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ORIGINAL CONTRIBUTION

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# Potential distribution around a charged spherical colloidal particle in a medium containing its counterions and a small amount of added salts

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**Abstract** A theory is developed for the potential distribution around a charged spherical colloidal particle carrying ionized groups on the particle surface in a medium containing its counterions (i.e., counterions produced from dissociation of the particle surface groups) and a small amount of added salts on the basis of the theory of Imai and Oosawa. Numerical solutions to the Poisson–Boltzmann equation for the potential distribution are obtained for the case of dilute (but not infinitely dilute) particle suspensions of volume fraction $\phi \ll 1$ for $\kappa a \ll 1$ (where $\kappa$ is the Debye–Hückel parameter and $a$ is the particle radius). Here we have taken into account the effects of (i) counterions from the particle surface groups, and (ii) the finite particle volume fraction. These effects, which are usually neglected in the conventional Poisson–Boltzmann equation, are found to be important. It is found that, as in the case of completely salt-free media, there is a certain critical value of the particle charge (which is the same as that for the completely salt-free case). When the particle charge is lower than the critical value, the potential is given by a Coulomb potential. If the particle charge is higher than the critical value, then counterions are accumulated in the vicinity of the particle surface (counterion condensation) and the potential becomes less dependent on the particle charge. The above behaviors can be observed even for the case where the electrolyte concentration is higher than the concentration of counterions from the particle surface groups, if the conditions $\phi \ll 1$ and $\kappa a \ll 1$are both satisfied.

**Keywords** Surface potential · Salt-free medium · Spherical particle · Counterion condensation · Added salt

## Introduction

The potential distribution around a charged colloidal particle in an electrolyte solution, which plays an essential role in various electric phenomena observed in colloidal suspensions, can be described by the Poisson–Boltzmann (PB) equation. Consider a particle carrying ionized groups on the particle surface in an electrolyte solution. In the suspension, in addition to electrolyte ions, there are counterions produced by dissociation of the particle surface groups. The following two assumptions are usually made: (i) the concentration of counterions from the surface groups can be neglected as compared with the electrolyte concentration, and (ii) the suspension is assumed to be infinitely dilute so that any effects resulting from the finite particle volume fraction can be neglected. The assumption (i) becomes invalid where the electrolyte concentration is as low as or lower than that of counterions from the particle. The assumption (ii) does not hold when the concentration of all ions (electrolyte ions and counterions from the particle) is very low, since in this case the potential around each particle becomes quite long-range and the effects of the finite particle volume fraction become appreciable.

The PB equation for the potential distribution around a spherical particle without recourse to the above two assumptions for the limiting case of completely salt-free suspensions containing only particles and their counterions was studied by Imai and Oosawa [1, 2, 3]. Although the exact analytic solution was not derived, Imai and Oosawa studied the analytic properties of the PB equation for dilute particle suspensions, showing, in their first paper [1], that there is a certain critical value of the particle charge separating two cases: the high-charge case and the low-charge case. When the particle charge is lower than the critical value, the particle surface potential is proportional to the particle charge, and the potential distribution is essentially given by a Coulomb potential as if counterions were absent. If, on the other hand, the particle charge is higher than the critical value, then counterions are accumulated in the vicinity of the particle surface (counterion condensation) and the surface potential becomes less dependent on the particle charge. The critical particle charge is found to be proportional to $\ln(1/\phi)$, $\phi$ being the particle volume fraction. The appearance of the high-charge case is thus the direct consequence of the finite particle volume fraction effect, since at the limit of infinite dilution ($\phi \to 0$) the high-charge case disappears. Ohshima [4] has recently solved numerically the PB equation in this system and derived its approximate analytic solutions. The results agree well with the theory of Imai and Oosawa [1].

The above theory [1, 4], however, is based on an idealized model assuming that there are only counterions from the particle and no other ions. Actually, even salt-free media may contain other ions rather than counterions from the particle surface groups. Salt-free water at pH 7, for example, contains $10^{-7}$ M $H^+$ and $OH^-$ ions. It is thus of interest to examine how the above behaviors of colloidal particles in a salt-free medium are influenced if a small amount of salts is added to the medium. In their second paper [2], Imai and Oosawa studied the analytic properties of the PB equation in the presence of added salts, which are found to exhibit similar behaviors to those of completely salt-free suspensions.

In the present paper, on the basis of the theory of Imai and Oosawa [2], we solve numerically the PB equation for the potential distribution around a spherical colloidal particle in a medium containing its counterions and a small amount of added salts, and derive some approximate expressions for the potential distribution for the case of dilute (but not infinitely dilute) particle suspensions.

## Poisson–Boltzmann equation

Consider a suspension of spherical colloidal particles of radius $a$ with monovalent ionized groups on their surface in a medium which contains counterions produced by dissociation of the particle surface groups and a small amount of monovalent symmetrical electrolytes. We may assume that the particles are positively charged without loss of generality. We treat the case in which $N$ ionized groups of valence $+1$ are uniformly distributed on the surface of each particle and $N$ counterions of valence $-1$ are produced by dissociation of the particle surface groups. Each particle thus carries a charge $Q = eN$, where $e$ is the elementary electric charge. We also assume that each particle is surrounded by a spherical free volume of radius $R$ (Fig. 1), within which electroneutrality as a whole is satisfied. The particle volume fraction $\phi$ is given by

$$\phi = (a/R)^3. \tag{1}$$

We treat the case of dilute (but not infinitely dilute) suspensions, viz.,

$$\phi \ll 1 \text{ or } a/R \ll 1. \tag{2}$$

We assume that the electrolyte is completely dissociated to give $M$ cations of valence $+1$ and $M$ anions of valence $-1$ in each free volume so that there are $N+M$ counterions and $M$coions in the free volume. Let the average concentration (number density) of total counterions be $n+m$ and that of coions be $m$, $n$ and $m$ being given by

$$n = \frac{N}{V}, \quad m = \frac{M}{V}, \tag{3}$$

where

$$V = \frac{4}{3}\pi\left(R^3 - a^3\right) \tag{4}$$

is the volume available for counterions and coions within each free volume. From the condition of electroneutrality in each free volume, we have

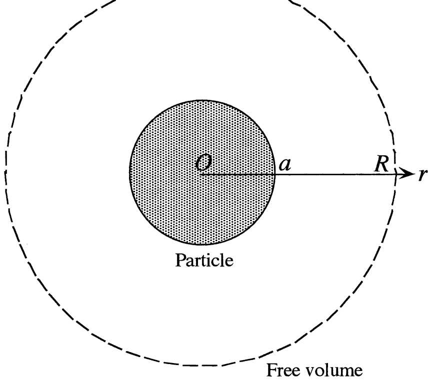


**Fig. 1** A spherical particle of radius $a$ in a free volume of radius $R$. $(a/R)^3$ equals the particle volume fraction $\phi$

$$Q = eN = Ven \tag{5}$$

We assume that the distribution of ions obeys a Boltzmann distribution so that the volume charge density $\rho(r)$ at position $r$, $r$ being the distance from the particle center ($r \geq a$), is given by

$$\rho(r) = e\left[-(n+m)e^{y}\frac{V}{4\pi\int_a^R e^{y}r^2dr} + me^{-y}\frac{V}{4\pi\int_a^R e^{-y}r^2dr}\right] \tag{6}$$

where

$$y(r) = \frac{e\psi(r)}{kT} \tag{7}$$

is the scaled potential, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. Note that Eq. 6 satisfies the electroneutrality condition of a free volume, viz.,

$$4\pi\int_a^R \rho(r)r^2dr = e\{-(N+M)+M\} = -eN = -Q. \tag{8}$$

We set the electric potential $\psi(r)$ to zero at points where the concentration of total counterions equals its average value $n+m$ so that

$$4\pi\int_a^R e^{y}r^2dr = V = \frac{4\pi}{3}\left(R^3 - a^3\right) \tag{9}$$

and Eq. 6 becomes

$$\rho(r) = en\left[-(1+p)e^{y} + \frac{p}{W}e^{-y}\right] \tag{10}$$

with

$$W = \frac{4\pi\int_a^R e^{-y}r^2dr}{V} = \frac{\int_a^R e^{-y}r^2dr}{(R^3 - a^3)/3} \tag{11}$$

and

$$p = \frac{m}{n}, \tag{12}$$

where $p$ is the ratio of the concentration of counterions (or coions) resulting from the added electrolytes to that of counterions from the particle. The case of $p=0$ corresponds to the completely salt-free case.

The Poisson equation relating $\rho(r)$ to $\psi(r)$ is given by

$$\frac{d^2\psi(r)}{dr^2} + \frac{2}{r}\frac{d\psi(r)}{dr} = -\frac{\rho(r)}{\varepsilon_r\varepsilon_0}, \tag{13}$$

where $\varepsilon_r$ is the relative permittivity of the medium and $\varepsilon_0$ is the permittivity of a vacuum. By combining Eqs. 10 and 13, we obtain the following PB equation:

$$\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = \frac{\kappa^2}{1+2p}\left[(1+p)e^{y} - \frac{p}{W}e^{-y}\right], \tag{14}$$

where $\kappa$ is the Debye–Hückel parameter defined by

$$\kappa = \left[\frac{e^2(n+2m)}{\varepsilon_r\varepsilon_0kT}\right]^{1/2} = \left[\frac{3Q^*\phi(1+2p)}{a^2(1-\phi)}\right]^{1/2} \tag{15}$$

and

$$Q^* = \frac{Q}{4\pi\varepsilon_r\varepsilon_0a}\left(\frac{e}{kT}\right) = \frac{\kappa^2a^2(1-\phi)}{3\phi(1+2p)} \tag{16}$$

is the scaled particle charge. Note that $\kappa$ generally depends on $Q^*$, $p$, $a$, and $\phi$ and that when $n \ll m$, $\kappa$ becomes the usual Debye–Hückel parameter of a 1–1 electrolyte of concentration $m$, given by

$$\kappa = \left[\frac{2e^2m}{\varepsilon_r\varepsilon_0kT}\right]^{1/2}. \tag{17}$$

The boundary conditions are expressed as

$$\left.\frac{d\psi}{dr}\right|_{r=a} = -\frac{\sigma}{\varepsilon_r\varepsilon_0} \tag{18}$$

and

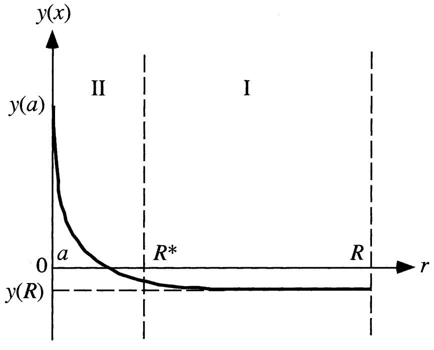
$$\left.\frac{d\psi}{dr}\right|_{r=R} = 0, \tag{19}$$

where $\sigma = Q/4\pi a^2$ is the surface charge density of the particle. Equation 18 can be rewritten as

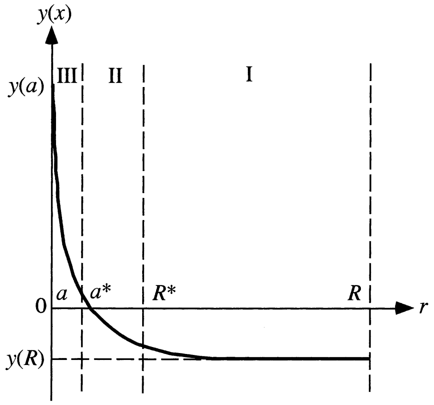
$$\left.\frac{dy}{dr}\right|_{r=a} = -\frac{Q^*}{a}. \tag{20}$$

## Approximate solution

Before we present numerical solutions to the PB Eq. 14, which cannot be solved analytically, we derive some approximate solutions. The analytic properties of Eq. 14 for the case of dilute suspensions ($\phi \ll 1$) have been studied by Imai and Oosawa [1, 2]. They showed [1] that for the special case of $p=0$ (salt-free media containing only counterions), there are two distinct cases, that is, case 1 (the low-charge case) and case 2 (the high-charge case), as schematically shown in Fig. 2. For case 1, there are two regions I ($R^* \leq r \leq R$) and II ($a \leq r \leq R^*$), while for case 2, there are three regions I ($R^* \leq r \leq R$), II ($a^* \leq r \leq R^*$), and III ($a \leq r \leq a^*$). That is, for case 1, $a^*$ reduces to $a$ so that region III disappears. For case 1, counterion condensation occurs so that counterions are condensed in the narrow region III between $r=a$ and $r=a^*$, where $a^*$ is found to be very close to $a$, and the potential sharply decreases in this region. In region II the potential is essentially a Coulomb potential. In region I the potential is almost constant at $y(r)=y(R)$, which is the potential at the outer boundary of the free



Case 1



Case 2

**Fig. 2** Three possible regions I, II, and III in the potential distribution around the particle surface for the dilute case. For case 1 (the low-charge case), there are two regions I ($R^* \le r \le R$) and II ($a \le r \le R^*$), whereas for case 2 (the high-charge case), there are three regions I ($R^* \le r \le R$), II ($a^* \le r \le R^*$), and III ($a \le r \le a^*$). The scaled particle surface potential $y_s$ is defined by $y_s \equiv y(a) - y(R)$

volume of radius $R$. Imai and Oosawa in their second paper [2] showed that the above behaviors are observed also when a small amount of salts are added to the suspension. We below extend the theory of Imai and Oosawa [1, 2, 3] as well as our previous theory [4] to obtain analytic approximate solutions to the PB Eq. 14.

For the dilute case ($\phi \ll 1$), as will be seen later, region I (where $y(r) \approx y(R)$) is found to be much wider than regions II and III, and in region III the potential is very high so that there are essentially no coions. We may thus safely approximate Eq. 11 as

$$W \approx \frac{e^{-y(R)} \int_a^R r^2 dr}{(R^3 - a^3)/3} = e^{-y(R)}, \text{ (for } \phi \ll 1). \tag{21}$$

Thus Eq. 14 can be approximated by

$$\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = \frac{\kappa^2}{1+2p}\left[(1+p)e^{y(r)} - pe^{-\{y(r)-y(R)\}}\right] \tag{22}$$

or, equivalently,

$$\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = \frac{3aQ^*}{R^3(1-\phi)}\left[(1+p)e^{y(r)} - pe^{-\{y(r)-y(R)\}}\right] \tag{22a}$$

For $p = 0$, Eq. 22 tends to the PB equation for the completely salt-free case [1, 4]. For large $p \gg 1$, $y(R)$ approaches 0 (as shown later by Eq. 45) and Eq. 22 tends to

$$\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = \kappa^2 \sinh y \tag{23}$$

with $\kappa$ given by Eq. 17. Equation 23, which ignores counterions from the particle, is the familiar PB equation for media containing ample salts [5, 6, 7, 8].

In region I, $y(r) \approx y(R)$ so that Eq. 22 can further be approximated by, for the dilute case ($\phi \ll 1$),

$$\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = \frac{3aQ^*}{R^3}\left[(1+p)e^{y(R)} - p\right] \tag{24}$$

which, subject to Eq. 19, can be solved to give

$$y(r) = Q^*\left[(1+p)e^{y(R)} - p\right]\left(\frac{a}{r}\right)\left(1 + \frac{r^3}{2R^3} - \frac{3r}{2R}\right) + y(R), \quad (R^* \leqslant r \leqslant R). \tag{25}$$

In the dilute case ($a/R \ll 1$), as $r$ decreases to $R^*$, approaching region II, the term proportional to $1/r$ in Eq. 25 becomes dominant, that is, $y(r)$ becomes an unscreened Coulomb potential. Since $y(r)$ must be continuous at $r = R^*$, $y(r)$ in region II should be of the form

$$y(r) = Q^*[(1+p)e^{y(R)} - p]\left(\tfrac{a}{r}\right) + y(R), \quad (a^* \leqslant r \leqslant R^*). \tag{26}$$

Note that Eq. 26 satisfies

$$\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = 0 \tag{27}$$

and that Eq. 22 becomes Eq. 27, if the following two conditions are both satisfied in addition to Eq. 2: (i) the terms on the right-hand side of Eq. 22 are very small as compared with $a^2$ and (ii) these terms are also much smaller than the second term of the left-hand side of Eq. 22. The first condition may be expressed as

$$\kappa a \ll 1, \tag{28}$$

or equivalently,

$$(1 + 2p)Q^*\phi \ll 1, \tag{29}$$

and the second condition as

$$\left|\frac{1}{r}\frac{dy}{dr}\right| \gg \frac{3aQ^*}{R^3}\left[(1+p)e^{y(r)} - pe^{-\{y(r)-y(R)\}}\right]. \tag{30}$$

By evaluating Eq. 30 at $r = a^*$ using Eq. 26, we obtain

$$(1+p)e^{y(R)} - p \gg \frac{3a^{*3}}{R^3}\left[(1+p)e^{y(a^*)} - pe^{-\{y(a^*)-y(R)\}}\right], \tag{31}$$

which yields, by taking the logarithm of both sides,

$$y(a^*) - y(R) < \ln\left[1 - \frac{p}{1+p}e^{-y(R)}\right] + \ln\left(\frac{R^3}{a^{*3}}\right) \approx \ln(1/\phi), \quad (\text{for } \phi \ll 1) \tag{32}$$

Equation 32 implies that the value of $y(a^*)-y(R)$ cannot exceed $\ln(1/\phi)$, which is thus the possible maximum value of $y(a^*)-y(R)$. From Eq. 26, on the other hand, we obtain

$$y(a^*) - y(R) = -a^* \left.\frac{dy}{dr}\right|_{r=a^*}. \tag{33}$$

By combining Eqs. 32 and 33, we obtain

$$-a^* \left.\tfrac{dy}{dr}\right|_{r=a^*} < \ln(1/\phi), \quad (\text{for } \phi \ll 1). \tag{34}$$

We must thus consider two cases 1 and 2 separately, depending on whether $-a\left.\frac{dy}{dr}\right|_{r=a} = Q^*$ is larger or smaller than $\ln(1/\phi)$.

Case 1 (The low-charge case)

Consider first case 1, in which the following condition holds:

$$Q^* \leqslant \ln(1/\phi). \tag{35}$$

In this case, region II can extend up to $r = a$, that is, $a^*$ can reduce to $a$. Thus the entire region of $r$ can be covered only with regions I and II and one does not need region III. For the low-charge case, Eq. 24, which is now applicable essentially for the entire region of $r$, can further be simplified by using the method given in a previous paper [4], to give

$$y(r) = Q^*\left(\tfrac{a}{r}\right)\left(1 + \tfrac{r^3}{2R^3} - \tfrac{9r}{5R}\right), \quad (a \leqslant r \leqslant R), \tag{36}$$

which is independent of $p$. For the dilute case ($\phi \ll 1$), Eq. 36 gives $y(R) \approx 0$ and becomes essentially a Coulomb potential, viz.,

$$y(r) = Q^* \tfrac{a}{r}, \quad (a \leqslant r \leqslant R). \tag{37}$$

The scaled particle surface potential $y_s = y(a)-y(R) = y(a)$ in case 1 is thus given by

$$y_s = Q^*. \tag{38}$$

The above results do not depend on $p$ and agree with those for the completely salt-free case [4].

Case 2 (The high-charge case)

Consider next case 2, in which the condition

$$Q^* > \ln(1/\phi) \tag{39}$$

is satisfied so that

$$Q^* > -a^* \left.\frac{dy}{dr}\right|_{r=a^*}. \tag{40}$$

That is, region II cannot extend up to $r = a$. Therefore the entire region of $r$ cannot be covered only with regions I and II and thus one needs region III very near the particle surface between $r = a$ and $r = a^*$, where counterions are condensed (counterion condensation). In region III, $y(r)$ is very high so that Eq. 22 becomes

$$\frac{d^2y}{dr^2} = \frac{3\phi Q^*}{a^2}(1+p)e^{y(r)}. \tag{41}$$

By integrating Eq. 41, we obtain for the dilute case

$$y(a) = \ln\left[\frac{Q^*}{6\phi(1+p)}\right]. \tag{42}$$

The value of $y(R)$ can be obtained as follows. In case 2, $y(a^*)-y(R)$ has already reached its maximum $\ln(1/\phi)$ so we find that Eq. 25 becomes

$$y(r) = Q^*_{\text{eff}}\tfrac{a}{r} + y(R), (a^* \leqslant r \leqslant R^*), \tag{43}$$

where

$$Q^*_{\text{eff}} = y(a^*) - y(R) = Q^*[(1+p)e^{y(R)} - p] = \ln(1/\phi) \tag{44}$$

is the scaled effective particle charge and the value of $y(R)$ is given by

$$y(R) = \ln\left[\frac{\ln(1/\phi) + pQ^*}{Q^*(1+p)}\right], \tag{45}$$

which is obtained from the last equation of Eq. 44. We see from Eq. 45 that $y(R)$ tends to zero as $p$ increases. Equation 43 implies that in region II the potential distribution around the particle is a Coulomb potential produced by the scaled particle charge $Q^*_{\text{eff}} = \ln(1/\phi)$. In other words, the particle behaves as if the particle charge were $Q^*_{\text{eff}}$ instead of $Q^*$ for regions I and II, in which regions Eq. 25 may be expressed as

$$y(r) = Q^*_{\text{eff}}\left(\tfrac{a}{r}\right)\left(1 + \tfrac{r^3}{2R^3} - \tfrac{3r}{2R}\right) + y(R), (a^* \leqslant r \leqslant R). \tag{46}$$

The particle surface potential $y_s = y(a)-y(R)$ in case 2 is found to be, from Eqs. 42 and 45,

$$y_s = \ln\left[\frac{Q^{*2}}{6\phi\{\ln(1/\phi) + pQ^*\}}\right]. \tag{47}$$

When $p = 0$, Eqs. 42, 45, and 47 all reduce back to results obtained for the completely salt-free case [4]. Also note that the critical value separating cases 1 and 2 is $\ln(1/\phi)$, which is the same as that for the completely salt-free case [1, 4].

## Results and discussion

We give in Figs. 3, 4, and 5 some of the numerical solutions to the PB Eq. 22, which is obtained by approximating $W$ as 1 in the original PB Eq. 14. This approximation is found to be good for the dilute case ($\phi \ll 1$). In Figs. 3 and 4 we plot the potential distribution $y(r)$ for the high-charge case, $Q^* = 30$ (Fig. 3) and the low-charge case, $Q^* = 5$ (Fig. 4) at $\phi = 10^{-6}$ and $p = 0$ and 5. The values of $\kappa a$ in these examples are 0.0095 (at $Q^* = 30$ and $p = 0$), 0.031 (at $Q^* = 30$ and $p = 5$), 0.0039 (at $Q^* = 5$ and $p = 0$), and 0.013 (at $Q^* = 5$ and $p = 5$), all of which satisfy $\kappa a \ll 1$ (Eq. 28). In Figs. 3 and 4 we also give the approximate results calculated with Eqs. 36 and 46, which are in good agreement with the numerical results. We thus see that for the low-charge case the potential is given by a Coulomb potential produced by a scaled charge $Q^*$ and for the high-charge case it is given by a Coulomb potential by the scaled effective charge $Q^*_{\mathrm{eff}} = \ln(1/\phi)$ except in the region very near the particle surface (region III), in which region counterion condensation occurs.

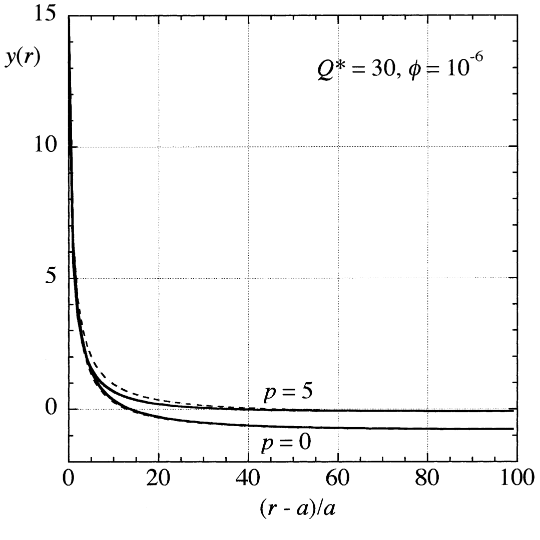


**Fig. 3** Potential distribution $y(r)$ for $Q^* = 30$ (the high-charge case) at $\phi = 10^{-6}$ and $p = 0$ and 5. *Solid curves* stand for numerical results obtained by solving Eq. 22 and *dotted curves* for approximate results (Eq. 46)

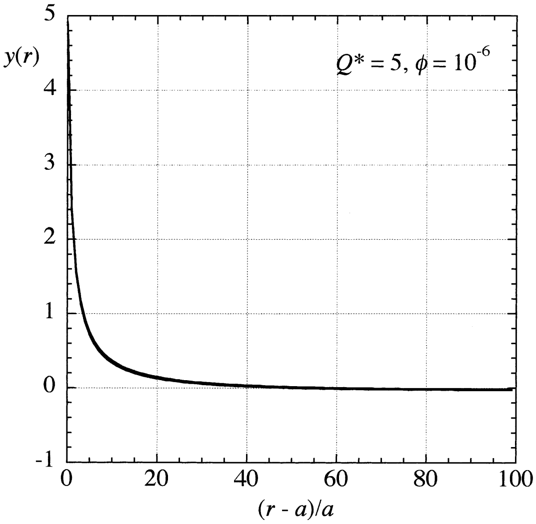


**Fig. 4** The same as Fig. 3, but for $Q^* = 5$ (the low-charge case). *Solid curves* for numerical results obtained by solving Eq. 22 and *dotted curves* for approximate results calculated with $p = 0$ and 5 (Eq. 36) all coincide with each other within the line width

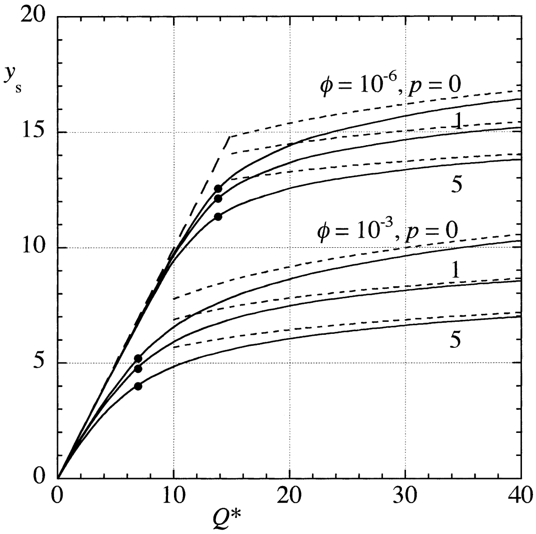


**Fig. 5** Scaled surface potential $y_s = e\psi_s/kT$, defined by $y_s \equiv y(a) - y(R)$, as a function of $Q^*$ at $\phi = 10^{-3}$ and $\phi = 10^{-6}$ for various values of $p$. *Solid lines* represent numerical results. *Dotted lines* are approximate results calculated by Eq. 38 (case 1: the low-charge case) and *dashed line* by Eq. 47 (case 2: the high-charge case). *Closed circles* represent the values of $y_s$, corresponding to the critical particle charge $Q^* = \ln(1/\phi)$

In Fig. 5 we plot numerical results for the scaled surface potential $y_s = y(a) - y(R)$ as a function of the scaled particle charge $Q^*$ for several values of $p$ at $\phi = 10^{-3}$ and $\phi = 10^{-6}$. It is clearly seen that even for the case of nonzero $p$ there are two distinct cases 1 and 2, that is, the low-charge case and high-charge case, and that the magnitude of $y_s$decreases as $p$ increases. In the low-charge case (case 1) the surface potential is essentially proportional to the particle charge. For the high-charge case (case 2) the dependence of $y_s$ upon $Q^*$ becomes suppressed because of counterion condensation. In accordance with the analytical results derived in the previous section, the numerical results also demonstrate that the critical value of the scaled particle charge $Q$ separating cases 1 and 2 is located around $Q = \ln(1/\phi)$, which is independent of $p$ and the same as that for the completely salt-free case ($p = 0$). The above behaviors can be observed when the conditions $\phi \ll 1$ (Eq. 2) and $\kappa a \ll 1$ (Eq. 28) are both satisfied. This implies that the range of the value of $p$ that gives the appearance of cases 1 and 2 as well as counterion condensation may become very wide as long as the condition $\kappa a \ll 1$ (or equivalently, $p \ll 1/Q^*\phi$) is satisfied. Indeed, we see in Fig. 5 that the cases of $p = 0$, 1, and 5 all exhibit similar behaviors.

Fig. 5 also shows approximate results obtained from Eq. 38 for the low-charge case and Eq. 47 for the high-charge case. The agreement with the numerical results is good except in the transition region between cases 1 and 2. Note again that at the limit of infinite dilution $\phi \to 0$, the critical value $\ln(1/\phi)$ tends to infinity so that there appears only the low-charge case and thus the high-charge case disappears, indicating that the high-charge case is the direct consequence of the finite particle volume fraction.

## Conclusion

We have shown both numerically and analytically that, as in the case of the completely salt-free case, there appears a critical value $\ln(1/\phi)$ of the particle charge separating the low-charge case and the high-charge case when the conditions $\phi \ll 1$ and $\kappa a \ll 1$ are both satisfied. The analytical results are summarized as follows. If $Q^* \leq \ln(1/\phi)$ (the low-charge case), then $y_s = y(a) = Q^*$ and $y(R) = 0$, whereas if $Q^* > \ln(1/\phi)$ (the high-charge case), then

$$y(a) = \ln\left[\frac{Q^*}{6\phi(1+p)}\right], \quad y(R) = \ln\left[\frac{\ln(1/\phi) + pQ^*}{Q^*(1+p)}\right],$$

$$y_s = \ln\left[\frac{Q^{*2}}{6\phi\{\ln(1/\phi) + pQ^*\}}\right].$$

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