Charge Reversal of Sulfate Latex Induced by Hydrophobic Counter-ion: Effects of Surface Charge Density

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Abstract

We studied experimentally and theoretically the charge reversal of sulfate latex colloid in the presence of monovalent hydrophobic counter-ion TPP^+ (tetraphenylphosponium). The intrinsic or chemical energy of adsorption of TPP^+ on the latex was evaluated from the concentration at charge reversal. The iso-electric point (IEP) increases with increasing the surface or electrokinetic charge density of sulfate latex spheres. That is, at low surface or electrokinetic charge density, the charge inversion concentration is low, and IEP shifts to higher values with the increase of surface or electrokinetic charge density. The intrinsic energy of adsorption decreases with increasing the surface or electrokinetic charge density. Finally our experimental and theoretical results suggest that the hydrophobicity is a determining factor for the charge inversion of hydrophobic colloids, and the intrinsic energy of adsorption also varies with the variations of surface or electrokinetic charge density.

Keywords: hydrophobicity, charge density, charge inversion, intrinsic/chemical energy of adsorption

Introduction

Controlling aggregation and dispersion of colloidal particles are one of the important subjects from scientific and industrial points of view. Colloidal particles bear the surface electric charge, which affects the interaction between particles and thus determines the aggregation-dispersion. Aggregation occurs at a charge neutralization condition induced by the interaction between oppositely charged interface and ionic substances such as polyelectrolytes [1-3], clays [4], multivalent ions [5, 6], and surfactants [7, 8]. While the attachment of strongly attracted and oppositely charged substances effectively realizes the charge neutralization, the overdose of such substances often results in the charge reversal and re-dispersion of colloidal particles. In the measurements of electrophoretic mobility, charge reversal or overcharging is observed as a reverse of migration of charged particles.

Charge reversal or overcharging is induced by the overcompensation of counter-ions adjacent to the surface of oppositely charged particle. The overcompensation by counter-ions is considered to be driven by ion-ion correlation, specific binding, hydrophobic interaction, and so on [5-7, 9]. The importance of the effect of hydrophobicity and hydrophilicity was clearly demonstrated by some studies, where the electrophoretic mobility of hydrophobic and hydrophilic particles were measured in the presence of big hydrophobic ions [10-12]. A simple theoretical analysis considering the adsorption at the Stern layer showed that the chemical or intrinsic energy of adsorption and electrostatic energy are responsible for the charge reversal, and the iso-electric point (IEP) is determined by the intrinsic energy of adsorption and the surface charge density [7, 10]. Several studies found the iso-electric point of different hydrophobic and hydrophilic surfaces with hydrophobic counter ions and also evaluated the energy of adsorption [7, 10, 11]. The obtained energy was comparable to the half of the energy of transfer of hydrophobic ions from water to non aqueous solvent [11]. Also, a molecular dynamics simulation showed that the IEP is proportional to the surface charge density [10]. However, experimental evidence about the effects of surface charge density and intrinsic/chemical energy of adsorption on the charge reversal is still lacking. Therefore, we focus on the relation among surface charge density of latex colloids and the intrinsic/chemical energy of adsorption of hydrophobic counter-ion with charge reversal concentration or IEP.

In this study, we examine the experimental and theoretical relationship between the charge inversion of hydrophobic latex colloids in the presence of hydrophobic tetraphenylphosponium

cations (TPP$^+$) and the intrinsic/chemical energy of adsorption of TPP$^+$ to latex particles of different charge density.

Experimental

Materials

Three IDC surfactant-free polystyrene sulfate latex spheres (Thermo-Fischer) were used as colloidal particles in this study. The manufacturer reported parameters of the three latex spheres that are listed in Table 1. Before use, the three sulfate latex particles were dialyzed in a Visking tube, which was pre-cleaned in a boiled NaHCO$_3$ (kanto Chemical Co., Inc.) and EDTA (Sigma-Aldrich) solution, against pure water. During the dialysis, the electric conductivity of outer water was measured by an electric conductivity meter (CM-30G TOA-DKK). The dialysis was carried out until the electrical conductivity reduced to less than 2 µS/cm. After the dialysis, the three latex suspensions were standardized using UV-Vis spectrophotometer (UV-1650PC, Shimadzu).

Two different electrolytes, KCl (JIS special grade, Wako Pure Chemical Industries) and hydrophobic tetraphenylphosphonium chloride (TPPCl) (EP grade, Tokyo Chemical Industry Co.), were used to control salt concentration. In every preparation of the solution, these two electrolyte solutions were filtered (DISMIC 25HP 0.2 µm, ADVANTEC). Before the experiment of electrophoretic mobility, used solution and suspension were degassed under reduced pressure (GCD-051X, ULVAC). The colloidal suspensions and salt solutions were prepared by using pure water (Elix, Millipore).The pH of the suspension was maintained at pH 4 with 0.1 mM HCl (JIS special grade, Wako Pure Chemical Industries) to avoid the dissolving effects of CO$_2$.

Experimental procedure

We measured electrophoretic mobility of the latex particles as a function of salt concentration. The electrophoretic mobility was measured with a Zetasizer Nano ZS apparatus (Malvern Instruments). Measurements of electrophoretic mobility were carried out as a function of salt concentration, 0.0001-100 mM (TPPCl) and 0.1-100 mM (KCl), at a temperature of 20ºC and pH 4. The concentration of sulfate latex particles was maintained 5 mg/L in every measurement. Samples were prepared from the latex suspension by adding appropriate volumes of water and stock salt solutions to adjust the particle and salt concentrations. The values of the suspension pH were checked by a combination electrode (ELP-035, TOA-DKK) and maintained a value

at pH 4. We measured the electrophoretic mobility of these three sulfate latex spheres in KCl and TPPCl salts separately to compare the effect of hydrophobicity.

Theoretical modelling

Surface charge- surface potential relationship

Experimental values of electrophoretic mobilities are compared with theoretical values. Theoretical mobility is calculated by using the theoretical models based on the standard electrokinetic theories and the double layer model with Poisson-Boltzmann (PB) equation. The Gouy-Chapman model is used for the evaluation of surface potential ψ_0 from the surface charge density σ_0 in KCl solution. That is, we use Eq. (1)

$$\sigma_0 = \frac{2k_BT\varepsilon\varepsilon_0\kappa}{e}\sinh\left(\frac{e\psi_0}{2k_BT}\right) \tag{1}$$

$$\frac{1}{\kappa} = \left(\frac{\varepsilon\varepsilon_0 k_B T}{2n_0 e^2}\right)^{\frac{1}{2}} \tag{2}$$

$1/\kappa$ is the Debye length in a solution with the concentration (number density) of electrolyte n_0. The Debye length $1/\kappa$ is considered as the thickness of the diffuse double layer. Other parameters $\varepsilon_r, \varepsilon_0$, T, k_B and e are the relative permittivity of liquid, the vacuum permittivity, the absolute temperature, the Boltzmann constant, and the elementary charge, respectively. We assume $\psi_0 = \zeta$, where ζ is the zeta potential in KCl solution. This assumption was verified by experiments [13, 14]. In some cases, however the reduction of charge or shift of slipping plane is needed [4, 13-15]. As a result, electrophoretic mobility in KCl solution is calculated from the surface charge density.

The TPP$^+$ ion is adsorbed strongly on the surfaces of the polystyrene latex, and thus we introduce the Stern layer as the following Eq. (3) followed by [7, 11]

$$\Gamma_S = 2r_s C_s \exp\left(-\frac{e\psi_d - \Phi}{k_B T}\right) \tag{3}$$

where the Γ_s is the amount of adsorbed TPP ion in the Stern layer, r_s is the radius of adsorbed TPP$^+$ ion, here we use $2r_s = 0.94$ nm [11], C_s is the bulk concentration of TPP$^+$ ion, ψ_d is the diffuse layer potential, Φ is the chemical/intrinsic adsorption energy per ion. Here, we use the term intrinsic/chemical energy of adsorption to indicate the energies other than electrostatic part for the adsorption energy.

Therefore, the charge density of the Stern layer σ_s is thus

$$\sigma_s = eN_A\Gamma_s \tag{4}$$

where N_A is the Avogadro number.

The diffuse layer charge σ_d is related to the diffuse layer potential ψ_d by using the Gouy-Chapman theory following [5]

$$\sigma_d = -\frac{2k_BT\varepsilon\varepsilon_0\kappa}{e}\sinh\left(\frac{e\psi_d}{2k_BT}\right) \tag{5}$$

According to charge neutrality

$$\sigma_0 + \sigma_s + \sigma_d = 0 \tag{6}$$

Finally, the zeta potential ζ is obtained as follows [15]

$$\zeta = \psi(x_s) = \frac{4k_BT}{e}\operatorname{arctanh}\left[\tanh\left(\frac{e\psi_d}{4k_BT}\right)\exp(-\kappa x_s)\right] \tag{7}$$

where x_s is the distance to the slipping plane. From Eqs. (3)-(7), in the presence of TPP$^+$, the zeta potential is evaluated.

At an iso-electric point, $\psi_d = 0$, a simple relation can be obtained between the charge reversal concentration C_s^I and the adsorption energy per ion Φ at iso-electric point followed by [10, 11, 16]. That is,

$$C_s^I = \frac{\sigma_0}{e2r_s}\exp\left(-\Phi/k_BT\right) \tag{8}$$

Electrophoretic mobility

We use an approximate formula called Henry's equation, which is applicable for low zeta potential ζ to convert zeta potential to electrophoretic mobility of a sphere with a radius a

$$\mu = \frac{\varepsilon_r\varepsilon_0}{\eta}\zeta f(\kappa a) \tag{9}$$

where η is the viscosity of medium and $f(\kappa a)$ is called Henry's function. An Ohshima's appropriate expression for Henry's function is [17]

$$f(\kappa a) = \frac{2}{3}\left[1 + \frac{1}{2\left(1 + \frac{2.5}{\kappa a\{1 + 2\exp(-\kappa a)\}}\right)^3}\right] \tag{10}$$

$f = 1$ corresponds to the Smoluchowski equation. The Eqs.(9) and (10) assume that during electrophoresis the potential distribution in the double layer around a spherical particle remains spherically symmetric. In the case of high zeta potential, however, the double layer around the particle is deformed. This double layer asymmetry is called relaxation effect which is not taken into account in Eqs. (9) and (10). In the presence of relaxation effect we can calculate the mobility of a sphere with a radius a by using O'Brien and White theory [18] through the computer program.

An analytical equation of the mobility of a sphere with larger zeta potential can be obtained by using Ohshima's expressions [17, 19, and 20]. It is known that taking account of the relaxation is necessary to describe the electrophoretic mobility of silica, latex, and lysozyme in previous researches [4, 14, 21-23]. If we take account of the relaxation effect, the electrophoretic mobility μ depends on the ionic drag coefficient of the i-th ion specie λ_i

$$\lambda_i = \frac{N_A e^2 |z_i|}{\Lambda_i^0} \tag{11}$$

where Λ_i^0 is the limiting conductance of i-th ion specie and z_i is the valance of the i-th ion specie . And the scaled drag coefficient of i-th ion specie m_i

$$m_i = \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\eta z_i^2 e^2} \lambda_i \tag{12}$$

The approximate mobility μ in a z-z symmetrical electrolyte $z=z_1=-z_2$ solution applicable to an order of $1/_{\kappa a}$ is given from the following semi-empirical mobility formula.

$$\mu = \text{sgn}(\zeta) \frac{\varepsilon_r \varepsilon_0}{\eta} \left\{ |\zeta| - \frac{2F}{1+F}\left(\frac{k_B T}{ze}\right) H \right\} \tag{13}$$

$$+ \text{sgn}(\zeta) \frac{2\varepsilon_r \varepsilon_0 \, k_B T}{3\eta e} \left[\frac{1}{\kappa a} \left\{ -18\left(t + \frac{t^3}{9}\right) K \right. \right.$$

$$+ \frac{15F}{1+F}\left(t + \frac{7t^2}{20} + \frac{t^3}{9}\right) - 6(1 + 3\overline{m})\left(1 - \exp\left(-\frac{\zeta}{2}\right)\right) G$$

$$+ \frac{12F}{(1+F)^2} H + \frac{9\overline{\zeta}}{1+F}(\overline{m}G + mH)$$

$$\left. \left. - \frac{36F}{1+F}\left(\overline{m}G^2 + \frac{m}{1+F}H^2\right)\right\}\right]$$

with

$$\overline{\zeta} = \frac{ze|\zeta|}{k_B T} \tag{14}$$

$$F = \frac{2}{\kappa a}(1 + 3m)\left(\exp\left(\bar{\zeta}/2\right) - 1\right) \tag{15}$$

$$G = \ln\left(\frac{1 + \exp\left(-\bar{\zeta}/2\right)}{2}\right) \tag{16}$$

$$H = \ln\left(\frac{1 + \exp\left(\bar{\zeta}/2\right)}{2}\right) \tag{17}$$

$$K = 1 - \frac{25}{3(\kappa a + 10)}\exp\left[-\frac{\kappa a}{6(\kappa a - 6)}\bar{\zeta}\right] \tag{18}$$

$$t = \tanh\left(\bar{\zeta}/4\right) \tag{19}$$

where $\bar{\zeta}$ is the magnitude of the scaled zeta potential; m and $\bar{m}$ are the scaled ionic drag coefficients of counterions and co-ions, respectively. In the case with TPPCl, m and $\bar{m}$ used for cations are molar average values of those for TPP$^+$ and H$^+$. The Eq.(13) is invalid for $\kappa a < 10$. Therefore, we need to use another expression available for the mobility to the third power of zeta potential in Henry's equation. According to Overbeek [24] the mobility expression to the order of ζ^3 is given as follows followed by Ohshima [17]

$$\mu = \frac{2\varepsilon_r\varepsilon_0\zeta}{3\eta}\left[f_1(\kappa a) - \left(\frac{ze\zeta}{k_BT}\right)^2\left\{f_3(\kappa a) + \left(\frac{m + \bar{m}}{2}\right)f_4(\kappa a)\right\}\right] \tag{20}$$

The first term on the right –hand corresponds to Henry's equation that is $(2/3)f_1(\kappa a)$ equals Henry's function $f(\kappa a)$ given by Eq.(10).

The final approximate expression of mobility of a sphere in a *z-z* type symmetrical electrolyte solution is given by Ohshima [17] is as follows

$$\mu = \frac{2\varepsilon_r\varepsilon_0\zeta}{3\eta}\left(1 + \frac{1}{2\left[1 + \frac{2.5}{\{\kappa a(1 + 2\exp{(-\kappa a)})\}}\right]^3}\right)$$

$$-\frac{2\varepsilon_r\varepsilon_0\zeta}{3\eta}\left(\frac{ze\zeta}{k_BT}\right)^2\left[\frac{\kappa a\{\kappa a + 1.3\exp(-0.18\kappa a) + 2.5\}}{2\{\kappa a + 1.2\exp(-7.4\kappa a) + 4.8\}^3}\right.$$

$$\left.+\left(\frac{m + \bar{m}}{2}\right)\frac{9\kappa a\{\kappa a + 5.2\exp(-3.9\kappa a) + 5.6\}}{8\{\kappa a - 1.55\exp(-0.32\kappa a) + 6.02\}^3}\right] \tag{21}$$

Table 1. Some parameters of studied particles reported from manufacturer.

Parameters	Particle 1	Particle 2	Particle 3
Particle diameter ($2a$) (μm)	0. 25	0.47	1.2
Density (g/cm^3)	1.055	1.055	1.055
Surface charge density σ_0 (C/m^2)	-0.006	-0.049	-0.096
Electrokinetic surface charge density σ_k(C/m^2)	-0.011	-0.037	-0.043

Results and discussion

Electrophoretic mobility in KCl solution

In this section, we describe the effect of KCl concentration on the electrophoretic mobility of sulfate latex of different surface charge density (Table 1). The values of electrophoretic mobility as a function of electrolyte concentration are shown in Figs. 1, 2 and, 3 for latex particles with manufacture's charge density of -0.006, -0.049, and -0.096 C/m^2, respectively. In Figs. 1-3, symbols are experimental data, the dashed and solid lines are obtained using the theoretical model with assumed electrokinetic charge densities of -0.011, -0.037, and -0.043 C/m^2 to fit the experimental data. The magnitude of experimental electrophoretic mobility (EPM) shows the maximum around 1-10 mM and decreases at lower and higher KCl concentrations. The solid lines are calculated by Ohshima's theory including the relaxation effect for large κa Eq.(13) and the dashed lines are drawn by the Smoluchowski equation, respectively. While the EPM by the Smoluchowski equation monotonically decreases with decreasing KCl concentration, the Ohshima equation captures the maximum in the magnitude of EPM as found for the experimental data. That is, the relaxation effect is significant at low KCl concentration.

From Figs 1-3, it is clear that the calculated values of mobility agree well with experimental data at salt concentrations 1-100 mM. At lower KCl concentrations, however, the magnitude of calculated EPM is higher than measured one. This disagreement indicates that there is a need to include additional effects to explain EPM behavior in the concentration below this range. The agreement between experiment and theory is acceptable for higher salts concentrations. For lower salts concentration of KCl (<10 mM), however, the agreement is less satisfactory. With the increase of surface charge density, the disagreement also increases at the lower concentrations (Figs.2 and 3). The clear reason for this disagreement is unknown.

While manufacture's charge density and the electrokinetic charge density fitted to experimental data do not agree, they are correlated. In the following section, we use both manufacturer's charge and electrokinetic charge in the analysis as possible charge densities.

Electrophoretic mobility in the presence of hydrophobic cation

In this section, we discuss the effect of tetraphenyl phosponium chloride (TPPCl) concentration on the electrophoretic mobility and charge reversal of polystyrene sulfate latex. The electrophoretic mobility of the latex sphere is shown as a function of the TPP concentration in Figs. 4, 5, and 6 for the three latex spheres with electrokinetic charge density -0.011 C/m^2, -0.037 C/m^2 and, -0.043 C/m^2. In Figs. 4-6, the symbols are experimental data, the dashed lines are evaluated without considering the double layer relaxation, and the solid lines are theoretical calculation including the double layer relaxation.

The EPM of sulfate latex is negative at low concentrations of TPP^+ ion. As the concentration of TPP^+ increases, the magnitude of the negative mobility decreases and the mobility reverses to positive; charge inversion is observed with TPP^+ ion. The inverted mobility increases, goes through the maximum, and decreases with increasing the TPP^+ concentration.

We observe a large inversion of the electrophoretic mobility of all the latex spheres. The concentrations of the mobility inversion or isoelectric points (IEPs) increase with increasing the surface charge density. The IEPs found from our experiments are 0.0018 mM, 0.45 mM, and 1.85 mM of TPP^+ ion concentration for the latex with the lowest, medium, and the highest charge density. This increase of IEP indicates that the higher amount of TPP^+ ions is necessary to neutralize the latex spheres of higher charge density. A previous study [11] showed that hydrophobic counter-ions gave rise to the mobility reversal of hydrophobic particles at a concentration higher than 1 mM of tetraphenyl arsonium chloride ($Ph_4As^+Cl^-$). Another study [10] showed the effect of hydrophilic and hydrophobic natures of colloids on the mobility reversal induced by hydrophobic counter-ion. They [10] explained that the charge inversion occurs only when hydrophobic surfaces interact with hydrophobic ions, and the charge

inversion disappears for hydrophilic colloids in the presence of organic or inorganic counter-ions. It is interesting to note that a previous study [12] also found the effect of hydrophobic anion and cation on the charge inversion and concluded that the anionic counter-ion causes much more notable inversion compared to cationic counter-ion. However, the charge density and hydrophobic interaction were unrevealed in their studies. In this study, we tried to reveal the influence of charge density on the charge reversal concentration in the presence of hydrophobic counter-ion (TPP$^+$) and found that the IEP or the charge inversion concentration of counter-ion increases with increasing surface charge density.

As for the theoretical calculation shown as the lines in Figs. 4-6, we use the model described above with the electrokinetic charge density of -0.011 C/m^2, -0.037 C/m^2 and, -0.043 C/m^2 and the intrinsic adsorption energy of 11 k_BT, 8.5 k_BT, and 5.5 k_BT for Figs. 4, 5, and 6, respectively. These values of the adsorption energy are selected to provide the reasonable agreement between theoretical IEP and experimental one. Figure 7 is the plot of the intrinsic energy against electrokinetic surface charge density. In this figure, we also plot the adsorption free energy evaluated using Eq.(8) from the iso-electric point with the surface charge density from manufacturer supplied (Table 1) (dashed line in Fig.7). In both cases using electrokinetic and manufacturer's surface charge densities, we found that the adsorption free energy (Φ) is not constant and decreases with surface charge density (Fig.7). To the best of the authors' knowledge, this is the first to report the dependence of the adsorption energy on the surface charge density. This result does not support the assumption of the previous study [10], which indicates that the bulk concentration of counter-ion at IEP is proportional to the surface charge density on the basis of molecular dynamics simulations with assuming a constant value of the intrinsic adsorption energy Φ= 8.5 k_BT. In this study, we found the highest intrinsic adsorption energy Φ = 11 k_BT for the lowest electrokinetic charge density (-0.011 C/m^2) and 11.2 k_BT by using Eq.(8) from the manufacturer's surface charge density (-0.006 C/m^2).Subsequently the lowest values of the intrinsic adsorption free energy were found 5.5 k_BT and 5.6 k_BT for electrokinetc and manufacturere's surface charge density of -0.043 C/m^2 and -0.096 C/m^2, respectively. The previous study [11] mentioned the typical value for the free energy of transfer for the family of some organic cations (Ph$_4$As$^+$,Ph$_4$Sb$^+$,Ph$_4$Ge$^+$, Ph$_4$C$^+$,…..) from water to non aqueous solvent as the order of 12 k_BT is closely related to the intrinsic energy of adsorption. It should be noted here that the previous study [11] introduced a scenario that the organic cation (Ph$_4$As$^+$) accumulate near the colloid (sulfonated latex) surfaces with 2 of 4 phenyl groups in contact (adsorbed) onto the hydrophobic latex surfaces, making for an hydration free energy 6 k_BT. In this study the maximum Φ is rather close to 12 k_BT. This means that nearly all the

phenyl groups from TPP$^+$ ion adsorb on the surfaces of latex spheres which carrying the lowest surface charge density. Surface roughness, irregularities of sphere shapes, co-ion effect near IEP, and the discrete distribution of charge layer around the latex spheres are probable factors for a little bit decrease of the intrinsic energy than 12 k_BT. In any case, from the above discussion of this section, it is clear that the adsorption free energy/ intrinsic energy of adsorption decreases with the increase of charge density.

In addition, we assume that the distance to the slipping plane is 1.25 nm in all the cases with TPP$^+$. The slipping plane distance used in this study is a little larger than the size of TPP$^+$ ion, 0.94 nm, indicating that some anomaly and irregularities of TPP$^+$ adsorption on the surface of hydrophobic latex spheres. It is probably due to the roughness of the latex surfaces or the uneven distribution of giant phenyl groups on the adsorbed surfaces. Also, dimerization of hydrophobic TPP$^+$ ions at the surface is a possible mechanism. In some cases in the point near neutralization there is a tendency to absorb the anions on the surface also; probably this uneven adsorption may cause some effect in slipping plane. We need more studies clarifying this matter by observing the molecular level observation and further experiments of other giant hydrophobic ions with hydrophobic colloids by viewing their pictorial representation in the molecular level.

Conclusions

In this study, the charge inversion of sulfate latex particles by hydrophobic monovalent counter-ions (TPP$^+$) was investigated experimentally and theoretically as a function of the surface charge density. We found that the charge inversion concentration or the iso-electric point for the latex with TPP$^+$ increases with the increasing of the charge density. Our simple theoretical analysis showed that the intrinsic energy of adsorption decreases with increasing the surface charge density of the particles.

Compliance with ethical standards
Conflict of interest: The authors declare that they have no conflict of interest

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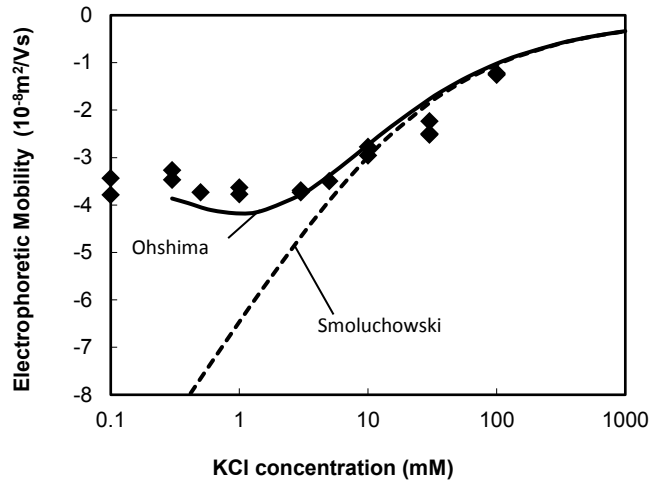Figure 1. Electrophoretic mobility of sulfate latex sphere (0.25 μm diameter) as a function of the concentration of KCl with HCl (10^{-4} M). Concentration of sulfate latex sphere : 5 mg/L. Symbols: Experimental data, Solid line: Theoretical model based on Eq.(13) and Dashed line: Smoluchowski equation.
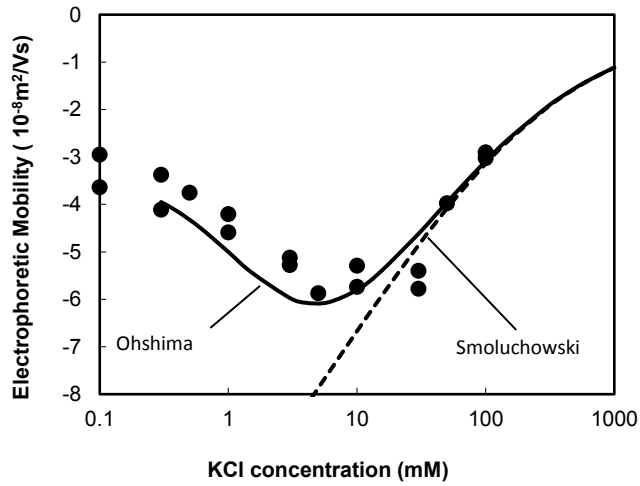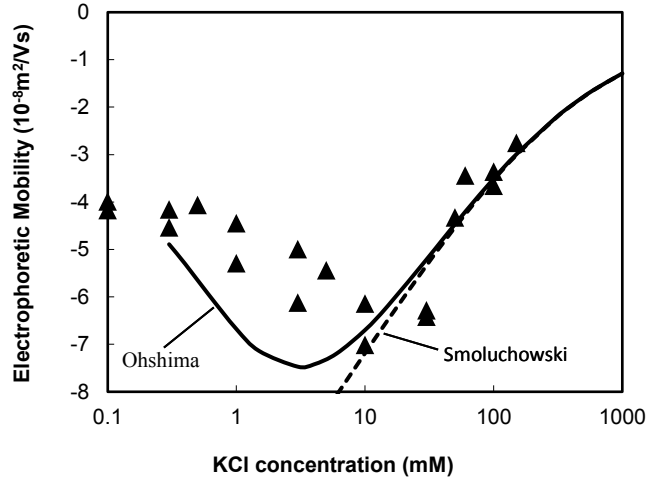

Figure 2. Electrophoretic mobility of sulfate latex sphere (0.47 μm diameter) as a function of the concentration of KCl with HCl (10^{-4} M). Concentration of sulfate latex sphere : 5 mg/L. Symbols : Experimental data, Solid line : Theoretical model based on Eq.(13) and Dashed line : Smoluchowski equation.
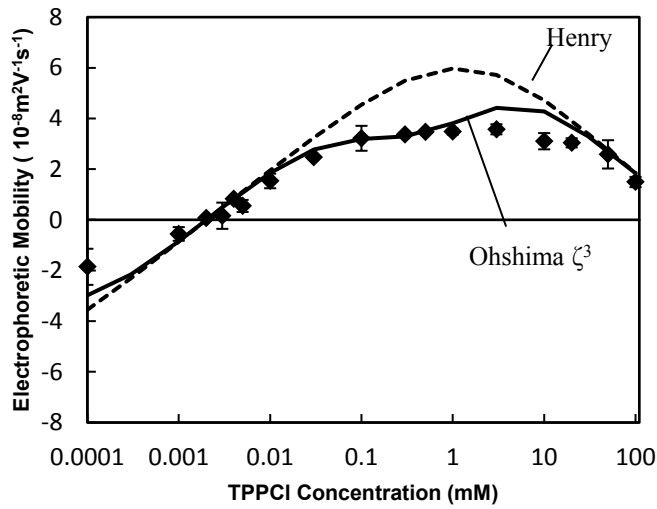
Figure 3. Electrophoretic mobility of sulfate latex sphere (1.2 μm diameter) as a function of the concentration of KCl with HCl (10^{-4} M). Concentration of sulfate latex sphere : 5 mg/L. Symbols : Experimental data, Solid line : Theoretical model based on Eq.(13) and Dashed line : Smoluchowski equation.

Figure 4. Electrophoretic mobility of sulfate latex sphere (0.25 μm diameter) as a function of the concentration of TPPCl with HCl (10^{-4} M). Concentration of sulfate latex sphere : 5 mg/L. Symbols: Experimental data, Solid line : Theoretical model based on Eq.(21) and Dashed line : Theoretical model based on Eq. (10). Error bars in experiment indicate the standard deviation of three measurements.
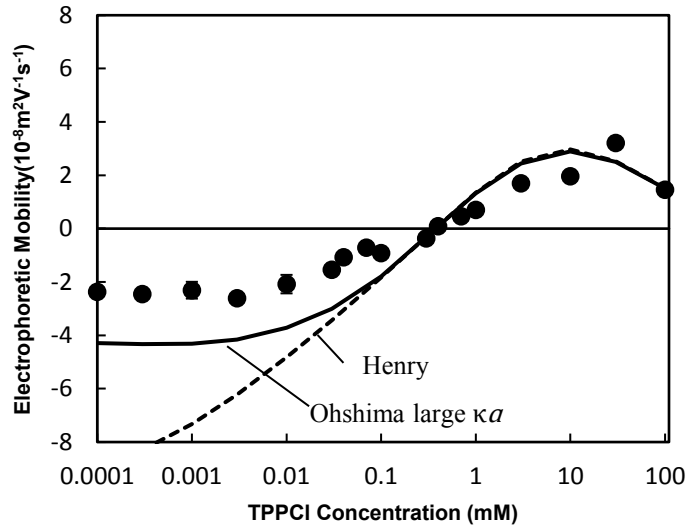
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Figure 5. Electrophoretic mobility of sulfate latex sphere (0.47 μm diameter) as a function of the concentration of TPPCl with HCl (10^{-4} M). Concentration of sulfate latex sphere : 5 mg/L. Symbols : Experimental data, Solid line : Theoretical model based on Eq.(13) and Dashed line : Theoretical model based on Eq. (10). Error bars in experiment indicate the standard deviation of three measurements.
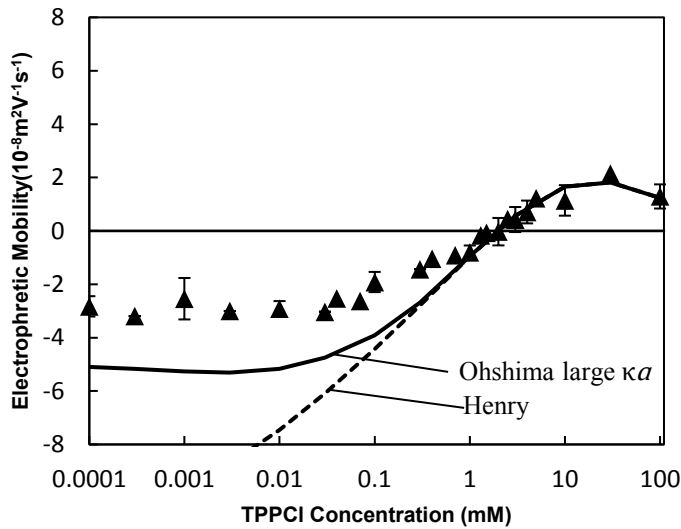

Figure 6. Electrophoretic mobility of sulfate latex sphere (1.2 μm diameter) as a function of the concentration of TPPCl with HCl (10^{-4} M). Concentration of sulfate latex sphere : 5 mg/L. Symbols : Experimental data, Solid line : Theoretical model based on Eq.(13) and Dashed line : Theoretical model based on Eq. (10). Error bar in experiment indicate the standard deviation of three measurements.
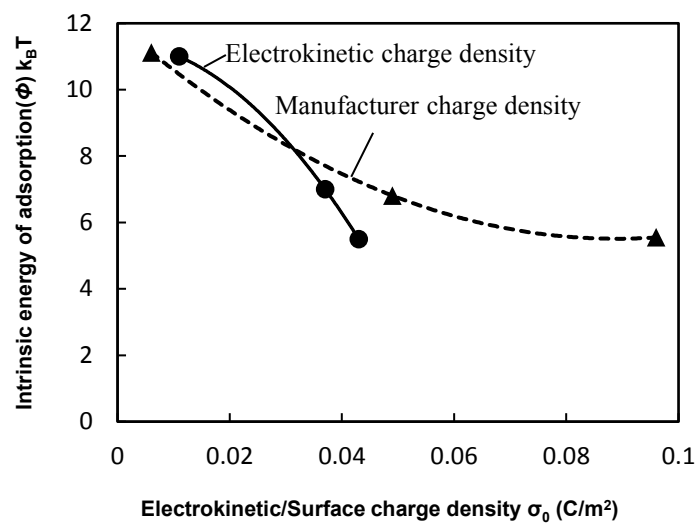
Figure 7. Intrinsic energy of adsorption (Φ) as a function of electrokinetic or surface charge density (σ₀).