Electrophoretic mobility of carboxyl latex particles: Effects of hydrophobic monovalent counter-ions

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Abstract

To investigate the effect of hydrophobicity on the charge reversal of colloidal particles, we measured and analyzed the electrophoretic mobility (EPM) of carboxyl latex particles in mixed electrolytes solutions containing potassium chloride KCl and tetraphenylphosphonium chloride TPPCl. Tetraphenylphosphonium (TPP^+) ion strongly adsorbs on the particle surface due to its hydrophobicity, and thus causes the charge reversal/overcharging. Measurements of EPM were carried out as functions of pH, ionic strength, and the mixed molar ratio of $X=[TPP^+]/[K^+]$ to unveil the influence of surface charge on hydrophobic interaction. Experimental EPM was analyzed by using 1-pK_H Stern Gouy Chapmann model with the Ohshima equation including the relaxation effect or the Smoluchowski equation neglecting the relaxation effect for calculating theoretical EPM values. Our results demonstrate that carboxyl latex particles show charge reversal indicated by positive EPMs at low pH due to the accumulation of TPP^+ ions on the surface and the reversed EPM values at low pH are augmented with increasing the mixed molar ratio of $X=[TPP^+]/[K^+]$. Also, we observed that charge re-reversal at higher pH as the deprotonation of surface carboxyl groups proceeded. The pH at which the charge re-reversal occurred increased with increasing the mixed molar ratio. From the comparison between our experiments and theoretical analysis, we found that the intrinsic energy of adsorption decreases with increasing the surface charge density to describe the observed charge re-reversal. These results indicate that the intrinsic adsorption energy of TPP^+, which is probably due to hydrophobic interaction, decreases with increasing the surface charge density.

Key words: Electrophoretic mobility; Charge reversal; Mixed electrolyte solution; hydrophobic interaction

1. Introduction

The stability of colloidal dispersion against aggregation-sedimentation is one of the important issues for scientific interest and industrial and technological applications such as foods storage, inks, paints, water treatment, and colloid-facilitated transport[1, 2]. The stability of colloids can be commonly explained by the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory [3, 4] in which interparticle interactions are composed of the van der Waals attraction and electrical double layer force. Particularly, the electrical double layer force is regulated by the charging behavior of colloidal particles. Therefore, one needs to estimate the surface charge of colloidal particles to predict their colloidal stability.

The surface charging properties of colloidal particles are strongly affected by the adsorption of oppositely-charging species such as polyelectrolytes[5, 6], surfactants[7, 8], and multivalent ions[9–11] onto the surfaces. Such adsorption can induce so-called charge reversal/overcharging which causes the change in sign of the net surface charges due to the excess accumulation of counter ionic species[12]. To reveal the mechanism of charge reversal, many studies have been done with the approaches of Monte-Carlo simulation and molecular dynamics including inter-ion correlation[13, 14], ionic specificity[15], and hydrophobic interaction[16]. The previous studies have demonstrated that the hydrophobicity of ions and colloids can significantly influence the surface/electrokinetic charge density in the presence of large hydrophobic ions[16–19]. Notably, the previous research with molecular dynamics simulation[16] has confirmed the linear relationship between the isoelectric point (IEP), which is the concentration where the charge reversal occurs, and the surface charge density by assuming a constant adsorption free energy of ions[17, 20]. Nevertheless, the intrinsic energy of adsorption for hydrophobic tetraphenylphosphonium (TPP$^+$) ions onto polystyrene sulfate latex surfaces decreases with increasing the surface charge density[19] even though the hydrophobic ion concentration at the IEP increases with the increase of the charge density as shown in the previous studies[16, 17]. This finding suggests that the adsorption energy of hydrophobic ions can be a function of surface charge density. However, the effect of charge density on the intrinsic energy of adsorption of hydrophobic ions remains ambiguous because the previous work used sulfate latex particles with different charge densities and sizes[19].

In the present study, to clarify the effect of surface charges on the adsorption of hydrophobic ions, which induces the reverse of sign in the surface (or zeta) potential, we measured and analyzed the electrophoretic mobilities of carboxylate polystyrene latex particles in the presence of hydrophobic tetraphenylphosphonium (TPP$^+$) ions. Carboxyl latex particles have carboxyl

groups on their surface, and thus the negative surface charge density increases with pH due to their deprotonation. This feature of carboxylated latex particles enables us to examine the effect of charge density and hydrophobic interaction on the adsorption of TPP$^+$ ions onto the surfaces.

2.   Material and Methods

2.1 Materials

Carboxylated polystyrene latex particles (Molecular Probes) were employed as model colloidal particles. The used carboxyl latex particles have pH-dependent negative charges due to the deprotonation of the carboxyl groups on the particle surface. The manufacturer reports that the chargeable site density on the surface Γ_{tot} is 1.136 /nm^2, the diameter $2a$ is 1.5±0.03 µm, and the density is 1.055 g/cm^3, respectively. KCl (JIS special grade, Wako Pure Chemical Industries) and tetraphenylphosphonium chloride TPPCl (EP grade, Tokyo Chemical Industry Co.) were used to prepare the electrolyte solutions. The pH was adjusted by the addition of HCl (JIS special grade, Wako Pure Chemical Industries) and KOH solutions. Carbonate free KOH solution was prepared by following the method described in the literature[21]. Before the sample preparation, all solutions were filtered with a 0.20 µm pore filter (DISMIC 25HP ADVANTEC). All solutions and suspensions were prepared from deionized water (Elix, MILLIPORE) and degassed before use.

2.2 Experimental Methods

EPM was measured by electrophoretic light scattering technique with Zetasizer NANO-ZS (Malvern). Measurements were carried out as a function of solution pH at different mixed molar ratio X = [TPP$^+$] /[K$^+$] with fixed ionic strength, where [TPP$^+$] and [K$^+$] denote the concentrations of TPP$^+$ and K$^+$. The pH was adjusted in the range from 3 to 11 with HCl and KOH solutions. Ionic strengths were 10 mM and 50 mM, and the mixed molar ratios X were 0, 0.01, 0.1, 0.5, 5 and ∞. The particle concentration was set to 50 mg/L in all experiments. The samples were prepared by mixing the required volumes of the suspension of the carboxyl latex particles, KCl solution, TPPCl solution, pH adjuster, and degassed water. The pH was measured with a combination electrode (ELP-035, TOA-DKK). All experiments were carried out at 20 ℃.

3.   Theoretical Analysis

3.1 Charging model

The surface charge of the used particle arises from the deprotonation of carboxyl group. That

is,

$$-\mathrm{COOH} \leftrightharpoons -\mathrm{COO}^- + \mathrm{H}^+ \qquad (1)$$

The dissociation equilibrium between the carboxyl groups and the proton in the electrolyte solution is characterized by the proton dissociation constant defined as[22]

$$\mathrm{p}K_\mathrm{H} = -\log_{10} K_\mathrm{H} = -\log_{10} \frac{\alpha_{-\mathrm{COO}^-}\alpha_{\mathrm{H}^+}^\mathrm{s}}{\alpha_{-\mathrm{COOH}}} \qquad (2)$$

where $\alpha_{-\mathrm{COO}^-}$, $\alpha_{-\mathrm{COOH}}$, and $\alpha_{\mathrm{H}^+}^\mathrm{s}$ are the surface activities of dissociated and protonated carboxyl groups, and proton, respectively. K_H is the acid dissociation constant. The value of $\mathrm{p}K_\mathrm{H}$ used in this study is 4.9 from the literature[1, 2]. The surface activity of proton is related to the bulk activity $\alpha_\mathrm{H}^\mathrm{b}$ and the surface potential ψ_0 via the Boltzmann equation

$$\alpha_\mathrm{H}^\mathrm{s} = \alpha_\mathrm{H}^\mathrm{b}\exp\left(-\frac{e\psi_0}{k_B T}\right) \qquad (3)$$

where e is the elementary charge, k_B is the Boltzmann constant, T is the absolute temperature. Since the surface charge density is attributed to the dissociated carboxyl groups on the surface, the relationship between the surface charge density and the surface potential due to deprotonation can be described as

$$\sigma_0 = -e\alpha_{-\mathrm{COO}^-} = -\frac{e\Gamma_{tot}}{1 + 10^{\mathrm{p}K_\mathrm{H}-\mathrm{pH}}\exp\left(-\frac{e\psi_0}{k_B T}\right)} \qquad (4)$$

where Γ_{tot} is the total site density of surface carboxyl groups including dissociated and protonated ones.

The TPP$^+$ ions strongly adsorb onto the surfaces of the polystyrene latex particles which are hydrophobic. To describe the adsorption of the TPP$^+$ ions, we introduce the Stern layer model with the following equation[2, 3]:

$$\Gamma_s = 2r_s C_{TPP}\exp\left(-\frac{-\phi + e\psi_d}{k_B T}\right) \qquad (5)$$

where the Γ_s is the amount of adsorbed TPP$^+$ ions in the Stern layer, r_s is the radius of adsorbed TPP$^+$ ion with the value of $2r_s = 0.94$ nm[17] used in present study, C_{TPP} is the bulk concentration of TPPCl, ψ_d is the diffuse layer potential, ϕ is the non-electrostatic chemical/intrinsic adsorption energy per ion. The term of chemical/intrinsic adsorption energy represents the energies other than from electrostatic origin. To incorporate the dependency of the non-electrostatic adsorption energy on the surface charge density proposed by the previous work [19], we have introduced the following simple linear interpolation to calculate the value of ϕ as

$$\phi = (\phi_{min} - \phi_{max})\frac{\sigma_0}{-e\Gamma_{tot}} + \phi_{max} \tag{6}$$

where ϕ_{min} and ϕ_{max} are the minimum and the maximum non-electrostatic chemical/intrinsic adsorption energy per ion. These values are determined below in Section 4.

With Eq. (5), we can express the Stern layer charge density σ_s as

$$\sigma_s = eN_A\Gamma_s \tag{7}$$

where N_A is the Avogadro number. This equation suggests that the adsorbed amount of TPP$^+$ ions in the Stern layer is in charge of the development of the Stern layer charge density σ_s.

The relationship between the diffuse layer charge density σ_d and the diffuse layer potential ψ_d for our system is given by the Grahame equation for monovalent salt as follows[24]:

$$\sigma_d = -\frac{2\varepsilon_r\varepsilon_0\kappa k_B T}{e}\sinh\left(\frac{e\psi_d}{2k_B T}\right) \tag{8}$$

with the inverse Debye parameter κ^{-1} as

$$\kappa^{-1} = \left(\frac{\varepsilon_r\varepsilon_0 k_B T}{2(C_{KCl} + C_{TPPCl})N_A e^2}\right)^{\frac{1}{2}} \tag{9}$$

where C_{KCl} and C_{KCl} are the concentrations of KCl and TPPCl, and ε_0 is the dielectric constant of vacuum, ε_r=80.4 is the relative dielectric constant of water. For the surface bearing weakly-acidic groups with the Stern layer, one needs to assume the following linear relationship[24]

$$\sigma_0 = C_s(\psi_0 - \psi_d) \tag{10}$$

where C_s is the Stern layer capacitance. And we set the value to $C_s = \epsilon_r\epsilon_r/r_s$ by assuming the thickness of the Stern layer is the radius of TPP$^+$ ion r_s.

According to the principle of electroneutrality, the sum of surface σ_0, the Stern layer σ_s, and diffuse layer charge densities σ_d must be zero which requires the condition below:

$$\sigma_0 + \sigma_s + \sigma_d = 0 \tag{11}$$

The set of Eqs. [2-11] is solved numerically to obtain the diffuse layer potential ψ_d for the successive calculation of the zeta potential ζ. Particularly, in a pure KCl solution, the above set of equation is solved with the conditions $\psi_d = \psi_0$, $\sigma_s = 0$, and $C_s \to \infty$ meaning no Stern layer for pure KCl case.

To calculate the electrophoretic mobility in the following section, the zeta potential ζ from ψ_d, which is set to $\psi_d = \psi_0$ for pure KCl solution, is calculated with the Gouy-Chapman theory via

$$\zeta = \psi(x_s) = \frac{4k_BT}{e}\tanh^{-1}\left[\tanh\left(\frac{e\psi_d}{4k_BT}\right)\exp(-\kappa x_s)\right] \tag{12}$$

where x_s is the distance to the slipping plane. The value of x_s for pure KCl case is set to $x_s=0.25$ nm[1, 2], while the value for mixed KCl and TPPCl case is set to $x_s=r_s=0.47$ nm with the assumption that the extent of the slipping plane coincides with the outer edge of the adsorbed TPP$^+$ ion on the surface.

3.2 Electrophoretic mobility (EPM)

The electrophoretic mobilities (EPMs) are calculated from the zeta potential using the Ohshima equation including the relaxation effect[25] and the Smoluchowski equation neglecting the relaxation effect.

First, the Smoluchowski equation is given by

$$\mu_m = \frac{\varepsilon_r\varepsilon_0}{\eta_s}\zeta \tag{13}$$

where μ_m is the electrophoretic mobility, η_s is the viscosity of the solution.

Second, an analytical expression for EPM of a negatively charged particle in 1:1 electrolyte solution such as KCl derived by the Ohshima, Healy, and White[25] is

$$
\begin{aligned}
\mu_m = {} & \mathrm{sgn}(\zeta)\frac{\varepsilon_r\varepsilon_0}{\eta_s}\left\{|\zeta| - \frac{2F}{1+F}\left(\frac{k_BT}{e}\right)H\right\} \\
& + \mathrm{sgn}(\zeta)\frac{2\varepsilon_r\varepsilon_0 k_BT}{3\eta_s e}\left[\frac{1}{\kappa a}\left\{-18\left(t + \frac{t^3}{9}\right)K\right.\right. \\
& + \frac{15F}{1+F}\left(t + \frac{7t^2}{20} + \frac{t^3}{9}\right) \\
& - 6(1+3\widetilde{m})\left(1 - \exp(-\tilde{\zeta}/2)\right)G + \frac{12F}{(1+F)^2}H \\
& \left.\left. + \frac{9\tilde{\zeta}}{1+F}(\widetilde{m}G + mH) - \frac{36F}{1+F}\left(\widetilde{m}G^2 + \frac{m}{1+F}H^2\right)\right\}\right]
\end{aligned}
\tag{14}
$$

With

$$H = \ln\frac{1 + \exp(\tilde{\zeta}/2)}{2} \tag{15}$$

$$K = 1 - \frac{25}{3(\kappa a + 10)}\exp\left(-\frac{\kappa a}{6(\kappa a - 6)}\tilde{\zeta}\right) \tag{16}$$

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

$$G = \ln \frac{1 + \exp(-\tilde{\zeta}/2)}{2} \tag{17}$$

$$t = \tanh(\tilde{\zeta}/4) \tag{18}$$

$$\tilde{\zeta} = \frac{e\zeta}{k_B T} \tag{19}$$

$$m = \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\eta_s e^2}\lambda, \quad \widetilde{m} = \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\eta_s e^2}\tilde{\lambda}, \tag{20}$$

$$\lambda = \tilde{\lambda} = \frac{N_A e^2 |z_i|^2}{\Lambda_i^\circ} \tag{21}$$

where sgn(x) is 1 when $x > 0$ or -1 when $x < 0$, m and $\widetilde{m}$ are the scaled drag coefficients of counter-ions and co-ions, respectively, N_A is the Avogadro constant, and Λ_i° is the values of the limiting molar conductance of the i-th ionic species. Eq. (13) is valid for $\kappa a > 10$ and this condition is satisfied in all experiments since the smallest κa is 245.65 in our experiment. In this study, the values of Λ_i° (10^{-4} S m^2/mol) used are 66.17 for K$^+$, 20.7 for TPP$^+$, and 68.68 for Cl$^-$ which are taken from the literature[10, 11].

4. Results and Discussion

We plot the EPMs of carboxyl latex particles as a function of the solution pH at different ionic strengths in Fig. 1 (a,b) for 10 mM and Fig. 1 (c,d) for 50 mM, respectively. In Fig. 1, the symbols are experimental values, the solid lines are the theoretical values calculated by the Ohshima equation including the relaxation effect, and the dashed lines are the theoretical values calculated by the Smoluchowski equation neglecting the relaxation effect. While the lines in Fig. 1 (a,c) are drawn with the constant non-electrostatic intrinsic energy of TPP$^+$ adsorption of $\phi = 6\,k_B T$, the lines in Figure 1 (b,d) are obtained with the assumption that the energy for TPP$^+$ adsorption linearly varies with the surface charge density from $6\,k_B T$ to $4\,k_B T$. The value of 6 $k_B T$ is taken from the literature[17]. They also reported that the free energy of transfer for a phenyl group from water to organic solvents is approximately 3 $k_B T$ and it is closely related to the adsorption energy. It should be noted that the value of 6 $k_B T$ corresponds to the situation where two of four phenyl groups on TPP$^+$ ions adsorb onto hydrophobic polystyrene latex surfaces[17]. These values used in the literature are comparable with the values we used.

In the case of pure KCl solution, X=[TPP$^+$]/[K$^+$]=0, the electrophoretic mobility in magnitude increases with pH. It shows that the particles are highly negatively charged at high pH due to the deprotonation of carboxyl groups. The experimental electrophoretic mobilities in

the solution including TPP$^+$ in Fig. 1 show positive values at low pH, indicating that the occurrence of charge inversion. This inversion is attributed to the adsorption of TPP$^+$ on the surfaces by hydrophobic interaction between phenyl groups of TPP$^+$ ions and the polystyrene surface. With increasing pH, the positive electrophoretic mobilities decrease. Then, the electrophoretic mobilities reverse again to negative values. This charge re-reversal means that the increased number of deprotonated carboxyl groups at high pH outnumbers the adsorbed amount of TPP$^+$ ions. In addition, the charge re-reversal pHs shift to higher pH with increasing the mixed molar ratio X and the ionic strength. This is because larger amounts of deprotonated carboxyl groups are required to compensate more adsorbed TPP$^+$ ions associated with abundant TPP$^+$ ions in bulk solution. However, the experimental electrophoretic mobilities at 50 mM and mixed molar ratios higher than $X=5$ in Fig. 1 (c,d) are positive and do not show the charge re-reversal regardless of pH. This can be ascribed to the existence of excess amounts of adsorbed TPP$^+$ ions even though all carboxyl groups are deprotonated at high pH.

From the comparison between calculated values with two different models, Smoluchowski equation and Ohshima equation, we confirm that differences in calculated electrophoretic mobilities between these two methods are not so significant for our case. This can be rationalized by relatively low zeta potentials which are induced by the charge reversal, and thus the relaxation effect is not significant.

In the comparison with theoretical values calculated by assuming the constant non-electrostatic intrinsic energy of adsorption in Fig. 1 (a,c), one finds that the calculations capture the experimental trends. However, the calculations with the constant adsorption energy overestimates the adsorption amounts of TPP$^+$ ions and cannot describe the experimentally observed charge re-reversal of electrophoretic mobilities at high pH with higher mixed molar ratios. In contrast, the calculated mobilities obtained by assuming that the intrinsic energy of adsorption in Fig. 1 (b,d) is proportional to the surface charge density can successfully reproduce the charge re-reversal for all the conditions and even in high mixed molar ratios. Therefore, our result suggests that the intrinsic energy of adsorption of TPP$^+$ decreases from 6 k_BT to 4 k_BT with increasing charge density. This finding is consistent with the result that the intrinsic energy of TPP$^+$ adsorption decreases with increasing the surface charge density of sulfate latex particles with different diameters[19], and complements their finding by monodisperse carboxylated latex particles with pH-variable surface charge.

Moreover, on the basis of our results above, we suggest the reason why the intrinsic energy of adsorption for TPP$^+$ ions can be dependent on the surface charge density as follows. As the deprotonation of surface carboxyl groups progresses with increasing pH, the particle surfaces become less hydrophobic. Such relatively low hydrophobicity can make difficult TPP$^+$ ions to be accumulated near the surfaces. Therefore, the adsorption energy decreases with the surface

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charge density, in other word, the number of dissociated surface groups. Hence, such reduction in the adsorption energy might cause the charge re-reversed electrophoretic mobilities from positive to negative due to the deprotonation of carboxyl groups. This suggestion also can rationalize the result of the previous study[19] because high surface charge densities of the sulfate latex particles mean larger number of surface sulfate groups on their surfaces.

Even though the proposed simple modeling captures the experimental trends represented by the charge re-reversal, there are still quantitative discrepancies in intermediate mixed molar ratios, for instance, X=0.01 and 0.1 at 10 and 50 mM. This could suggest that the adsorption behavior in mixed solution of KCl and TPPCl can be more complex than the simple model used in this paper. The discrepancies in solution containing K^+ ions at higher pH could be explained by K^+ binding to the deprotonated carboxylic groups [28] by decreasing the amounts of surface charge, which decreases the magnitude of mobilities. However, such explanation is not applicable at lower pH because of less deprotonated groups. So, the discrepancies at lower pH within our simple modeling seem to be attributed to mixed effects due to mutual interaction between K^+ and TPP^+ ions. Since TPP^+ ions have larger hydrophobicity, in other words, higher affinity to the hydrophobic latex surfaces than K^+ ions, TPP^+ ions tend to accumulate near the surface than K^+ ions. In addition, K^+ ions experience electrical repulsion with TPP^+ ions and less attraction with the surface due to its lower surface charge density at low pH. These interactions between the surface and ions might cause the depletion of K^+ ions between the surface and TPP^+ ions, which can augment the TPP^+ adsorption by depletion forces. Related specific ionic effects have been examined in the previous work [15], however, mixed effects of ions with different surface affinity on the adsorption are still under consideration. Molecular dynamics and Monte Carlo simulation would help to clarify this enhanced adsorption in mixed solution.

Another possible effect, which can apparently reduce the adsorption energy in our modeling, is to consider ionic steric effect due to ionic saturation and finite size effects in adsorption process. Along with an approximated mean field model for the steric effect discussed in the previous research [17], an estimate for the excess chemical potential of TPP^+ at the Stern layer is given by $\mu_{ex} \approx k_B T \ln(1 + C_s v)$, where $C_s = \Gamma_s/(2r_s)$ calculated from Eq. (5) is the TPP^+ concentration at the Stern layer, and $v \approx 200\ \mathrm{cm}^3/\mathrm{mol}$ is the volume of the cation approximated as the value for $TPAs^+$ (tetraphenyl arsonium ion) [29]. In 50 mM solution of pure TPPCl with constant adsorption energy of $\phi = 6\,k_B T$, one estimates $C_s \approx 2.38$ M, and leads a repulsive free energy with $\mu_{ex} \approx 0.39\,k_B T$. This value is still smaller than the reduction of adsorption energy of $|\phi_{max} - \phi_{min}| = 2\,k_B T$, suggesting that the steric effect is not dominant in the TPP^+ adsorption. Therefore, our interpretation can be valid in the solution where TPPCl is dominant, although we need more sophisticated theoretical treatment for the reduction of adsorption energy in the future.
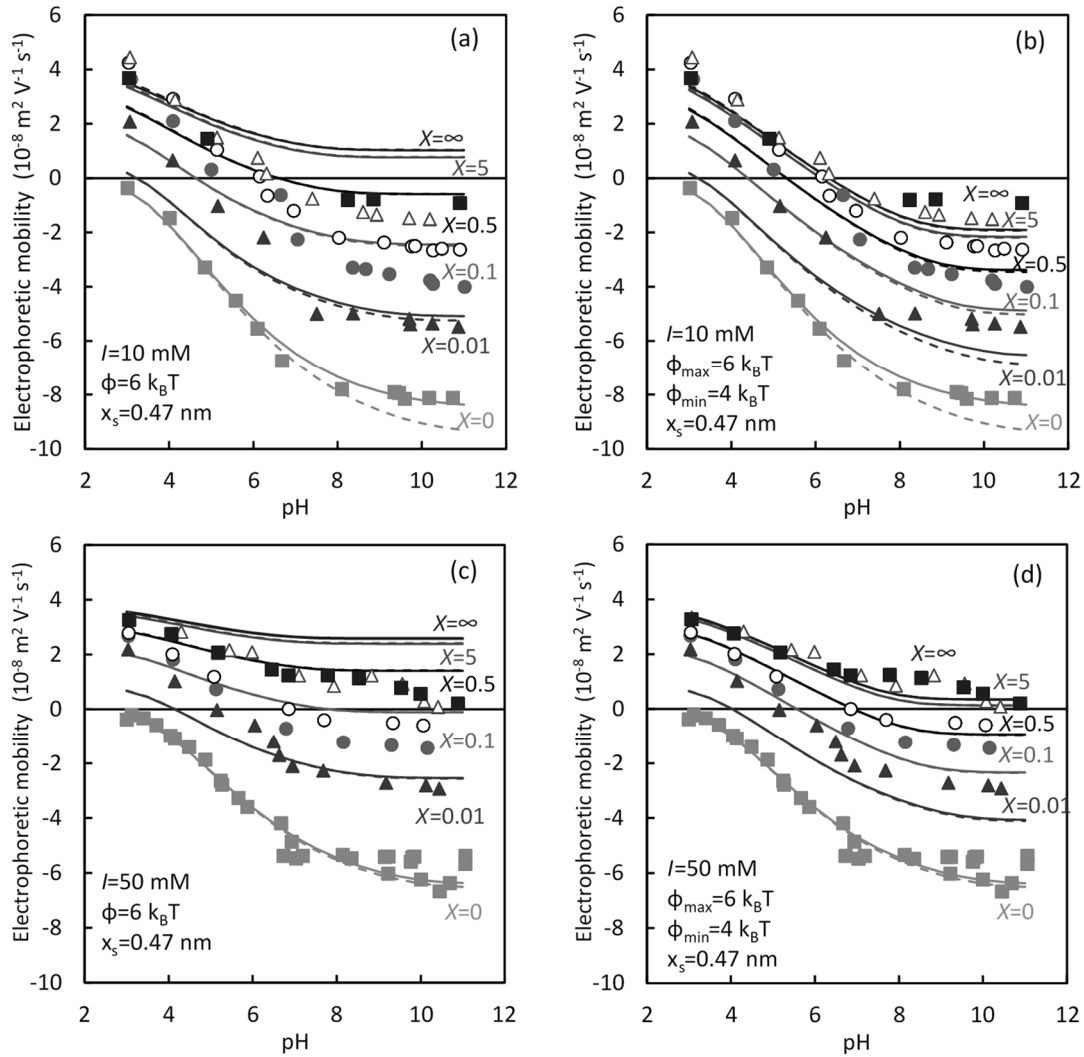
Figure 1 The relationship between electrophoretic mobility of carboxyl latex particles and pH in mixed solution of KCl and TPPCl at 10 mM for (a,b) and 50 mM for (c,d). Symbols are experimental values. Solid and dashed lines are theoretical values calculated by the Ohshima equation and the Smoluchowski equation, respectively. Mixed molar ratios $X= [TPP^+] / [K^+]$ are 0, 0.01, 0.1, 0.5, 5 and ∞ from lower to upper lines. Calculated values in (a,c) are obtained by assuming the constant non-electrostatic intrinsic energy of TPP^+ adsorption and theoretical values in (b,d) are calculated by assuming pH-dependent intrinsic energy of TPP^+ adsorption.

5. Conclusion

Electrophoretic mobilities of carboxyl latex particles were measured in mixed solutions of KCl and TPPCl as a function of the pH, the ionic strength, and the mixed molar ratio of $X=[TPP^+]/[K^+]$ to reveal the effect of hydrophobicity on the charge reversal. We observed that the charge reversal of the latex occurred at low pH in the presence of hydrophobic TPP^+ ions because of hydrophobic interaction. With increasing pH, the EPMs were reversed again due to

the increased deprotonation of carboxylic groups and the reduction of hydrophobic interaction. With the theoretical analysis describing such charge re-reversal, we found the reduction in the intrinsic energy of adsorption of TPP$^+$ with increasing the charge density from $6k_BT$ at the lowest charge density to $4k_BT$ at the highest charge density. This finding supports the conclusion in the previous work [19] and suggests that the non-electrostatic energy of adsorption of TPP$^+$ is dependent on the surface charge density of adsorbents.

Conflict of interest
The authors declare that they have no conflict of interest associated with this article.

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