

Electrophoretic mobility of carboxyl latex particles in the mixed solution of 1:1 and 2:1 electrolytes or 1:1 and 3:1 electrolytes: experiments and modeling

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1. Introduction

Colloidal particles aggregate when the solution condition is close to the isoelectric point of the particles and/or the ionic strength is high. Also, the critical coagulation concentration, which is the minimum electrolyte concentration inducing fast coagulation, decreases with increasing the valence of counter-ion. These trends found experimentally are theoretically explained by the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory [1,2]. The DLVO theory assumes that the interparticle interaction is given by the sum of electrostatic double layer force and the van der Waals attractive force. The former force is a function of surface electric potential, electrolyte concentration, and valence of ions. Therefore, to discuss the aggregation-dispersion behavior, we need to quantitatively evaluate charging behaviors of the particle in solutions having different ionic composition.

Measurement of electrophoretic mobility (EPM) is widely used to characterize the charging behavior of colloidal particles. While the EPM reflects the sign and magnitude of surface potential, proper theories must be used to evaluate EPM from surface charge of the particle. EPM of monodisperse latex spheres as model colloidal particles has been extensively researched over the years [3-6]. For the latex particles bearing a constant surface charge density in 1:1 electrolyte solution, the dependence of EPM on salt concentration can be described by the O'Brien-White (OW) theory or the Ohshima equation that calculates EPM from the surface or electrokinetic potential, which is obtained from the charge density with the Gouy-Chapman (GC) theory derived from the Poisson-Boltzmann equation [4]. Such methodology can be successfully applied to EPM in a solution containing divalent ions [7,8]. For carboxyl latex particles in KCl solution, measured values of pH-dependent EPM were compared with theoretical ones calculated using $1-pK_H$ GC model and OW theory [9]. The $1-pK_H$ GC model is applied for the evaluation of surface charge and potential as a function of pH. Their result demonstrated that theoretical EPM reasonably agrees with experimental data. A similar result was obtained by Sugimoto *et al.*[10]. Ottewill and Shaw measured the EPM of carboxyl latex particles with various diameters and surface charge densities as a function of $La(NO_3)_3$ and $Nd(NO_3)_3$ concentration [11], and they showed that the charge reversal occurred in a solution containing trivalent ions. James and Healy also observed the charge reversal for SiO_2 in $La(NO_3)_3$ at high pH [12]. However, these researchers did not sufficiently focus on the effect of surface charge density and did not report on a comparison with the theoretical calculation assuming the presence of multivalent ions.

In soil and aquatic environments, colloidal dispersions contain multiple ionic species with different valences. The ionic composition significantly affects the charging and aggregation of colloidal particles [13,14]. Therefore, it is important to understand the charging properties of

colloidal particles in a mixed solution of multiple ionic species. Chow and Takamura measured EPMs of bitumen-in-water emulsion particles in mixed solutions of NaCl and CaCl₂ or MgCl₂ [15]. Their experimental values were compared with theoretical ones calculated using the OW theory and a charging model taking account of the counter-ion binding to the surface charge group. However, they did not obtain quantitative agreement between the experimental and theoretical values. Kobayashi and Sasaki showed the results of measurements and analysis of the EPM of sulfate latex in mixed solutions of KCl and MgCl₂ [16]. The experiments were carried out as functions of the concentration ratio of Mg²⁺ to K⁺ and of the total concentration of electrolytes. From the comparison of theoretical and experimental data, they suggested that the position of the slipping plane, where the zeta or electrokinetic potentials are defined, was needed to shift from the particle surface in the presence of MgCl₂, indicating that the presence of multivalent ions significantly affect EPM compared to monovalent ions. Several studies pointed out the occurrence of counter-ion adsorption to the surface [5,6], counter-ion association on the surface groups [17], reduction of the surface charge [7], and ion-ion correlation [18,19]. However, systematic measurements and modeling of EPMs of colloidal particles in mixed electrolyte solutions containing divalent and trivalent counter-ions are still lacking.

In this study, the EPM of carboxyl latex particles was measured as functions of pH, the ionic strength, and the mixing molar ratio of Ca²⁺ to K⁺ ($X = [\text{Ca}^{2+}] / [\text{K}^+]$) or La³⁺ to K⁺ ($X = [\text{La}^{3+}] / [\text{K}^+]$). The obtained experimental data were compared with theoretical ones calculated by using 1-p \bar{K}_H model with or without Ca²⁺ or La³⁺ association, the diffuse double layer model, and the Ohshima equation and the CellMobility program including the relaxation effect or the Smoluchowski equation neglecting the relaxation effect. From comparisons of experiments and the theory, we demonstrate the significance and limitation of the theoretical model assuming the binding of multivalent counter-ion to the particle surface.

2. Material and methods

2.1 Materials

Carboxylated polystyrene latex particles (Interfacial Dynamics Corporation) were used as colloidal particles. Carboxyl latex particles bear pH-dependent negative charge due to the deprotonation of the carboxyl groups on the particle surface. The manufacturer reports that the maximum surface charge density is -182 mC/m², the diameter is $2a = 1.5 \pm 0.03 \mu\text{m}$, and the density is 1.055 g/cm³, respectively. KCl, CaCl₂ · 2H₂O and LaCl₃ · 7H₂O (JIS special grade, Wako Pure Chemical Industries) 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 [20]. Before sample preparation, all solutions were filtered with a 0.20 μm pore filter (Millex-LG, MILLIPORE). All solutions and suspensions were prepared from pure water (Elix, MILLIPORE) and degassed before use.

2.2 Experimental Methods

EPM was measured by electrophoretic light scattering using Zetasizer NANO-ZS (Malvern). Measurements were carried out as a function of solution pH at different mixed molar ratio $X = [\text{Ca}^{2+}] / [\text{K}^+]$ or $X = [\text{La}^{3+}] / [\text{K}^+]$ with fixed ionic strength. The pH was adjusted in the range from 3 to 11 with HCl and KOH solutions. In mixed electrolyte solutions containing Ca^{2+} , ionic strengths were 1 mM, 10 mM, and 50 mM, and mixed molar ratios X were 0, 0.01, 0.1, and 0.5. In mixed electrolyte solutions containing La^{3+} , ionic strengths were 1 mM and 10 mM, and mixed molar ratios X were 0, 0.001, 0.01, 0.1, and 0.5. The particle concentration was 50 mg/L. The samples were prepared by mixing the suspension of latex particles, KCl solution, CaCl_2 solution or LaCl_3 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 $^\circ\text{C}$.

3. Theoretical Analysis

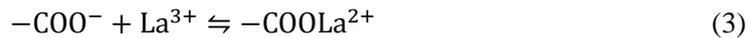
1- pK_{H} model with or without $\text{Ca}^{2+}/\text{La}^{3+}$ association and the Ohshima equation were used to calculate theoretical EPM.

3.1 1- pK model

In the 1- pK_{H} model without $\text{Ca}^{2+}/\text{La}^{3+}$ association, the surface charge arises from the deprotonation of carboxyl groups. On the one hand, in the 1- pK_{H} model with $\text{Ca}^{2+}/\text{La}^{3+}$ association, the surface charge is developed by the deprotonation of carboxyl groups and the binding of $\text{Ca}^{2+} / \text{La}^{3+}$ to the deprotonated carboxyl groups. That is,



or



The association and dissociation equilibria between the carboxyl groups and the cationic species in the electrolyte solution are characterized by the proton dissociation constant and the ion-association constant defined as [17]

$$pK_{\text{H}} = -\log_{10} K_{\text{H}} = -\log_{10} \frac{\alpha_{[-\text{COO}^-]} \alpha_{[\text{H}^+]}}{\alpha_{[-\text{COOH}]}} \quad (4)$$

$$\log_{10} K_{Ca} = \log_{10} \frac{\alpha_{[-COOCa^+]}}{\alpha_{[-COO^-]}\alpha_{[Ca^{2+}]}} \quad (5)$$

$$\log_{10} K_{La} = \log_{10} \frac{\alpha_{[-COOLa^{2+}]}}{\alpha_{[-COO^-]}\alpha_{[La^{3+}]}} \quad (6)$$

where α_{H^+} , $\alpha_{Ca^{2+}}$ and $\alpha_{La^{3+}}$ are the surface activities of proton, calcium and lanthanum ions, K_H is the acid dissociation constant, K_{Ca} and K_{La} are the association constants of Ca^{2+} and La^{3+} . The value of pK_H used in this study is 4.9 from the literature [9,10]. The values of $\log K_{Ca}$ and $\log K_{La}$ are determined to fit experimental data. The surface charge density is derived from the deprotonation of the carboxyl group and the binding of Ca^{2+} and La^{3+} to the deprotonated carboxyl group. That is,

$$\sigma = -e\Gamma_{[-COO^-]} \quad (7)$$

$$\sigma = -e\{\Gamma_{[-COO^-]} - \Gamma_{[-COOCa^+]}\} \quad (8)$$

$$\sigma = -e\{\Gamma_{[-COO^-]} - 2\Gamma_{[-COOLa^{2+}]}\} \quad (9)$$

where e is the elementary charge. These surface activities are related to the bulk activity and the surface potential by the Boltzmann distribution

$$\alpha_i = \alpha_i^b \exp\left(-\frac{z_i e \psi_0}{k_B T}\right) \quad (10)$$

where α_i^b is the activity of the i -th ionic species in the bulk, z_i is the valence of the i -th ionic species, k_B is the Boltzmann constant, T is the absolute temperature, and ψ_0 is the surface potential. The relationship between the surface charge density σ and the surface potential ψ_0 is given by the Poisson-Boltzmann equation as follows: [21]

$$\sigma = \frac{\varepsilon_r \varepsilon_0 \kappa k_B T}{e} f(y_0) \quad (11)$$

with

$$\kappa = \left(\frac{1}{\varepsilon_r \varepsilon_0 k_B T} \sum_{i=1}^N z_i^2 e^2 n_i \right)^{1/2} \quad (12)$$

where ε_r is the relative permittivity of the liquid, ε_0 is the permittivity of vacuum, $1/\kappa$ is the Debye length, N is the number of ionic species, and n_i is the concentration of the i -th ionic species. For a 1:1 electrolyte solution, $f(y_0)$ as follows [21]

$$f(y_0) = 2 \sinh\left(\frac{y_0}{2}\right) \quad (13)$$

with

$$y_0 = \frac{e\psi_0}{k_B T} \quad (14)$$

In 1:1 and 2:1 mixed electrolyte solution, [21]

$$f(y_0) = (1 - \exp(-y_0)) \left[\left(1 - \frac{\eta}{3}\right) \exp(-y_0) + \frac{\eta}{3} \right]^{1/2} \quad (15)$$

with

$$\eta = \frac{3n_2}{n_1 + 3n_2} \quad (16)$$

where n_1 is the concentration of 1:1 electrolyte solution and n_2 is the concentration of 2:1 electrolyte solution.

For a mixed electrolyte solution of 1:1 and 3:1,[21]

$$f(y_0) = (1 - \exp(-y_0)) \left[\left(1 - \frac{\eta'}{2}\right) \exp(-y_0) + \frac{\eta'}{3} + \frac{\eta'}{6} \exp(-y_0) \right]^{1/2} \quad (17)$$

with

$$\eta' = \frac{6n_3}{n_1 + 6n_3} \quad (18)$$

where n_3 is the concentration of 3:1 electrolyte solution.

Eqs. (13), (15), and (17) neglects the curvature of the surface, it is equivalent to assume planar geometry. However, the curvature have negligible effects on electrical potential distribution around a sphere which have been shown by the numerical calculation [22] in the case of large $\kappa a (> 10)$. This condition is satisfied in all our experiments, since the smallest value of κa is 77.8. Therefore, for simplicity, we utilize following equations derived for planar surfaces to spherical particles to calculate the electrical potential distribution near the surface. The electrostatic potential at a distance from the surface is related to the surface potential ψ_0 . The zeta potential can be calculated as the electrostatic potential at the slipping plane from the particle surface.

In a 1:1 electrolyte solution, the zeta potential at a distance from the surface is related to the surface potential by [21]

$$\zeta = \psi(x_s) = \frac{4k_B T}{e} \tanh^{-1} \left[\tanh \left(\frac{e\psi_0}{4k_B T} \right) \exp(-\kappa x_s) \right] \quad (19)$$

where x_s is the distance of slipping plane from the particle surface.

For 1:1 and 2:1 mixed electrolyte solution, the relationship between the zeta potential and the surface potential is written by [21]

$$\zeta = \psi(x_s) = \frac{k_B T}{e} \ln \left[\frac{1}{1 - \eta/3} \left(\frac{1 + (1 - \eta/3) \gamma^n \exp(-\kappa x_s)}{1 - (1 - \eta/3) \gamma^n \exp(-\kappa x_s)} \right)^2 - \frac{\eta/3}{1 - \eta/3} \right] \quad (20)$$

with

$$\gamma'' = \left(\frac{1}{1 - \eta/3} \right) \frac{[(1 - \eta/3)\exp(e\psi_0/k_B T) + \eta/3]^{1/2} - 1}{[(1 - \eta/3)\exp(e\psi_0/k_B T) + \eta/3]^{1/2} + 1} \quad (21)$$

For a mixed solution of 1:1 and 3:1 electrolytes, the zeta potential is calculated from the following Eqs. (22)-(24) [21] by the Runge–Kutta method.

$$\frac{dy}{dx} = -\kappa f(y) \quad (22)$$

with

$$f(y) = (1 - \exp(-y)) \left[\left(1 - \frac{\eta'}{2} \right) \exp(y) + \frac{\eta'}{3} + \frac{\eta'}{6} \exp(-y) \right]^{1/2} \quad (23)$$

$$y(x_s) = \frac{e\psi(x_s)}{k_B T} = \frac{e\zeta}{k_B T} \quad (24)$$

where $y(x)$ is the scaled potential. The value of x_s used in this study is kept 0.25 nm taken from the literature [9,10].

3.2 Electrophoretic mobility (EPM)

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

The Smoluchowski equation is given by

$$\mu_m = \frac{\varepsilon_r \varepsilon_0}{\eta_s} \zeta \quad (25)$$

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

EPM for a negatively charged particle in 1:1 electrolyte solution such as KCl is written by the Ohshima, Healy, White equation [23].

$$\begin{aligned} \mu_m = \text{sgn}(\zeta) \frac{\varepsilon_r \varepsilon_0}{\eta_s} & \left\{ |\zeta| - \frac{2F}{1+F} \left(\frac{k_B T}{e} \right) H \right\} \\ & + \text{sgn}(\zeta) \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\eta_s e} \left[\frac{1}{\kappa a} \left\{ -18 \left(t + \frac{t^3}{9} \right) K \right. \right. \\ & + \frac{15F}{1+F} \left(t + \frac{7t^2}{20} + \frac{t^3}{9} \right) \\ & - 6(1 + 3\tilde{m}) \left(1 - \exp(-\tilde{\zeta}/2) \right) G + \frac{12F}{(1+F)^2} H \\ & \left. \left. + \frac{9\tilde{\zeta}}{1+F} (\tilde{m}G + mH) - \frac{36F}{1+F} \left(\tilde{m}G^2 + \frac{m}{1+F} H^2 \right) \right\} \right] \end{aligned} \quad (26)$$

with

$$H = \ln \frac{1 + \exp(\tilde{\zeta}/2)}{2}, \quad K = 1 - \frac{25}{3(\kappa a + 10)} \exp\left(-\frac{\kappa a}{6(\kappa a - 6)} \tilde{\zeta}\right) \quad (27)$$

$$F = \frac{2}{\kappa a} (1 + 3m) (\exp(\tilde{\zeta}/2) - 1), \quad G = \ln \frac{1 + \exp(-\tilde{\zeta}/2)}{2} \quad (28)$$

$$t = \tanh(\tilde{\zeta}/4), \quad \tilde{\zeta} = \frac{e\zeta}{k_B T} \quad (29)$$

$$m = \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\eta_s e^2} \lambda, \quad \tilde{m} = \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\eta_s e^2} \tilde{\lambda}, \quad (30)$$

$$\lambda = \tilde{\lambda} = \frac{N_A e^2}{\Lambda_i^\circ} \quad (31)$$

where $\text{sgn}(x)$ is 1 when $x > 0$ or -1 when $x < 0$, m and \tilde{m} are the scaled drag coefficient of counter-ions and co-ions, respectively, N_A is the Avogadro constant, and Λ_i° is the values of the limiting equivalent conductance of the i -th ionic species. In Eq.(26), the relative error is decreased to $<1\%$ for $\kappa a > 10$ as compared to the O'Brien-White theory [23]. Therefore, Eq.(26) can be used to calculate the EPM since the smallest value of κa is 77.8 in our experiments.

In mixed solutions of 1:1 and 2:1 electrolytes such as KCl and CaCl₂ is given by [24]

$$\begin{aligned} \mu_m = \frac{\varepsilon_r \varepsilon_0}{\eta_s} \left[\zeta + \left(\frac{1}{1 + F_{+1}} + \frac{1}{1 + F_{+2}} - 2 \right) \left\{ \frac{\zeta}{2} - \left(\frac{k_B T}{e} \right) \ln \left(\frac{1 + \beta}{2} \right) \right\} \right. \\ \left. + \left(\frac{1}{1 + F_{+1}} - \frac{1}{1 + F_{+2}} \right) H(\zeta, \alpha) \right] \end{aligned} \quad (32)$$

where

$$F_{+1} = \frac{2}{\kappa a} (1 + 3m_{+1}) \left\{ \exp\left(\frac{e|\zeta|}{2k_B T}\right) - 1 \right\} \quad (33)$$

$$F_{+2} = \frac{\sqrt{3}}{\kappa a} (1 + 3m_{+2}) \left\{ \exp\left(\frac{e|\zeta|}{k_B T}\right) - 1 \right\}$$

$$m_{+1} = \frac{2\varepsilon_r \varepsilon_0 k_B T}{3\eta_s e^2} \lambda_{+1} = \frac{2N_A \varepsilon_r \varepsilon_0 k_B T}{3\eta_s \Lambda_{+1}^\circ} \quad (34)$$

$$m_{+2} = \frac{\varepsilon_r \varepsilon_0 k_B T}{6\eta_s e^2} \lambda_{+2} = \frac{N_A \varepsilon_r \varepsilon_0 k_B T}{3\eta_s \Lambda_{+2}^\circ}$$

$$\alpha = \frac{3n_2}{n_1 + 3n_2}, \quad \beta = \sqrt{\frac{\alpha}{3} + \left(1 - \frac{\alpha}{3}\right) \exp\left(\frac{e\zeta}{k_B T}\right)} \quad (35)$$

$$\frac{\phi_{+1}(a)}{a} = \frac{3}{2(1+F_{+1})}, \quad \frac{\phi_{+2}(a)}{a} = \frac{3}{2(1+F_{+2})}, \quad \frac{\phi_{-1}(a)}{a} = \frac{3}{2} \quad (36)$$

$$\begin{aligned} H(\zeta, \alpha) = & \frac{(1-\alpha)}{2} \sqrt{\frac{3}{\alpha}} \left\{ \left(\frac{e\zeta}{k_B T} \right) \ln \left[\left(\frac{1+\sqrt{\alpha/3}}{1-\sqrt{\alpha/3}} \right) \left(\frac{1-\beta}{1+\beta} \right) \right] \right. \\ & - 2 \ln \left(\frac{\beta + \sqrt{\alpha/3}}{1 + \sqrt{\alpha/3}} \right) \cdot \ln \left(\frac{1-\beta}{1+\beta} \right) - Li_2 \left(\frac{\beta + \sqrt{\alpha/3}}{1 + \sqrt{\alpha/3}} \right) \\ & + Li_2 \left(\frac{\beta - \sqrt{\alpha/3}}{1 - \sqrt{\alpha/3}} \right) - Li_2 \left(-\frac{\beta - \sqrt{\alpha/3}}{1 + \sqrt{\alpha/3}} \right) \\ & + Li_2 \left(-\frac{\beta + \sqrt{\alpha/3}}{1 - \sqrt{\alpha/3}} \right) - Li_2 \left(-\frac{1 + \sqrt{\alpha/3}}{1 - \sqrt{\alpha/3}} \right) \\ & \left. + Li_2 \left(-\frac{1\sqrt{\alpha/3}}{1 + \sqrt{\alpha/3}} \right) \right\} - \frac{e\zeta}{2k_B T} + \ln \left(\frac{1+\beta}{2} \right) \\ & Li_2(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^2} \quad (37) \end{aligned} \quad (38)$$

where $Li_2(z)$ is a dilogarithm function. In this study, the values of Λ_i° (10^{-4} S m²/mol) used were 66.17 for K⁺, 53.55 for Ca²⁺, 62.64 for La³⁺, and 68.68 for Cl⁻. These values were obtained from the literature [25]. Eq.(32) is applicable to $\kappa a > 30$ with tolerable errors [24]. Thus, Eq.(32) can be applied to estimate the EPM since the smallest value of κa is 77.8 in our experiments.

For an 1:1 and 3:1 mixed electrolyte solution, the EPM is obtained using the CellMobility program provided by the authors of refs.[26–28]. The program takes account of the relaxation effect.

4. Result and discussion

4.1 Mixed solution of KCl and CaCl₂

Figure 1 and Figure 2 show the EPMs of carboxyl latex particle as a function of the solution pH at different ionic strengths. In Fig.1 and Fig.2, the symbols are experimental values, the solid lines are the theoretical values calculated by the Ohshima equation including 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) and Fig.2 (a-c) are drawn by neglecting Ca²⁺ association, the lines in Fig. 2 (d-f) are obtained with taking account of Ca²⁺ association. As pH increases, the absolute value of the EPM increases. The magnitude of the EPM is large at high pH due to the deprotonation of the carboxyl groups on the particle. At low pH, EPMs are almost on a single curve irrespective of the ratio X . This result means that the charging behavior is controlled by ionic strength at low pH even in the presence of Ca²⁺. At low

pH, the surface potential is low due to the weak deprotonation of carboxyl groups. Therefore, Ca^{2+} ions are weakly attracted to the surface, and Ca^{2+} ions do not condense on the surface. Thus the binding of Ca^{2+} to the deprotonated carboxyl group is negligible. On the one hand, at high pH, as the ratio X increases at fixed ionic strength, the absolute value of the EPM decreases. This reduction is attributed to the increase of Ca^{2+} concentration near the surface. At high pH, the negative surface potential becomes high because the number of deprotonated carboxyl groups is large. As a result, Ca^{2+} is strongly attracted to the surface. A similar tendency is also observed at 1 mM, 10 mM, and 50 mM.

Comparing theoretical values to measured data, one can notice that the theoretical EPMS calculated by the Smoluchowski equation neglecting the relaxation effect (dashed lines) are much larger in magnitude than EPM at low ionic strength and low ratio X . In contrast, the EPMS calculated by the Ohshima equation including the relaxation effect (solid lines) qualitatively agree with experimental EPMS at all conditions. Additionally, the theoretical EPMS calculated by the Ohshima equation using $1-pK_H$ without Ca^{2+} association model show the same tendency as the experimental ones (Fig. 2 (a)). Thus, the effect of screening of double layer is significant in mixed solutions containing Ca^{2+} . At high pH, however, the magnitude of the theoretical EPMS without Ca^{2+} association is still larger than the experimental ones. On the other hand, the theoretical EPMS calculated by using $1-pK_H$ model with Ca^{2+} association quantitatively agree with the experimental ones (Fig. 2 (d)). Therefore, the binding of Ca^{2+} with deprotonated carboxyl groups is crucial when describing the charging behavior of the particle. That is, the binding of Ca^{2+} reduces the net surface charge. The present $\log K_{\text{Ca}}$ values were found to be 1.8 for 1 mM, 0.83 for 10 mM and 0.53 for 50 mM ionic strengths (Table 1). Using the constant $\log K_{\text{Ca}}$ value is successful when describing EPM at different ratios X at each ionic strength. However, the $\log K_{\text{Ca}}$ depends on the ionic strength; with increasing the ionic strength, $\log K_{\text{Ca}}$ value decreases. David *et al.* reported that $\log K_{\text{Ca}}$ of the polyacrylic acid, which has carboxyl groups, depends on the ionic strength in mixed solution of KNO_3 and $\text{Ca}(\text{NO}_3)_2$ [29]. Moreover, the $\log K_{\text{Ca}}$ of acetic acid is 0.59 [25]. Thus, we consider $\log K_{\text{Ca}}$ values of this study are reasonable. From the context of competition for ion adsorption, the model developed by Miklavic *et al.* [30] might be useful for taking into account for different finite hydrated sizes of monovalent and divalent counter-ions on the surface. However, the hydration behavior of ions near the charged surfaces is still an open question in detail. So, we remain including the finite ionic sizes and ion correlation into the modeling as a future issue.

4.2 Mixed solution of KCl and LaCl_3

Figure 3 and Figure 4 show the relationship between the EPM and pH in mixed solution of KCl and LaCl_3 at different ionic strengths. In Fig. 3 and Fig. 4, the symbols are experimental values,

the solid lines are the theoretical values calculated by the CellMobility program including the relaxation effect, and the dashed lines are the theoretical values evaluated using the Smoluchowski equation neglecting the relaxation effect. While the lines in Fig. 3 (a,b) and Fig. 4 (a,b) are drawn by neglecting La^{3+} association, the lines in Fig. 4 (c,d) are obtained taking account of La^{3+} association. At low pH, the experimental values of mobility are negative and are on a single curve irrespective of the ratio X . These tendencies are observed in a mixed solution of KCl and CaCl_2 as described above. Therefore the charging behavior of weakly charged surface is controlled by the ionic strength even in the presence of trivalent ions. In contrast, at high pH, the absolute value of the EPM decreases with increasing pH and the ratio X . The main reason for this reduction is the increase of La^{3+} concentration near the surface. At high pH, the number of the deprotonated carboxyl groups is large. Accordingly, the concentration of La^{3+} at the near surface increases because La^{3+} is strongly attracted to the surface. Although the charge reversal is not observed in a mixed solution of KCl and CaCl_2 , the EPM is reversed to a positive value at high pH with La^{3+} ; the charge reversal occurs at pH 6 to 7, and then the positive value of EPM increases. Moreover, as the mixing ratio X increases, the charge reversal occurs at lower pH and the positive value of the EPM increases. However, the charge reversal does not occur when La^{3+} concentration is low even at high pH. Previous researchers reported that EPM of negatively charged particles is reversed to positive at high pH in LaCl_3 [6,28], $\text{La}(\text{NO}_3)_3$ [12], or KCl and LaCl_3 solutions [32]. Additionally, Martin-Molina *et al.* showed that EPM of highly charged particles, which have sulfonate groups, was reversed at high $\text{La}(\text{NO}_3)_3$ concentration [19]. Thereby, our results confirm that the EPM of carboxyl latex becomes positive only when the carboxyl groups are highly deprotonated and the La^{3+} concentration is high in mixed electrolyte solution containing La^{3+} .

In comparison with the measured data, the theoretical EPMs calculated by using $1-pK_H$ without La^{3+} association model do not agree with the experimental ones (Fig. 4 (a) and (b)). On the other hand, at low pH, as seen in Fig. 4 (c) and (d), the theoretical EPMs calculated by using $1-pK_H$ model with La^{3+} association reasonably agree with the experimental ones. That is, the binding of La^{3+} reduces the surface negative charge. Therefore, for the weakly charged surface, the modeling of La^{3+} association is effective for the evaluation of the charging behavior of the particle. Constant $\log K_{\text{La}}$ values are available for different mixing ratios X at each ionic strength (Table 1). As the ionic strength increases, $\log K_{\text{La}}$ value decreases. Similar tendencies are observed in a mixed solution of KCl and CaCl_2 as discussed above. Also, we refer to that the chosen values for $\log K_{\text{La}}$ in this study are reasonable compared to the $\log K_{\text{La}}=2.44$ for acetic acid [23]. The Poisson-Boltzmann equation successfully describes the behavior of trivalent counter-ions for the interaction with the weakly charged surface. At high pH, however, theoretical values by our model do not show the occurrence of charge reversal in spite of taking

account of La^{3+} association. The present model with the binding of La^{3+} is unable to describe EPM at high pH, because the reversed surface potential prevents further binding of La^{3+} . To confirm this observation, we have tried to calculate the model with extremely high $\log K_{\text{La}}$. Consequently, we found that increasing $\log K_{\text{La}}$ value gives rise to the charge reversal at unreasonably very low pH and does not fit the experiment. Therefore, trivalent La^{3+} ions are strongly attracted and over-compensated by highly charged surface through interactions which cannot be described by the Poisson-Boltzmann equation. In the Poisson-Boltzmann equation, ions are considered as point charges and the ion-ion interaction is neglected. Martin-Molina *et al.* calculated the diffuse layer potential by taking into account the size of the ion and the interaction energy between ion and ion/the charged wall in the presence of $\text{La}(\text{NO}_3)_3$ [19]. Their results showed the charge reversal occurs at high charge density. Meanwhile, the influence of hydrolysis of metal cations is definitely one of the important subjects. Jiménez *et al.* suggested that the charge reversal occurs mainly due to the specific adsorption of hydrolyzed Al^{3+} ions when they appear [33]. From their discussion, we judge that the effect of hydrolysis of trivalent cations becomes significant when the ratio of hydrolyzed cation specie exceeds few % in the total cations. For La^{3+} , Ottewill and Shaw [11] showed that the ratio of hydrolyzed species reaches few % at pH 7-8. Therefore, we should consider the hydrolysis effect at pH beyond 7-8. Also, Jiménez *et al.* mentioned that when the hydrolysis of trivalent cations is likely to be absent, at pH probably lower than 7-8 in our study, overcharging can be attributed to ion-ion correlation or adsorption of bare multivalent ions such as La^{3+} ion. The usefulness of the latter concept is successfully demonstrated for the mobility in the presence of La^{3+} at lower pH in our study. Thus, at high pH, to improve the modeling of La^{3+} behavior used in this study, we need to include additional factors, which are sensitive to the density of deprotonated carboxyl groups, and the adsorption of hydrolysis products.

5. Conclusion

Electrophoretic mobility (EPM) of carboxyl latex particles was measured in mixed electrolyte solution of KCl and CaCl_2 or KCl and LaCl_3 as functions of the solution pH, the mixed molar ratio of Ca^{2+} to K^+ ($X = [\text{Ca}^{2+}] / [\text{K}^+]$), or La^{3+} to K^+ ($X = [\text{La}^{3+}] / [\text{K}^+]$) and the ionic strength. Experimental EPM was analyzed by using 1- $\text{p}K_{\text{H}}$ with or without Ca^{2+} / La^{3+} association model, diffuse double layer model, and the Ohshima equation and the CellMobility program including the relaxation effect or the Smoluchowski equation neglecting the relaxation effect. In the mixed solution of KCl and CaCl_2 , the theoretical EPMs calculated by using 1- $\text{p}K_{\text{H}}$ model with Ca^{2+} association and the Ohshima equation including the relaxation effect quantitatively agree with the experimental ones. This result demonstrates that the surface charge reduces through the binding of Ca^{2+} to deprotonated carboxyl groups. For a mixed solution of KCl and LaCl_3 , the

theoretical EPMs calculated by using 1-pK_H model with La³⁺ association and EPM theory including the relaxation effect reasonably agree with the experimental ones at low pH, i.e. low charge density. However, the theoretical calculation underestimates the experimental one at high pH. We found that, in mixed electrolyte solution of KCl and CaCl₂ as well as KCl and LaCl₃ at low charge density, the EPMs are reasonably described by the theoretical models including the deprotonation and the binding of Ca²⁺/La³⁺ to deprotonated carboxyl groups, the diffuse double layer model, and the Ohshima equation including the relaxation effect for calculating theoretical EPM value. The Poisson-Boltzmann equation successfully describes the behavior of trivalent counter-ions for the interaction with weakly charged surface. On the contrary, the model with the binding of La³⁺ is unable to describe EPM at high pH. Trivalent La³⁺ ions are strongly attracted by highly charged surface through interactions which cannot be described by the Poisson-Boltzmann equation.

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Conflict of interest

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

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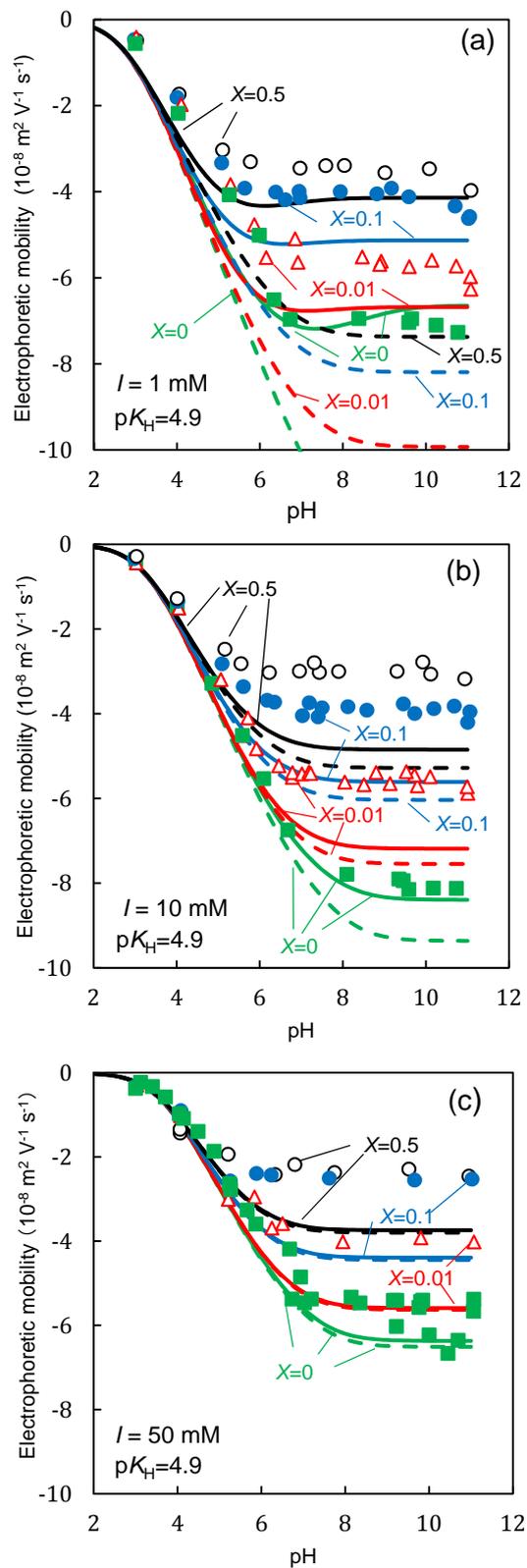


Fig. 1 The relationship between electrophoretic mobility of carboxyl latex particles and pH in mixed solution of KCl and CaCl₂. Symbols are experimental values. Lines are theoretical values calculated by the Ohshima equation (solid lines) and the Smoluchowski equation (dashed lines) without Ca²⁺ association. Mixed molar ratios $X = [\text{Ca}^{2+}] / [\text{K}^+]$ are 0, 0.01, 0.1, and 0.5 from lower to upper lines.

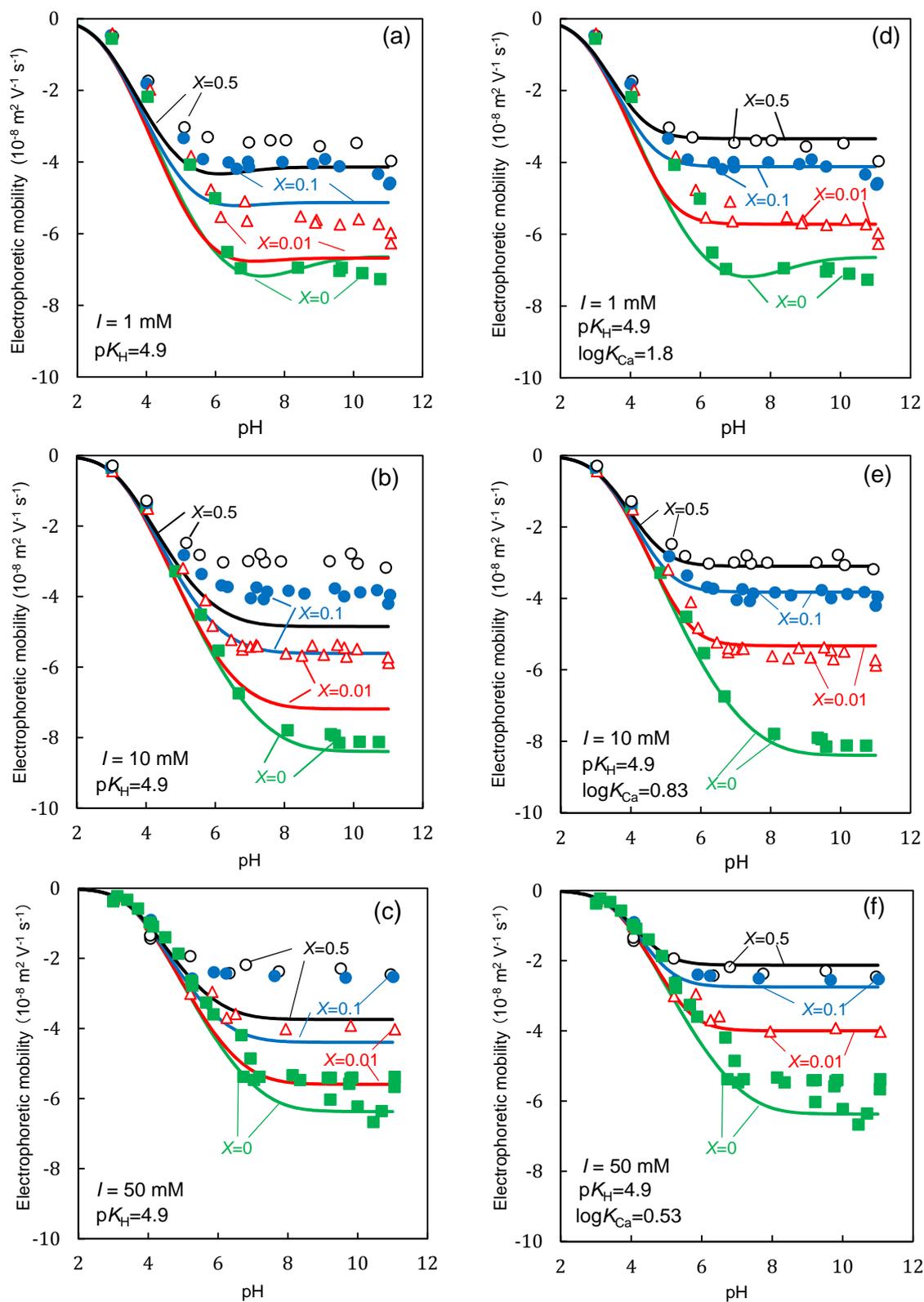


Fig. 2 The relationship between electrophoretic mobility of carboxyl latex particles and pH in mixed solution of KCl and CaCl₂. Symbols are experimental values. Lines are theoretical values calculated by the Ohshima equation. Mixed molar ratios $X = [\text{Ca}^{2+}] / [\text{K}^+]$ are 0, 0.01, 0.1, and 0.5 from lower to upper lines. Calculated values in (a), (b), and (c) are obtained without Ca²⁺ association and theoretical values in (d), (e), and (f) are calculated with Ca²⁺ association.

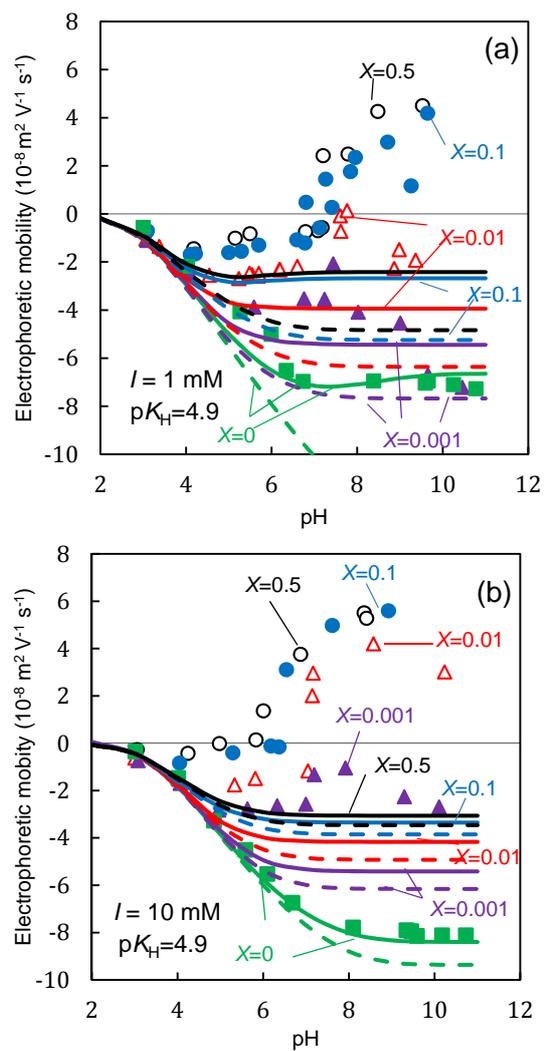


Fig. 3 The relationship between electrophoretic mobility of carboxyl latex particles and pH in mixed solution of KCl and LaCl₃. Symbols are experimental values. Lines are theoretical values calculated by the Ohshima equation (solid lines) and the Smoluchowski equation (dashed lines) without La³⁺ association. Mixed molar ratios $X = [\text{La}^{3+}] / [\text{K}^+]$ are 0, 0.001, 0.01, 0.1, and 0.5 from lower to upper lines.

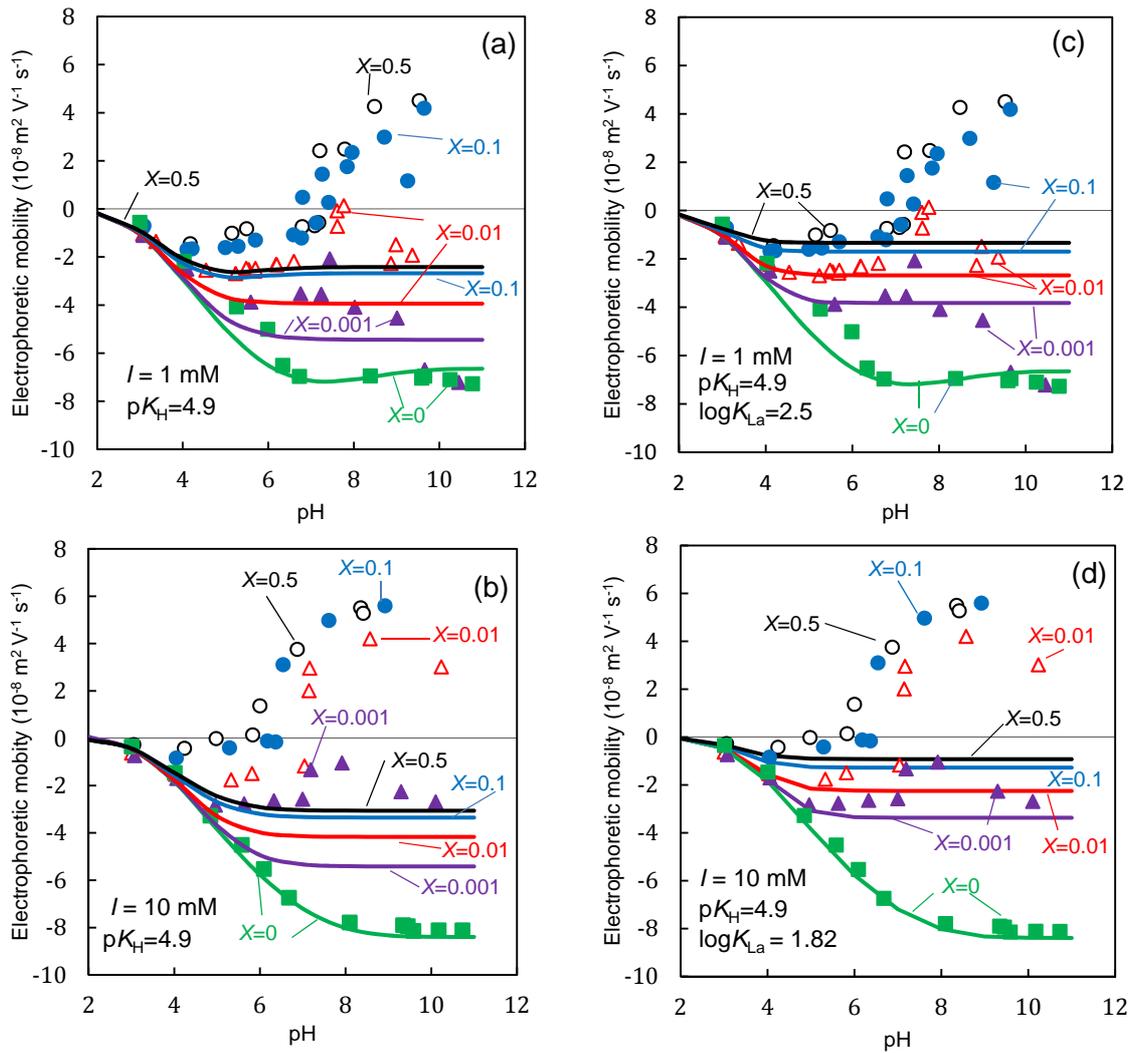


Fig. 4 The relationship between electrophoretic mobility of carboxyl latex particles and pH in mixed solution of KCl and LaCl_3 . Symbols are experimental values. Lines are theoretical values calculated by the Ohshima equation. Mixed molar ratios $X = [\text{La}^{3+}] / [\text{K}^+]$ are 0, 0.001, 0.01, 0.1, and 0.5 from lower to upper lines. Calculated values in (a) and (b) are obtained without La^{3+} association and theoretical values in (c) and (d) are calculated with La^{3+} association.

Table 1 Parameters used in the theoretical model

Ionic strength (mM)	pK_H	$\log K_{Ca}$	$\log K_{La}$
1	4.9	1.8	2.5
10	4.9	0.83	1.82
50	4.9	0.53	-