

# Charge reversal of sulfate latex induced by hydrophobic counterion: 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 counterion TPP<sup>+</sup> (tetraphenylphosphonium). The intrinsic or chemical energy of adsorption of TPP<sup>+</sup> on the latex was evaluated from the concentration at charge reversal. The isoelectric 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 two 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 counterions adjacent to the surface of oppositely charged particle. The overcompensation by counterions 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 was 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 isoelectric point (IEP) is determined by the intrinsic energy of adsorption and the surface charge density [7, 10]. Several studies found the isoelectric point of different hydrophobic and hydrophilic surfaces with hydrophobic counterions 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 nonaqueous solvent [11]. Also, a molecular dynamic 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

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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 counterion 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 tetraphenylphosphonium cations (TPP<sup>+</sup>) and the intrinsic/chemical energy of adsorption of TPP<sup>+</sup> 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<sub>3</sub> (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<sub>2</sub>.

### Experimental procedure

We measured electrophoretic mobility of the latex particles as a function of salt concentration.

**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 <sup>3</sup> )	1.055	1.055	1.055
Surface charge density $\sigma_0$ (C/m <sup>2</sup> )	-0.006	-0.049	-0.096
Electrokinetic surface charge density $\sigma_k$ (C/m <sup>2</sup> )	-0.011	-0.037	-0.043

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 20 °C 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 modeling

#### 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  $\psi_0$  from the surface charge density  $\sigma_0$  in KCl solution. That is, we use Eq. (1):

$$\sigma_0 = \frac{2k_B T \varepsilon_r \varepsilon_0 \kappa}{e} \sinh\left(\frac{e\psi_0}{2k_B T}\right) \quad (1)$$

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

$1/\kappa$  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  $\zeta$  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<sup>+</sup> 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  $\Gamma_s$  is the amount of adsorbed TPP ion in the Stern layer,  $r_s$  is the radius of adsorbed TPP<sup>+</sup> ion, here we use  $2r_s = 0.94$  nm [11],  $C_s$  is the bulk concentration of TPP<sup>+</sup> ion,  $\psi_d$  is the diffuse layer potential, and  $\Phi$  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  $\sigma_s$  is thus

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

where  $N_A$  is the Avogadro number.

The diffuse layer charge  $\sigma_d$  is related to the diffuse layer potential  $\psi_d$  by using the Gouy-Chapman theory [5]:

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

According to charge neutrality

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

Finally, the zeta potential  $\zeta$  is obtained as follows [15]:

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

where  $x_s$  is the distance to the slipping plane. From Eqs. (3)–(7), in the presence of TPP<sup>+</sup>, the zeta potential is evaluated.

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

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

### Electrophoretic mobility

We use an approximate formula called Henry’s equation, which is applicable for low zeta potential  $\zeta$  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  $\eta$  is the viscosity of medium and  $f(\kappa a)$  is called Henry’s function. An Ohshima’s appropriate expression for Henry’s function is as follows[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  $\mu$  depends on the ionic drag coefficient of the  $i$ -th ion specie  $\lambda_i$

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

where  $\Lambda_i^0$  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 species  $m_i$  is as follows:

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

The approximate mobility  $\mu$  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 semiempirical mobility :

$$\begin{aligned} \mu = & \operatorname{sgn}(\zeta) \frac{\varepsilon_r \varepsilon_0}{\eta} \left\{ |\zeta| - \frac{2F}{1+F} \left( \frac{k_B T}{ze} \right) H \right\} \\ & + \operatorname{sgn}(\zeta) \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\eta e} \left[ \frac{1}{\kappa a} \left\{ -18 \left( t + \frac{t^3}{9} \right) K + \frac{15F}{1+F} \left( t + \frac{7t^2}{20} + \frac{t^3}{9} \right) - 6(1+3\bar{m}) \left( 1 - \exp\left(-\frac{\zeta}{2}\right) \right) G + \frac{12F}{(1+F)^2} H + \frac{9\zeta}{1+F} (\bar{m}G + mH) - \frac{36F}{1+F} \left( \bar{m}G^2 + \frac{m}{1+F} H^2 \right) \right\} \right] \end{aligned} \tag{13}$$

with

$$\bar{\zeta} = \frac{ze|\zeta|}{k_B T} \quad (14)$$

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

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

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

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

$$t = \tanh \left( \frac{\bar{\zeta}}{4} \right) \quad (19)$$

where  $\bar{\zeta}$  is the magnitude of the scaled zeta potential and  $m$  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  $\text{TPP}^+$  and  $\text{H}^+$ . 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  $\zeta^3$  is given as follows followed by Ohshima [17]:

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

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 given by Ohshima [17] is as follows:

$$\mu = \frac{2\varepsilon_r \varepsilon_0 \zeta}{3\eta} \left( 1 + \frac{1}{2 \left[ 1 + \frac{2.5}{\{\kappa a(1+2\exp(-\kappa a))\}} \right]^3} \right) - \frac{2\varepsilon_r \varepsilon_0 \zeta}{3\eta} \left( \frac{ze\zeta}{k_B T} \right)^2 \left[ \frac{\kappa a \{ \kappa a + 1.3 \exp(-0.18\kappa a) + 2.5 \}}{2 \{ \kappa a + 1.2 \exp(-7.4\kappa a) + 4.8 \}^3} + \left( \frac{m + \bar{m}}{2} \right) \frac{9\kappa a \{ \kappa a + 5.2 \exp(-3.9\kappa a) + 5.6 \}}{8 \{ \kappa a - 1.55 \exp(-0.32\kappa a) + 6.02 \}^3} \right] \quad (21)$$

## Results and discussion

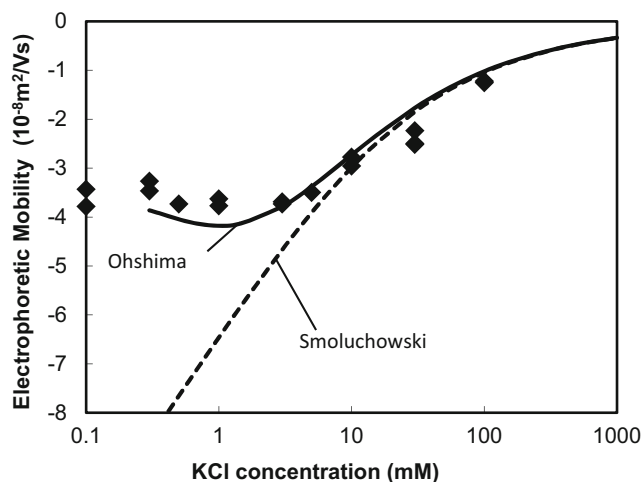
### Electrophoretic mobility in KCl solution

In this section, we describe the effect of KCl concentration on the electrophoretic mobility of sulfate latex of different surface charge densities (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 manufacturer's charge density of  $-0.006$ ,  $-0.049$ , and  $-0.096$  C/m<sup>2</sup>, respectively. In Figs. 1, 2, and 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<sup>2</sup> 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  $\kappa$ . 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

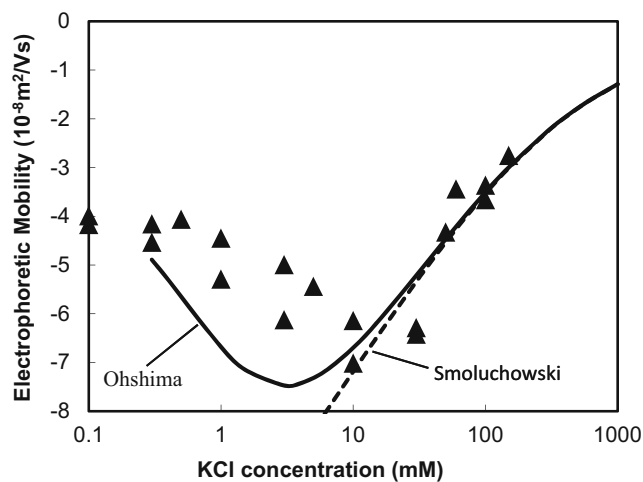
the magnitude of EPM as found for the experimental data. That is, the relaxation effect is significant at low KCl concentration.

From Figs. 1, 2, and 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 that of the 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 salt concentrations. For lower salt 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 the manufacturer'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.



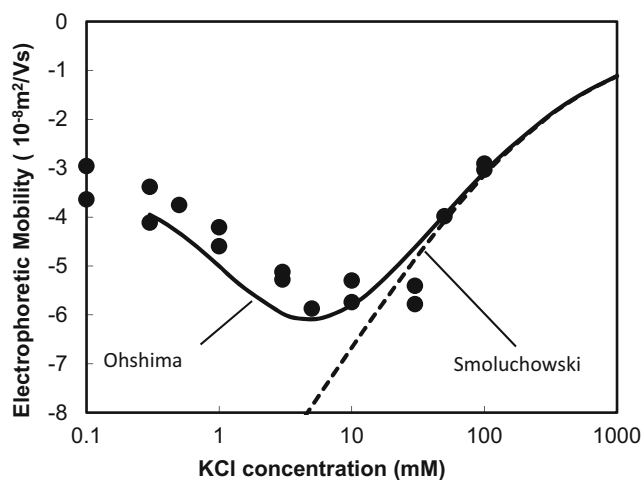
**Fig. 1** Electrophoretic mobility of sulfate latex sphere (0.25 μm diameter) as a function of the concentration of KCl with HCl (10<sup>-4</sup> M). Concentration of sulfate latex sphere : 5 mg/L. Symbols: experimental data, solid line: theoretical model based on Eq. (13), and dashed line: Smoluchowski equation



**Fig. 3** Electrophoretic mobility of sulfate latex sphere (1.2 μm diameter) as a function of the concentration of KCl with HCl (10<sup>-4</sup> 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

**Electrophoretic mobility in the presence of hydrophobic cation**

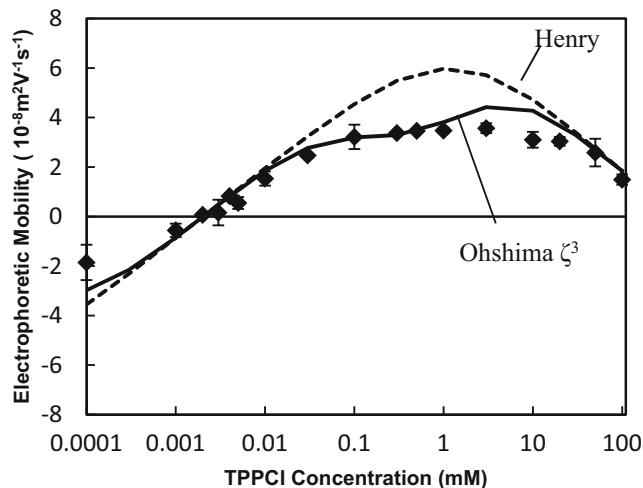
In this section, we discuss the effect of tetraphenylphosphonium chloride (TPPCI) concentration on the electrophoretic mobility and charge reversal of polystyrene sulfate latex. The electrophoretic mobility of the latex sphere is shown as a function of the TPP concentration in Figs. 4, 5, and 6 for the three latex spheres with electrokinetic charge density -0.011, -0.037, and -0.043 C/m<sup>2</sup>. In Figs. 4, 5, and 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.



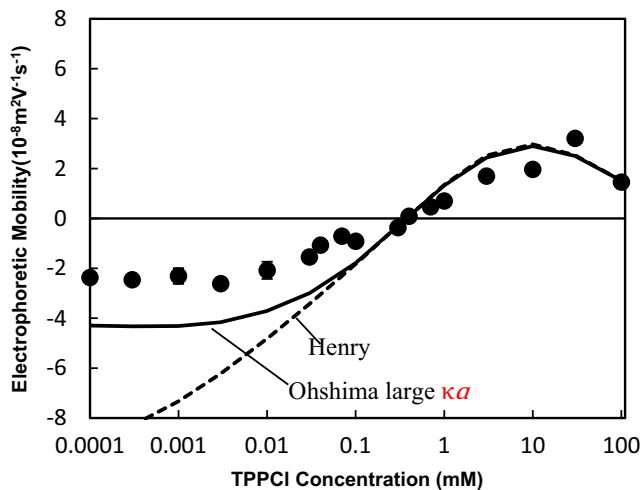
**Fig. 2** Electrophoretic mobility of sulfate latex sphere (0.47 μm diameter) as a function of the concentration of KCl with HCl (10<sup>-4</sup> M). Concentration of sulfate latex sphere : 5 mg/L. Symbols: experimental data, solid line: theoretical model based on Eq. (13), and dashed line: Smoluchowski equation

The EPM of sulfate latex is negative at low concentrations of TPP<sup>+</sup> ion. As the concentration of TPP<sup>+</sup> increases, the magnitude of the negative mobility decreases and the mobility reverses to positive; charge inversion is observed with TPP<sup>+</sup> ion. The inverted mobility increases, goes through the maximum, and decreases with increasing the TPP<sup>+</sup> 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, 0.45, and 1.85 mM of TPP<sup>+</sup> ion concentration for the latex with the lowest, medium, and the highest

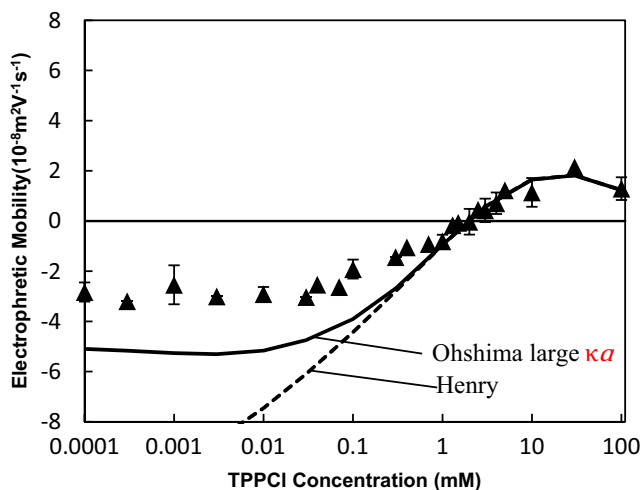


**Fig. 4** Electrophoretic mobility of sulfate latex sphere (0.25 μm diameter) as a function of the concentration of TPPCI with HCl (10<sup>-4</sup> M). Concentration of sulfate latex sphere: 5 mg/L. Symbols: experimental data, solid line: theoretical model based on Eq. (21), and dashed line: theoretical model based on Eq. (10). Error bars in experiment indicate the standard deviation of three measurements

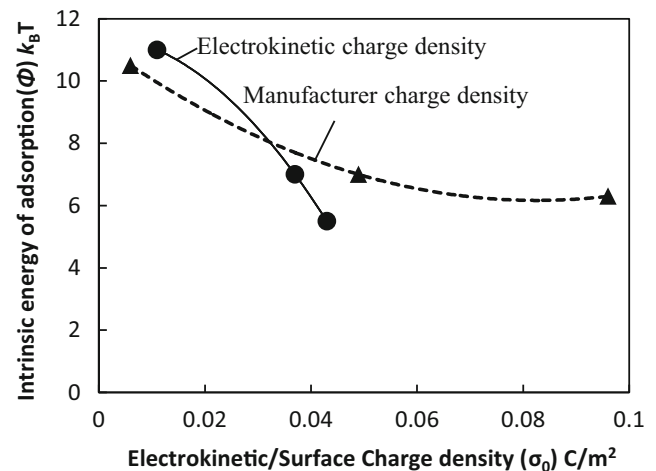


**Fig. 5** Electrophoretic mobility of sulfate latex sphere (0.47  $\mu\text{m}$  diameter) as a function of the concentration of TPPCI with HCl ( $10^{-4}$  M). Concentration of sulfate latex sphere: 5 mg/L. Symbols: experimental data, solid line: theoretical model based on Eq. (13), and dashed line: theoretical model based on Eq. (10). Error bars in experiment indicate the standard deviation of three measurements

charge density. This increase of IEP indicates that the higher amount of TPP<sup>+</sup> ions is necessary to neutralize the latex spheres of higher charge density. A previous study [11] showed that hydrophobic counterions gave rise to the mobility reversal of hydrophobic particles at a concentration higher than 1 mM of tetraphenyl arsonium chloride ( $\text{Ph}_4\text{As}^+\text{Cl}^-$ ). Another study [10] showed the effect of hydrophilic and hydrophobic natures of colloids on the mobility reversal induced by hydrophobic counterion. They [10] explained that the charge inversion occurs only when hydrophobic surfaces interact with hydrophobic ions, and the charge inversion



**Fig. 6** Electrophoretic mobility of sulfate latex sphere (1.2  $\mu\text{m}$  diameter) as a function of the concentration of TPPCI 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



**Fig. 7** Intrinsic energy of adsorption ( $\Phi$ ) as a function of electrokinetic or surface charge density ( $\sigma_0$ ).

disappears for hydrophilic colloids in the presence of organic or inorganic counterions. 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 counterion causes much more notable inversion compared to cationic counterion. 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 counterion (TPP<sup>+</sup>) and found that the IEP or the charge inversion concentration of counterion increases with increasing surface charge density.

As for the theoretical calculation shown as the lines in Figs. 4, 5, and 6, we use the model described above with the electrokinetic charge density of  $-0.011$ ,  $-0.037$ , and  $-0.043$  C/m<sup>2</sup> and the intrinsic adsorption energy of 11, 7 and 5.5  $k_B T$  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 isoelectric point with the surface charge density from manufacturer's supply (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 ( $\Phi$ ) 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 counterion at IEP is proportional to the surface charge density on the basis of molecular dynamic simulations with assuming a constant value of the intrinsic adsorption energy  $\Phi = 8.5 k_B T$ . In this study, we found the highest intrinsic adsorption energy  $\Phi = 11 k_B T$  for the lowest electrokinetic charge

density ( $-0.011 \text{ C/m}^2$ ) and  $10.5 k_B T$  by using Eq. (8) from the manufacturer's surface charge density ( $-0.006 \text{ C/m}^2$ ). Subsequently, the lowest values of the intrinsic adsorption free energy were found  $5.5$  and  $6.3 k_B T$  for electrokinetic and manufacturer's surface charge density of  $-0.043$  and  $-0.096 \text{ C/m}^2$ , respectively. The previous study [11] mentioned the typical value for the free energy of transfer for the family of some organic cations ( $\text{Ph}_4\text{As}^+$ ,  $\text{Ph}_4\text{Sb}^+$ ,  $\text{Ph}_4\text{Ge}^+$ ,  $\text{Ph}_4\text{C}^+$ , ...) from water to non-aqueous solvent as the order of  $12 k_B T$  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 ( $\text{Ph}_4\text{As}^+$ ) accumulates near the colloid (sulfonated latex) surfaces with two of four phenyl groups in contact (adsorbed) onto the hydrophobic latex surfaces, making a hydration free energy  $6 k_B T$ . In this study, the maximum  $\Phi$  is rather close to  $12 k_B T$ . This means that nearly all the phenyl groups from  $\text{TPP}^+$  ion adsorb on the surfaces of latex spheres which carry 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  $12 k_B T$ . 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  $1.25 \text{ nm}$  in all the cases with  $\text{TPP}^+$ . The slipping plane distance used in this study is a little larger than the size of  $\text{TPP}^+$  ion,  $0.94 \text{ nm}$ , indicating that some anomaly and irregularities of  $\text{TPP}^+$  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  $\text{TPP}^+$  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 counterions ( $\text{TPP}^+$ ) was investigated experimentally and theoretically as a function of the surface charge density. We found that the charge inversion concentration or the isoelectric point for the latex with  $\text{TPP}^+$  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.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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