration, given by \( n = n_0 e \), was at \( r_1 = 2.08a = 92 \) nm. The electrostatic energy is larger than the thermal energy in the domain \( r < 2a \). The concentration at the cell boundary \( r = b \) is only about 0.034\% for volume fractions less than 1%. This value is close to the current ratio described in the Introduction (feature c). It is therefore plausible that the concentration at the cell boundary is responsible for the voltammetric current.

Two-Layer Model. When the latex diffuses to the electrode, maintaining electrical neutrality except in the double layer at the electrode, it should generate a concentration distribution. Therefore, the local volume fraction in the diffusion layer decreases or the local value of \( b \) increases as the latex approaches the electrode. As shown in Figure 4, the concentration of hydrogen ion at the cell boundary, \( c_{H}^b/c_{H}^d \), decreases rapidly with \( b \). Since the cell volume, \((4\pi/3)b^3\), is, by definition, inversely proportional to the concentration of the latex, Figure 4 represents implicitly the relation of the concentrations of both species. The primary relationship of concentrations is a reaction order. To evaluate the reaction order, a logarithmic plot is shown in the inset of Figure 4, exhibiting excellent linearity with the slope \(-2.68\). It follows that \( 2.68/3 = 0.89 \) is the number of latex particles required to release one hydrogen ion through the equilibrium \( c_0^b = K_0^b \), where \( c_0 \) is the local concentration of the latex and \( K \) is the equilibrium constant. As the hydrogen ion is in equilibrium with the latex, the flux, \( dc_0/d\tau \), at the electrode should be proportional to \( dc_0/d\tau \). However, a given value of \( dc_0/d\tau = k \) provides \( c_0 = [k(r - a)]^{1.089} \), which leads to \( dc_0/d\tau \) or no current. Consequently, the stoichiometric coefficient should be unity. This contradiction leads to the following argument. The noninteger stoichiometry 0.89 was based on the assumption that only the concentration of hydrogen ion at the cell boundary could participate in the electrode reaction. We therefore assume that \( c_0 \) in a wider domain participates in the electrode reaction. We searched the domain of the concentration so that the stoichiometry was unity by averaging spatially the concentration as follows

\[
(c_0)_{av} = \frac{3}{4\pi(b^3 - \frac{1}{12}r_1^3)}\int_{r_1}^{b} 4\pi r^2 c_0 \, dr \tag{12}
\]

Figure 4. Dependence of the concentration at the cell boundary, \( c_{H}^b/c_{H}^d \), on \( b \), and the logarithmic plot (inset). It was calculated from eq 9 for various values of \( b \) at the volume fraction of the latex 2.37% and \( a = 44 \) nm.

Figure 5. Variation of \((c_0)_{av}\) with the volume fraction \( \nu_l \) of the latex for \( a = 44 \) nm. Circles denote the ratio of the measured steady-state current in the deionized latex suspension to the current in a 0.1 M LiClO4 + latex suspension. The solid curve was computed from eq 12.

Figure 6. Chronoamperometric curves and Cottrell plots (inset, taken from 15 data points) for the reduction of hydrogen ion at a Pt disk, \( r_p = 10.5 \) \( \mu \)m in 70 \( \mu \)M HClO4 solution (C), and in the deionized latex suspension (A), containing 1.26 mM hydrogen ion (volume fraction 2.25%). In both experiments the potential was stepped from \(-0.4 \) V to \(-0.1 \) V versus Pt wire. Then the concentration averaged from radius \( r_1 = 4.2a \) to \( b \) showed unity stoichiometry, regardless of values of \( b \). In other words, the hydrogen ion in this shell can be charge-transferred at the electrode, whereas those ions in the domain from a to 4.2a are trapped electrostatically by the latex. This separability of the domain proposes a two-layer model: the electrochemically inactivated hydrogen ion for \( r < 4.2a \) and the activated hydrogen ion between 4.2a and \( b \). The boundary of the two layers depends on \( b \) rather than \( b \), being independent of the volume fraction. Figure 5 shows the variation of \((c_0)_{av}\), the volume fraction of the latex. The predicted value is close to the experimental values of the current ratio. To estimate the freedom of the hydrogen ion in the outer shell, chronoamperometry was carried out at the microdisk electrode in the latex suspension and the HClO4 solution without supporting electrolyte. It is intuitively predicted that the decay of the current in the latex suspension is slower than that in the HClO4 because the ratio of the diffusion coefficient of the latex to that of ClO4- is estimated to be 0.003. The concentration of HClO4 was 70 \( \mu \)M, at which the steady-state current was the same as that in the latex suspension. Figure 6 shows that the transient curves in both systems exhibit similar decays. As shown in the inset of Figure 6, the plot of \( I \) at short times against \( t^{-1/2} \) fell on a straight line, demonstrating
simple diffusion-control. Subtraction of the background current in a solution of 70 μM LiClO₄ was also confirmed to be Cottrellian. Six Cottrell plots measured in the deionized latex and four Cottrell plots measured in HClO₄ were averaged to give slope values of 2.4 ± 0.2 and 2.1 ± 0.3 nA s¹/², respectively, with correlation coefficients ranging from 0.992 to 0.996. According to a forthcoming theory of chronoamperometry in a Z:1 strong acid without supporting electrode, the slope of the Cottrell plot is given by

\[ \frac{dl}{dt^{1/2}} = \left( 1 + \frac{1}{Z} \right) F c^* \sqrt{\frac{(ZD_L + D_H)D_L}{\pi(Z + 1)D_L}} \]  

For a large value of \( Z \), eq 13 tends to \( F c^*[D_H/\pi]^{1/2} \). For \( Z = 1 \) and \( D_L \ll D_H \), eq 13 becomes \( F c^*[2D_H^2/\pi D_L]^{1/2} \) in the case of HClO₄, where \( c^* \) is a few percent of \( c^* \) owing to the loss of freedom. If we assign \( D_H/D_L \) as 1660 and \( c^*/c^* \) as 0.017, the slopes of the latex and the HClO₄ solution are identical. This agreement with the prediction of the theory is within experimental errors.

**Conclusions**

The Debye–Hückel theory does not explain the voltammetric properties of the latex suspension without supporting electrolyte because it does not take into account diffusion of the latex and hydrogen ion or the ordered structure of the latex. We proposed the non-neutralized charge distribution model, in which each cell is independent electrostatically. This is equivalent to the introduction of a unit cell, which accounts for the structural formation. This model suggests 38 nm as the thickness of the ionic atmosphere instead of the value of 0.35 nm predicted by the Debye–Hückel theory. A two-layer model is described from the discussion of the reaction order: the hydrogen ion in the inner layer (\( a < r < 4.2a \)) is bound by the latex and does not participate in the electrode reaction, whereas that in the outer layer (\( 4.2a < r < b \)) is sufficiently free from electrostatic energy to be transported to the electrode and reduced. The presence of the bound and unbound domains suggests behavior between those of a strong and weak acid. Since the concept of the two-layer model is valid only for voltammetric behavior, it does not necessarily agree with thermodynamic estimations. For instance, the inner layer is larger than the domain (\( a < r < 2a \)) in which the electric energy is larger in magnitude than the thermal energy.

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