

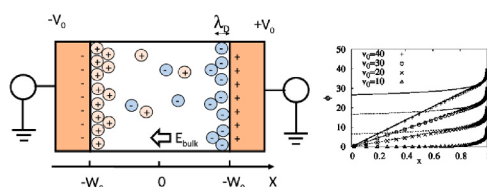


Expanded ion-conserving Poisson-Boltzmann theory at extremely-high voltages

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GRAPHICAL ABSTRACT



ABSTRACT

The solution of the Poisson-Nernst-Planck (PNP) equation does not exist in the region of extremely high applied voltages in which a bulk electric field remains, even for a steady-state. Thus, we propose an expanded ion-conserving Poisson-Boltzmann theory at the high voltages and show that it predicts steady PNP solutions precisely at the high applied voltages. Furthermore, the bulk electric fields and appropriate zeta potential are provided through this theory. We believe that our solution opens a new way to improve the various theories on the diffused charge dynamics and their applications at high applied voltages.

1. Introduction

Diffused charge dynamics [1] at extremely high voltages (~ 1 V) in electrolyte is important to consider microfluidic devices [2] (e.g., ac electro-osmotic pumps [3], valves [4], and mixers [5]), double-layer capacitors [6], batteries [7], nano-hole sensing [8], ion-exchange membranes [9], electrophoretic deposition [10], electrolysis [11,12], etc. To understand the diffused charge dynamics, two kinds of basic governing equations are known; i.e., one is the Poisson-Nernst-Planck (PNP) equation (e.g., Ref. [1,13]) and the other is the (nonlinear) Poisson-Boltzmann (PB) equation. On the one hand, although the mathematically exact solution of the PB equation is known as the Gouy and Chapman's (GC) solution [14,15], the GC solution provides unrealistic ion concentrations at high applied voltages [16]. On the other hand, the solution of the PNP equation at high voltages (> 25 mV) is not known except a formal Jacobi solution [17] and our previously-proposed steady PNP solution using an ion-conserving Poisson-Boltzmann (ICPB) theory [18]. However, even the ICPB theory cannot provide the PNP solution at an extremely high voltage region

(approximately, $V_0 > 0.25$ V) since the ICPB solution is the exact solution of the PNP equations under the condition that a bulk electric field E_{bulk} (at the mid-position between the electrodes) is zero [18]. Thus, the study to obtain the steady PNP solution at high voltages (e.g., ~ 1 V) is challenging. Here, as pointed out in [18], the steady PNP equation is equivalent to the PB equation under the ion-conserving condition; thus, by solving the PB equation with the ion-conserving condition, we obtained the exact PNP solution below the range of a moderately-high voltage region (approximately, $0.025 < V_0 \leq 0.25$ V) in the ICPB theory.

Although a numerical simulation for the PNP equation is a powerful tool, a demand for an analytical solution for the diffused charge dynamics is still large to institute more complex theories (e.g., theories on Faradaic reaction problems [7,11]). However, one uses Gouy and Chapman's (GC) solution [14,15] instead of the inexistent complete PNP solution, even though the GC solution is unrealistic. To overcome the unrealistic problem of the GC solution, various modified PB (MPB) theories [16,19] have been proposed and they succeeded in removing the difficulty to some extent. However, as pointed out in the modified ICPB (M-ICPB) theory [20] that considers a steric limit of ions with the

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ion-conserving condition, the ion clouding problem due to the steric limit occurs at much higher applied voltages than the predictions of ordinary MPB theories in the M-ICPB theory. Thus, it is important to expand the ICPB theory to obtain the PNP solution at extremely high voltages. In addition, as pointed out in [21], the ICPB solution is much more precise than the GC solution even for an open parallel electrode condition because of the generation of the edge vortex flows due to the steep gradient of ion concentrations around the edge region of the finite-size electrodes; i.e., ions cannot be inhaled by the electrodes infinitely even for the open electrode condition although one may consider that ions can be drawn from the surrounding region infinitely as the GC and MPB solutions implicitly assume. Thus, to know the shielding state of the external electric field and the effective zeta potential for the electrodes with the bulk electric field around the mid position, we need to know the PNP solution at extremely high voltages (~ 1 V).

In this study, we focus on obtaining the analytical solution of the steady PNP equations at extremely high applied voltages ($0.1 < V_0 \leq 1$ V) between parallel electrodes and clarify the effective zeta potential and the bulk electric field.

2. Theory

2.1. Problem definition

Fig. 1 shows a schematic view of the considered ion system in an electrolyte between parallel electrodes of the distance $2W_0$ at high applied voltages $2V_0$. In this study, we propose two kinds of models (Models A and B) based on the ICPB theory [18] for the steady PNP solution at the extremely high applied voltages. Here, the nondimensional PNP equation [11] consists of the nondimensional Poisson equation

$$-2\epsilon \frac{\partial^2 \phi}{\partial x^2} = \rho \quad (1)$$

and the nondimensional Nernst-Planck (NP) equation

$$\frac{\partial c_{\pm}}{\partial \tau} = \frac{\partial}{\partial x} \left(\frac{\partial c_{\pm}}{\partial x} \pm c_{\pm} \frac{\partial \phi}{\partial x} \right), \quad (2)$$

where $\phi (= \Phi/\Phi_c)$, $c_{\pm} (= C_{\pm}/C_0)$, $\rho (= c_+ - c_-)$, $\tau (= t/T_0)$, and $x (= X/W_0)$ are the nondimensional values of a potential Φ , ion concentration C_{\pm} , charge density ρ , and position X . Further, C_0 is the bulk

ion concentration at the initial state, $\epsilon = 1/\kappa = \lambda_D/W_0$, $\lambda_D (= \sqrt{\epsilon kT/2z^2 e^2 C_0})$ is the Debye length, $\epsilon \simeq 80\epsilon_0$ is the permittivity of water, ϵ_0 is the vacuum permittivity, $T_0 (= W_0^2/D)$ is a diffusion time, and $\Phi_c = kT/ze$, where k is the Boltzmann constant, T is the temperature, ze is the ion charge, and D ($\sim 10^{-9}$ m²/s for water) is the ion diffusivity; e.g., $\Phi_c = 25.85$ mV at $T = 300$ K. Since the NP equation includes the continuity equation, the steady NP equation consists of the ion-conserving (IC) condition

$$\int_0^1 (c_+ + c_-) dx = 2 \quad (3)$$

and the zero ion flux condition

$$\frac{\partial c_{\pm}}{\partial x} \pm c_{\pm} \frac{\partial \phi}{\partial x} = 0, \quad (4)$$

where we consider the symmetrical condition that $c_+(x) = c_-(-x)$ for Eq. (3). Thus, our problem is to solve the steady PNP equation consisting of Eqs. (1), (3), and (5) under the boundary condition that

$$\phi = v_0 = V_0/\Phi_c \quad \text{at } x = 1, \quad \phi = 0 \quad \text{at } x = 0. \quad (5)$$

2.2. Brief summary of the ICPB theory

Here, we briefly summarize the ICPB theory [18]. That is, by using the Boltzmann form

$$c_{\pm} = c_q e^{\mp \phi} \quad (6)$$

with Eq. (4), we obtain

$$\frac{\partial^2 \phi}{\partial x^2} = \kappa_q^2 \sinh \phi, \quad (7)$$

where $\kappa_q = \kappa \sqrt{c_q}$ and c_q is obtained from Eqs. (3) and (4); i.e., the IC condition

$$c_q \int_0^1 (e^{-\phi} + e^{+\phi}) dx = 2. \quad (8)$$

By differentiating Eq. (6), we obtain Eq. (4); thus, solving Eqs. (6)–(8) is equivalent to solve the steady PNP equation; thus, our problem is to solve Eqs. (6)–(8) under the boundary condition of Eq. (5). The PB equation is obtained if we consider that Eq. (6) is the Boltzmann's

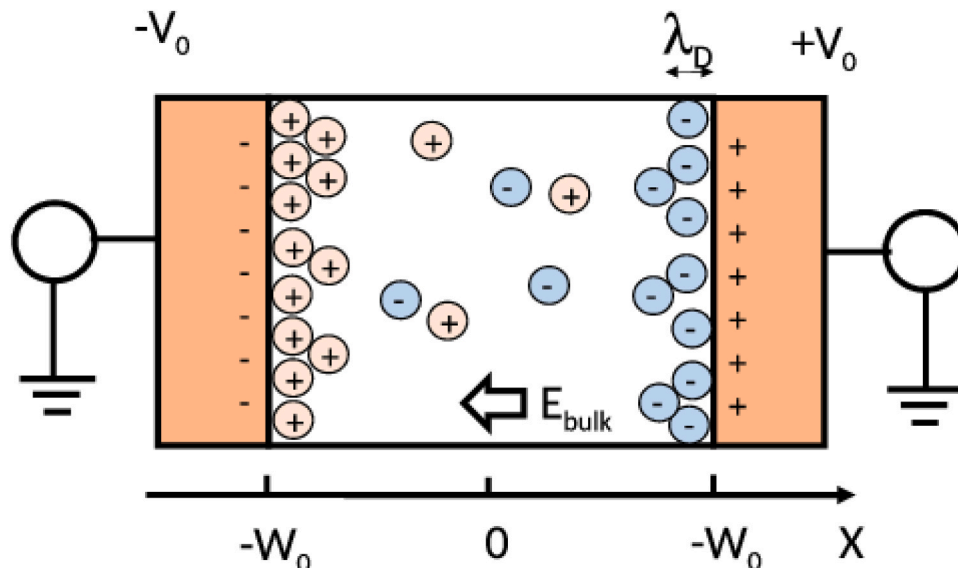


Fig. 1. Schematic view of the considered ion system in an electrolyte. Here, $2V_0$ is the applied voltage and $2W_0$ is the distance between the electrodes.

statistical equation and we assume that $c_q = 1$ by neglecting the IC condition of Eq. (8). However, the theory is intrinsically justified only when $\phi \ll 1$ from the limiting condition of the Boltzmann's statistical equation. On the contrary, since we consider that Eq. (6) is just the mathematical transformation, the ICPB equation [consisting of Eqs. (6)–(8)] that is equivalent to the steady PNP equation can be used even at high applied voltages; i.e., until the limit of the steric limit [16,19,20].

2.3. The ICPB solution at moderately-high voltages

In the previous study [18], we already obtained the ICPB solution under the condition that

$$\frac{\partial \phi}{\partial x} = 0 \quad \text{at} \quad x = 0. \quad (9)$$

That is,

$$\phi(x) = \phi_{icpb,0} = 2\ln\left(\frac{1 + \tanh(v_0/4)e^{-(1-x)\kappa_q}}{1 - \tanh(v_0/4)e^{-(1-x)\kappa_q}}\right), \quad (10)$$

$$\kappa_q = \frac{1}{\lambda_q} = \kappa\sqrt{c_q}, \quad (11)$$

$$c_q = (-A + \sqrt{1 + A^2})^2, \quad (12)$$

$$A = \frac{2\tanh^2(\frac{v_0}{4})}{\kappa(1 - \tanh^2(\frac{v_0}{4}))} = 2\epsilon\sinh^2\frac{v_0}{4}. \quad (13)$$

Here, since the collateral condition of Eq. (9) is realized when the external applied electric field is screened completely by the formation of the electric double layer near the electrodes, the ICPB solution of Eq. (10) is exact only under the moderately-high voltage range (approximately, $v_0 \leq 10$).

2.4. Model A for the PNP solution at extremely-high voltages

In this section, we propose a simple model (Model A) for the PNP solution at extremely high voltages; i.e., we consider a simple superposition-type solution in the extremely high voltage region, in which the screening effect becomes incomplete. In this region, as the analogy of the colloids science, we consider that the potential is approximated by the superposition of the double layer potential ϕ_D near the electrode and the external potential ϕ_e , as the first step. In Model A, the ICPB solution of Eq. (10) under the condition that $\frac{\partial \phi}{\partial x} = 0$ at $x = 0$ is considered to be ϕ_D and ϕ_e is described as $\phi_{e,1} \simeq (v_0 - \zeta_1)x$, where ζ_1 corresponds to the zeta potential in the colloid science and it is described as $\zeta_1 = v_0 - \phi_{icpb,0}(0)$. Thus, we summarize Model A as follows:

$$\phi^{model \ A} \simeq \phi_D + \phi_{e,1}, \quad (14)$$

$$\phi_D(x) = \phi_{icpb,0}(x) \quad (15)$$

$$\phi_{e,1}(x) \simeq \phi_D(0)x \quad (16)$$

Because of the simplicity, Model A is useful and it approximates the PNP solution reasonably to some extent, as will be explained later.

2.5. Model B for the PNP solution at extremely-high voltages

In this section, we propose a more precise model (Model B) for the PNP solution at extremely high voltages; i.e., in the extremely high voltage region, we consider a connecting-type solution consist of the solution in the bulk region and the solution in the electric double layer region near the electrode. Specifically, we consider the analytical continuum solution consists of the ICPB solution at $x_p \leq x \leq 1$ and the linear solution at $0 \leq x < x_p$ as the steady PNP solution at high voltages, where

$(x_p, \phi(x_p))$ is the junction point that satisfies the continuum condition. Note that we consider that the bulk region is in the region $0 \leq x < x_p$ ($< W_0$), while the (surface) electric double layer region is in the region $x_p W_0 \leq W_0$. Obviously, the solution near the electrode at $x_p \leq x \leq 1$ is provided by Eq. (10); thus, $\phi^{modelB}(x) = \phi_{icpb,0}(x)$ at $x_p \leq x \leq 1$. Further, in the extremely high voltage region, the ions in a bulk region are exhausted and thus we can assume $k_q \ll 1$. Therefore, for the low potential region, we can neglect the term of $k_q^2 \sinh \phi$ in Eq. (7); thus, we can approximate Eq. (7) as

$$\frac{\partial^2 \phi}{\partial x^2} \simeq 0. \quad (17)$$

Consequently, since $\phi = 0$ at $x = 0$, we obtain the solution in the bulk region at $x < x_p$ as

$$\phi \simeq Bx, \quad (18)$$

where $B = \phi_{icpb,0}(x_p)/x_p$. Furthermore, from the continuum condition of $\partial \phi / \partial x = 2\kappa_q \sinh \frac{\phi_{icpb,0}(x_p)}{2}$ [18] at $(x_p, \phi(x_p))$, we obtain the relation for the point as follows:

$$2\kappa_q \sinh \frac{\phi_{icpb,0}(x_p)}{2} = \frac{\phi_{icpb,0}(x_p)}{x_p}. \quad (19)$$

With this condition, we summarize Model B as

$$\phi^{model \ B}(x) = \begin{cases} \phi_{icpb,0} & (\text{at } x \geq x_p) \\ \frac{\phi_{icpb,0}(x_p)}{x_p}x & (\text{at } x < x_p). \end{cases} \quad (20)$$

Unfortunately, we could not solve Eq. (20) explicitly. However, since we can easily obtain x_p that satisfies Eq. (20) by using a bisection method, we propose Model B as the better analytical solution of the PNP equations.

3. Results

3.1. Evaluation of Model A

Fig. 2 shows the comparison between numerical PNP solutions and analytical results of Model A based on Eq. (14) at $\kappa = 20$ at the extremely high applied voltage ($v_0 = 40$) and at the moderately-high applied voltage ($v_0 = 9$). In Fig. 2(a), (c), and (e), we find that the analytical results of ϕ and $c_n (= c_-)$ obtained by Model A (solid line) using Eq. (14) agree with the numerical PNP results (circles) at the extremely high applied voltage ($v_0 = 40$), whereas the GC solution (broken line) does not agree with the PNP solution. In detail, the ICPB solution (dotted line) of ϕ using Eq. (10) agrees with the numerical PNP results only near the electrode, whereas Model A in the expanded ICPB (E-ICPB) theory predicts the whole outline of ϕ fairly well. Thus, Model A is useful to understand the bulk electric field and the zeta potential concerning the electrode. However, strictly speaking, the prediction of Model A for c_n near the electrode is worse than that of the previously proposed simple ICPB solution of Eq. (10) because of the extra superposition of $\phi_{e,1}$ in the region of the electric double layer; in addition, the prediction of the simple ICPB for c_n around the joint region between the bulk and electrode regions is not so bad compared to that of Model A. Thus, the improvement of Model A is required, although it is useful because of its simplicity. Further, in the E-ICPB theory, the solutions of Models A and B are equivalent to the simple ICPB solution of Eq. (10). Consequently, the analytical results using an ICPB theory (Models A and B) for ϕ and c_n agree with the numerical PNP results very well at the moderately-high applied voltage ($v_0 = 9$) as shown in Fig. 2(b), (d), and (f), whereas the GC solution also does not agree with the PNP solution. Namely, Models A and B cover the moderately-high applied voltage region and

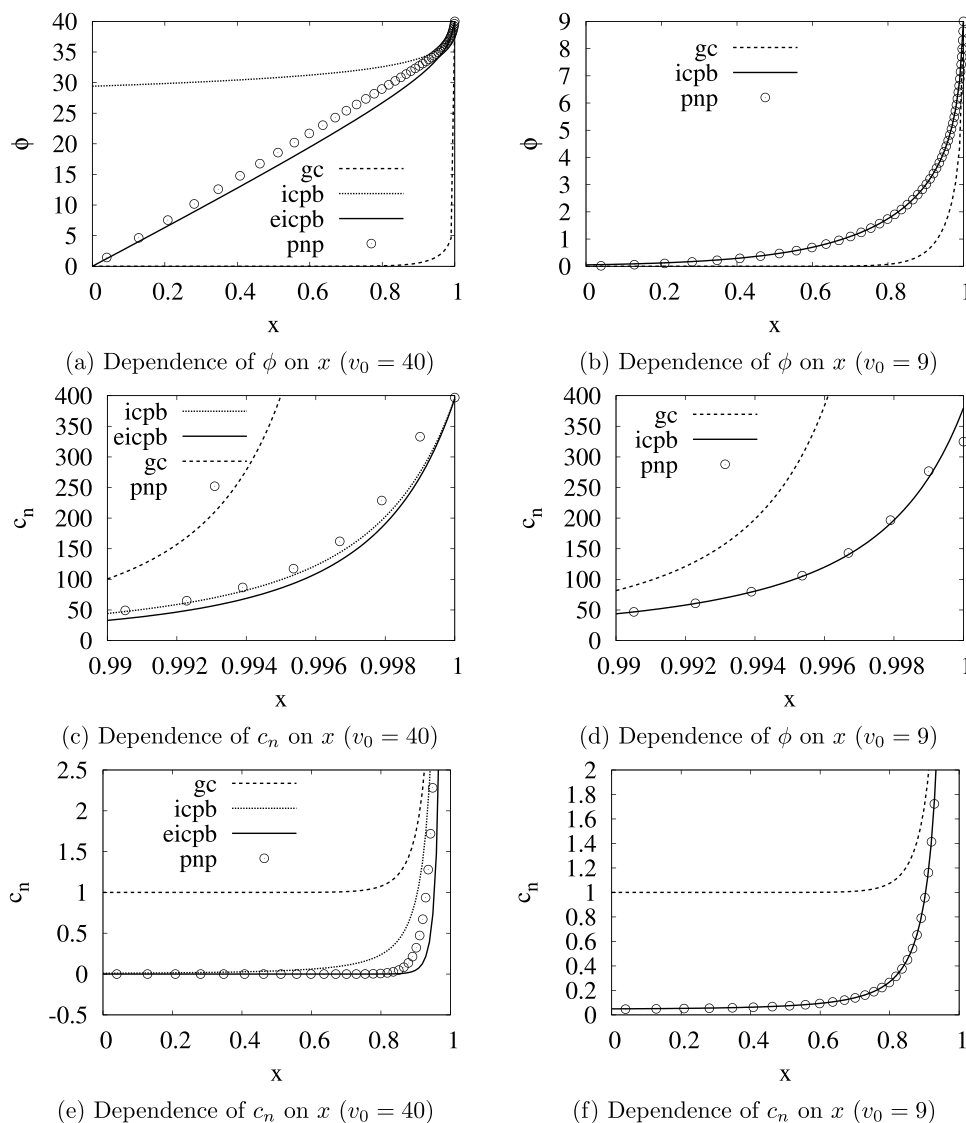


Fig. 2. Comparison between the numerical PNP solutions and the analytical results of Model A based on Eq. (14) at $\kappa = 20$ at the extremely high applied voltage ($v_0 = 40$) and at the moderately high applied voltage ($v_0 = 9$). Here, the lines show the analytical results, whereas the characters show the numerical PNP results.

they can predict the PNP solution precisely in a wide voltage range.

3.2. Evaluation of Model B

Fig. 3 shows the comparison between the numerical PNP solutions of ϕ and the analytical results of Model B based on Eq. (20) at extremely high applied voltages. Here, the lines show the analytical results, whereas the characters show the numerical PNP results. In Fig. 3(a) to (c), we find that the numerical PNP solutions for the dependence of ϕ on x in the extremely high voltage region are predicted excellently by Model B. Thus, Model B is useful. Further, Fig. 3(d) shows the dependence of x_p on v_0 . In Fig. 3(d), we find that x_p increases around zero to 0.94 as v_0 increases. Thus, we understand that it is difficult to consider the fixed width of the electric double layer concerning the electrode, although customary one often uses the Debye screening length λ_D to consider the joint-type solution (e.g., [11]) in colloid surface science.

Fig. 4 shows the comparison between numerical PNP solutions of c_n and analytical results of Model B based on Eq. (20) at extremely high applied voltages. Specifically, Fig. 4(a), (c), and (e) show the low concentration region, whereas Fig. 4(b), (d), and (f) show the high concentration region. In Fig. 4, we find that the numerical PNP solutions for the dependence of c_n on x in extremely high voltage region are predicted

excellently by Model B for both high and low concentration regions especially at large κ (e.g., $\kappa = 80$) and at relatively low v_0 (e.g., $v_0 = 20$). However, strictly speaking, there still exists a distinguishable discrepancy between the PNP solutions and the E-ICPB solutions of Model B for both high and low concentration regions at $\kappa = 20$ and $v_0 = 40$. This is because the ion-conserving condition using $\phi_{icpb,0}$ becomes incomplete at $\kappa = 20$ and $v_0 = 40$.

3.3. Appropriate zeta potential and bulk electric field

Fig. 5 (a) shows the dependence of $\phi_{icpb,0}(0)$ on v_0 . In Fig. 5(a), the region that $\phi_{icpb,0}(0) \neq 0$ is the extremely high applied voltage region that cannot be covered by the previously proposed simple ICPB theory [18]. However, in the E-ICPB theory especially of Model A, the simple ICPB solution describes the electric-double-layer potential concerning the electrode and $\zeta = v_0 - \phi_{icpb,0}(0)$ in Fig. 5(b) means the zeta potential of the electrode in the customary sense of colloid science. In Fig. 5(b), we find that ζ becomes constant at the extremely high voltages and the constant value of ζ becomes large, as κ becomes large. This is because ζ is related to the screening effect and it depends on the ion numbers in the considered region. In other words, the ions are exhausted at the extremely high applied voltages and thus ζ becomes constant

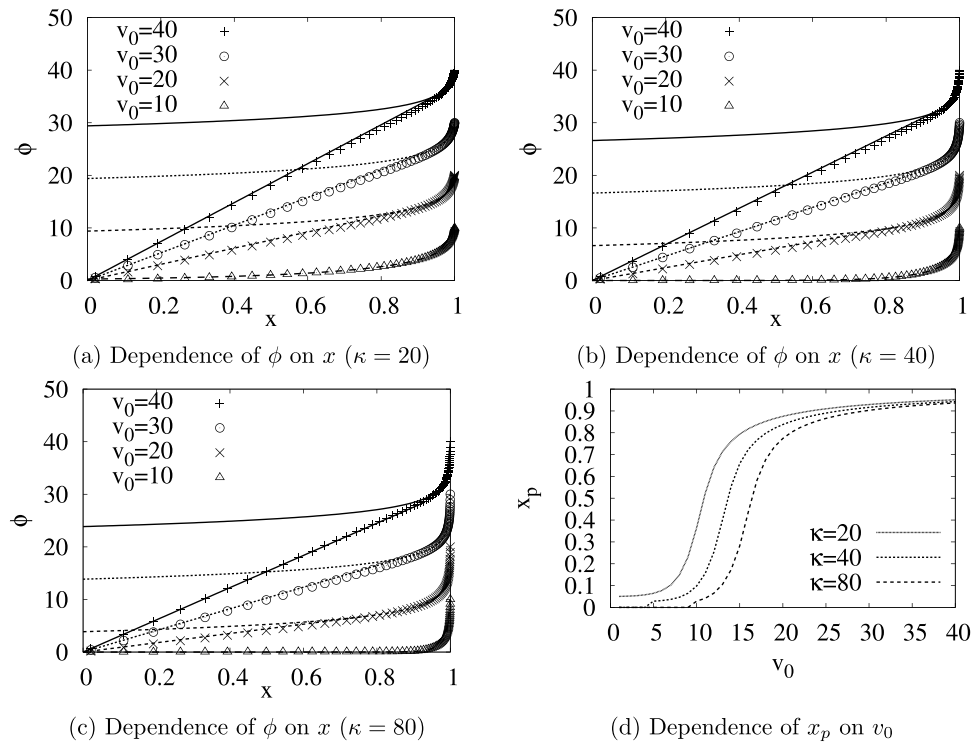


Fig. 3. Comparison between numerical PNP solutions of ϕ and analytical results of Model B based on Eq. (20) at extremely high applied voltages. Here, the lines show the analytical results, whereas the characters show the numerical PNP results.

approximately at $v_0 > 10$ at $\kappa = 20$ (at $v_0 > 15$ at $\kappa = 80$). Thus, the simple ICPB theory and the concept of ζ is still important at the extremely high applied voltages.

Nevertheless, the E-ICPB theory of Model B requires the more appropriate definition of zeta potential of the electrode to differentiate the bulk region ($0 \leq x < x_p$) and the double layer region ($x_p \leq x \leq 1$); i. e., the appropriate zeta potential ζ' in Fig. 5(c) is defined as $\zeta' \equiv v_0 - \phi_{icpb,0}(x_p)$. In Fig. 5(c), we find that ζ' increases in the moderately-high applied voltage region (e.g., approximately, $v_0 < 10$ at $\kappa = 20$) as v_0 increase, whereas ζ' decrease in the extremely high applied voltage region (e.g., approximately, $v_0 > 10$ at $\kappa = 20$). This is because x_p increases in the extremely high applied voltage region and thus a part of ζ is distributed to the bulk potential; i.e., $v_{bulk} \equiv \phi_{icpb,0}(x_p)$ in Fig. 5(d). In Fig. 5(d), we find that v_{bulk} is zero at the moderately-high applied voltage because of the screening effect and it increases as v_0 increases in the extremely high applied voltage region since the screening effect becomes incomplete in the region. From the values of ζ' and v_{bulk} , we obtain the average double-layer electric field $E_D = \zeta'/(1 - x_p)$ in Fig. 5(e) and the average bulk electric field $E_{bulk} = v_{bulk}/x_p$ in Fig. 5(f).

4. Discussion

4.1. About the electroneutrality condition

The reference point of electric potential is $x = 0$. At this point, the electric potential becomes zero and thus $c_{\pm} = c_q e^{\mp \phi}$ become their bulk values c_q . Therefore, at a glance, it may seem that the electroneutrality condition is satisfied only at $x = 0$. However, this kind of situation occurs even for the other models such as PB and MPB theories, and it does not become a problem since $\rho = c_+ - c_- \simeq 0$ in the so-called bulk region. In particular, since $c_q \ll 1$ in the extremely high voltage region in our model, the electroneutrality $\rho = c_+ - c_- = c_q(e^- - e^+) \simeq 0$ is rather satisfied stronger than the PB and MPB theories in the bulk region, although we should refer to it as the exhaustion of ions. That is, in our models, we assume that the ions in a bulk region are exhausted in the

extremely high voltage region in which region $\phi_{icpb,0}(0) \neq 0$. In other words, we assume $\phi \propto x$ in the bulk region and it means that $\rho \simeq 0$ in the Poisson equation of Eq. (1) for both Models A and B. That is, the electroneutrality condition is satisfied through Eqs. (16) and (18).

4.2. About the effect of high bulk concentration

In the sense that our theory is formulated by the non-dimensional parameters, our theory is not affected by the bulk concentration C_0 directly, and thus the results provide universal predictions. However, since our theory considers C_0 in the non-dimensional formulation, our theory is of course equally applicable under high bulk concentrations, as long as the ion concentrations do not exceed the steric limit. Specifically, the large value of $\kappa (= W_0/\lambda_D)$ corresponds to the high bulk concentration condition, while the low value of κ corresponds to the low bulk concentration condition. Thus, Fig. 5(a) and (b) show that as C_0 increases, the ratio of the shielded voltage ζ/v_0 increases, while the ratio of the bulk voltage $\phi_{icpb,0}(0)/v_0$ decreases. For example, $\lambda_D \simeq 1 \mu\text{m}$ for ideal water at $pH = 7$ (i.e., $C_0 = 10^{-7} \text{ mol/l}$) and the typical value of W_0 is $100 \mu\text{m}$ for the biomedical application. Thus, we obtain $\kappa = 100$ in this case. That is, from Fig. 5(a) and (b), we predicts that $\frac{\zeta}{v_0} V_0 \simeq \frac{\phi_{icpb,0}(0)}{v_0} V_0 \simeq 0.5 \text{ V}$ for $V_0 = 1 \text{ V}$ ($v_0 = 40$) when $\kappa = W_0/\lambda_D = 100$. Furthermore, from $\lambda_D \equiv \sqrt{\epsilon kT/2z^2 e^2 C_0}$, we obtain that $\lambda_D \simeq 0.1 \mu\text{m}$ and $\kappa = 1000$ at $C_0 = 10^{-5} \text{ mol/l}$. Thus, the complete shielded state appears and the bulk electric field becomes zero. That is, it turns out that the E-ICPB theory can predict such situations in a unified manner.

4.3. About the related experiments

Unfortunately, there is no explicit experimental data to which the present theory can be applied directly. However, there are many potential experiments related to the E-ICPB theory. For example, at least under a low-frequency condition, experiments of many so-called ICEO devices [2,22,23] that works under the parallel electrodes should consider the unshielded electric field that is clarified by our theory,

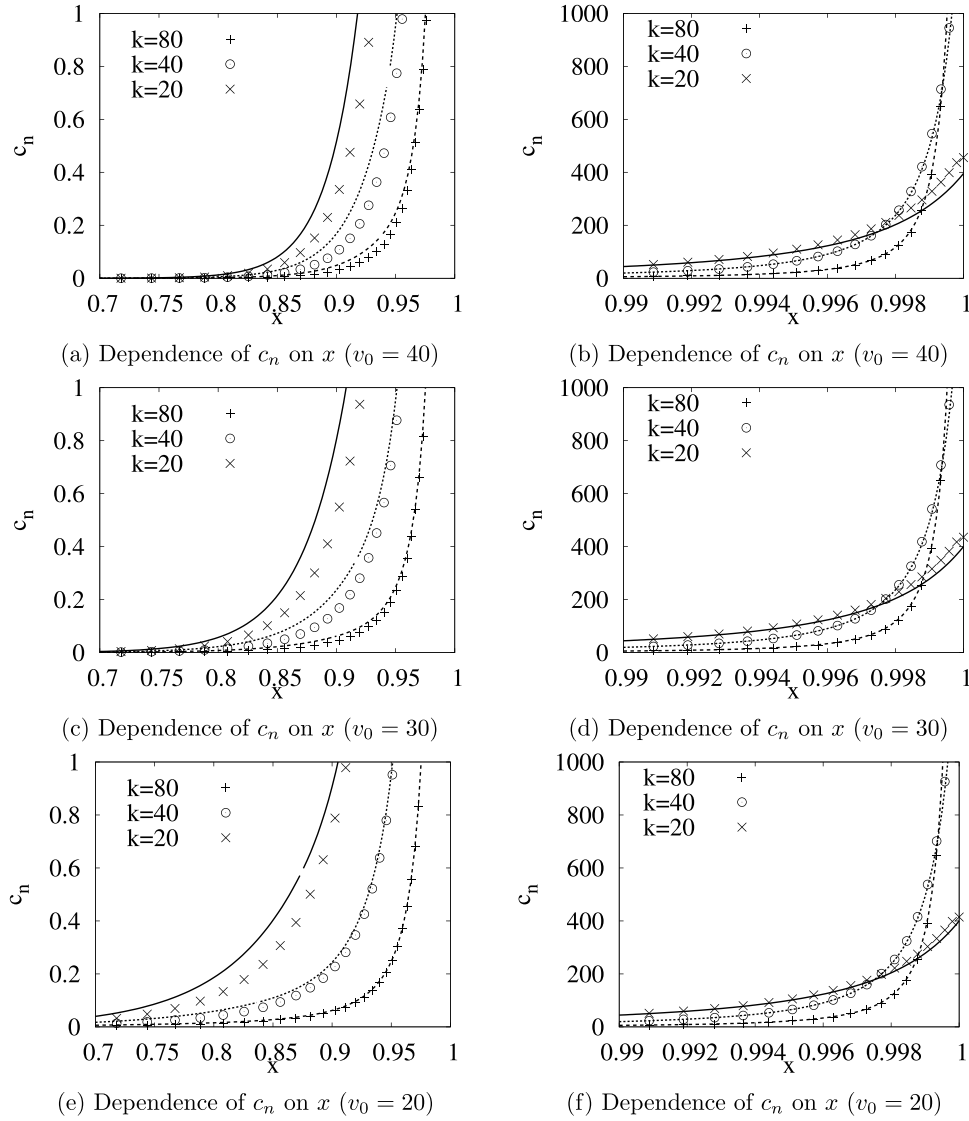


Fig. 4. Comparison between numerical PNP solutions of c_n and analytical results of Model B based on Eq. (20) at extremely high applied voltages. Here, the lines show the analytical results, whereas the characters show the numerical PNP results.

while experiments of many so-called ACEO devices [3,24,25] that use the diffused layer on the electrodes connecting to the electric power should consider the limited zeta potential that is clarified by our theory. In particular, if we observe the maximum ICEO flow velocity u_{ICEO} around the circular conductive cylinder between the electrodes under the condition that $W_0 \leq 100 \mu\text{m}$ and $V_0 \sim 1 \text{ V}$, the value of C_0 may affect u_{ICEO} strongly at least for DC applied voltages because the unshielded electric field changes largely by C_0 , as discussed in Section 4.2.

4.4. About the dielectric coefficient (relative permittivity)

It is well known that the dielectric coefficient is not a constant at extremely high electric fields [26,27]. Specifically, on the basis of theories of Onsager and Kirkwood, Booth [26] reported the formula (in SI units) for the relative permittivity of water as

$$\epsilon_r = n^2 + \frac{1}{4\pi\epsilon} \frac{28N_0\pi(n^2 + 2)\mu_v}{3\sqrt{73}E} L\left(\frac{\sqrt{73}E\mu_v(n^2 + 2)}{6kT}\right), \quad (21)$$

where $n = 1.334$ is the refractive index, $N_0 = \frac{1}{18} 10^6 N_A$ is the number of molecules per unit volume, N_A is the Avogadro constant, $\mu_v = 1.9$ Debye ($= 2.1 \times 3.33564 \times 10^{-30} \text{ C m}$) is the dipole moment of the water

molecule, E is the strength of the electric field, and $L(z) = \coth(z) - \frac{1}{z}$ is the Langevin function. From Eq. (21), we understand that ϵ_r decreases significantly at $E \geq 0.1 \text{ GV/m}$; e.g., $\epsilon_r = 80.4, 65, 26.1$, and 12.2 at $E = 0.1, 0.25, 1.0$, and 2.5 GV/m .

On the other hand, our theory tells us that the solution near the electrode is provided by the previously-proposed simple ICPB theory [18], and the simple ICPB theory tells us that there is a limitation for the increasing of c_{\pm} and $\frac{\phi}{x}$ near electrodes. That is, as explained in Ref. [18], the maximum electric field E_{\max} is provided as $E_{\max} = \kappa^2 \frac{\phi_0}{W_0}$, while the maximum ion concentration C_{\max} is provided as $C_{\max} = \kappa^2 C_0$. Thus, if $W_0 = 100 \mu\text{m}$, we obtain that $E_{\max} = 2.5 \times 10^5, 2.5 \times 10^7$, and $2.5 \times 10^9 \text{ V/m}$ ($C_{\max} = 10^{-3}, 10$, and 10^5 M) at $C_0 = 10^{-7}, 10^{-5}$, and 10^{-3} M (at $\kappa = 100, 1000$, and $10,000$), respectively. Thus, we find that the correction due to the decreasing of ϵ_r may require at $C_0 \geq 10^{-3} \text{ M}$. However, at the same time, we find that we need to consider the steric limit at $C_0 \geq 10^{-5} \text{ M}$ for the extremely high applied voltage. That is, we probably need to consider the steric limit that decreases the maximum electric field, before considering the dielectric saturation. In other words, in our understanding, it is seldom to encounter the real situation we need to consider the dielectric saturation at least for the interesting scales for biomedical applications. This situation is very different from

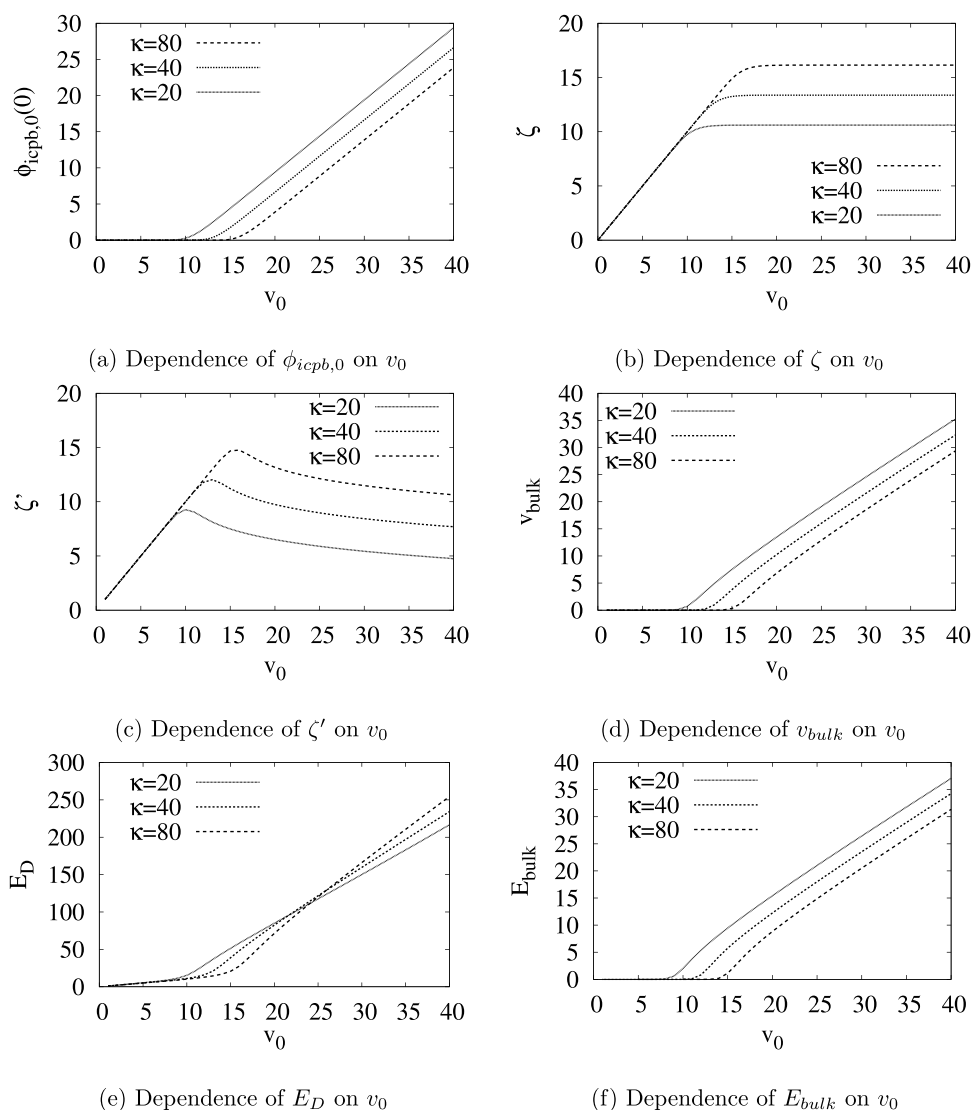


Fig. 5. The appropriate zeta potential and bulk electric field.

that of the GC solution, which provides unrealistic values of c_{\pm} and $\frac{\partial \phi}{\partial x}$. Nevertheless, if we need to consider the dielectric saturation within the framework of E-ICPB theory, we need to solve Eqs. (1)–(5) numerically with Eq. (21). Note that we solved the modified ICPB (M-ICPB) equations (that consider a steric limit with the ion-conserving condition) numerically in our previous study [20], and we believe that the theories of E-ICPB, ICPB [18], and M-ICPB [20] play complementary roles.

4.5. The meaning of E-ICPB theory

Although our previously-proposed simple ICPB theory [18] provided the exact PNP solution for the moderately-high applied voltage region (approximately, $1 \leq v_0 < 10$, or $0.025 \leq V_0 < 0.25$ V), we here first succeed in providing a precise analytical PNP solution that covers all applied voltages in a parallel electrode configuration. Further, the bulk electric field and appropriate zeta potential are first analyzed analytically and clarified through the E-ICPB theory. In other words, although the researchers in the field of colloid science often tend to consider that an external electric field in an electrolyte cell is completely screened, the screening effect becomes incomplete at the extremely high applied voltages and we first describe this incomplete screening state mathematically.

Reversely, when one considers the device using electric fields, one

often neglects the screening effect of the electric double layer. However, by using the E-ICPB theory, one can estimate the bulk electric field easily and it enables more precise analysis of one's device at least for the DC blocking electrode problems. Specifically, the screening potential is approximately 0.25–0.375 V at $\kappa = 20$ –80 and it increases as κ increases as shown in Fig. 5(b). Further, as mentioned in the introduction, we already clarified the open electrode problem in previous paper [21]; i.e., even in an open parallel electrode configuration, the region near the center is described on the basis of the one-dimensional (1D) PNP solution that satisfies the ion-conserving condition. Thus, the E-ICPB theory is useful for both open and closed electrode configurations.

Moreover, we clarify the physical picture of the simple PNP solution in ranging from a small voltage region to the extremely high voltage region through the E-ICPB theory. Thus, we safely use some conclusions of the simple ICPB theory and the relating theory even at the extremely high applied voltages. For example, we can expect that $c_h(1) \simeq \kappa^2$ at the extremely high voltages since the simple ICPB solution becomes the precise approximation of the potential and concentrations in the electric double layer near the electrode, as discussed in the E-ICPB theory. Thus, we can easily recognize when we should consider the steric effect [16, 19] due to the ion size; i.e., if $\kappa^2 C_0$ is larger than the steric-limit concentration $C_0^{steric-limit}$, we need to consider the steric effect along with the ion-conserving condition [20]. Further, by the same reason, we can also

use the electric circuit model [1,28] using the ICPB theory safely at the extremely high applied voltage region.

4.6. About the comparison of the numerical results

One may consider that the comparison in Figs. 1–4 is misleading because the PNP equation does not account for steric effects that become important at high applied voltage. However, this argument is off the point since we try to clarify the diffused ion phenomena that occur when the ions are insufficient owing to the high applied voltage. Note that ICPB should be corrected at extremely high voltages to the M-ICPB that considers the steric effect [20] only when the ions are sufficient to generate a condensation layer due to the steric effect, whereas ICPB should be corrected at extremely high voltages to the E-ICPB that considers non-screening effects when the ions are insufficient to screen the applied voltages, as discussed in this manuscript.

Further, one may consider that the “GC” results are irrelevant for the comparison in Fig. 2, because they are derived for systems that are connected to salt reservoirs. However, this argument is also off the point since the GC and MGC solutions are practically used as the 1D solutions for the diffused charge problems between parallel electrodes without arguing an ion conserving condition or a salt reservoir condition [1,16,18]. Thus, we compare the GC solutions with the ICPB solutions in Fig. 2. Note that one often consider that an open electrode system can be treated as the system that connects to salt reservoirs. However, Sugioka already showed that it is not true [21]. Moreover, the 1D parallel electrode problem intrinsically should be treated as an infinitely large electrode problem, which should be treated as the ion conserving system [18]. Figs. 2–4 implies that Models A and B have merits as mathematical approximations to the full PNP result. Based on our simulations and the above argument, we claim that this is always true for all applied voltages except in the case that the ions are sufficient to generate a condensation layer due to the steric effect. Note that although the specific function curves of the approximations change depending on V_0 and C_0 , the validity of the approximations does not change. In particular, we claim that the separation point between the bulk and surface regions change depending on V_0 and C_0 , although the length of the surface region is usually described by λ_D .

4.7. Future problems

We consider that our findings open a new way to improve various theories on the wide range of diffused charge problems. For example, Prieve [11] proposed an asymptotic steady PNP solution based on the GC solution under the nonzero ion flux condition and discussed the effect of current on the zeta potential. However, the nonzero ion flux condition suggests the extremely high applied voltage, at which Faradaic reaction occurs at the electrode. Thus, we may improve the theory by considering the E-ICPB solution instead of the GC solution. In addition, although Prieve [11] discussed electrophoretic deposition (EPD) from the viewpoint of the electroosmotic (EO) model with the nonzero ion flux condition, we believe that the bulk electric field discussed in the E-ICPB theory should be considered to understand the EPD phenomena more deeply.

Further, Soestbergen [29] clarified diffuse layer effects on the current in a galvanic cell by solving the PNP equation coupled to the generalized Frumkin-Butler-Volmer (g-FBV) boundary equation. However, they assumed the GC solution as the PNP solution by considering that $\kappa \rightarrow \infty$ and thus the solution will be improved for the finite κ condition by using the E-ICPB solution. In particular, since the ion concentration near the electrode affects the Faradaic current concerning the chemical reaction at the electrode, the theory considering the GC solution much overestimates the Faradaic current. In addition, since the Soestbergen's results for the PNP equation coupled with the g-FBV equation is used to model the diffused charge and Faradaic reactions in porous electrodes to develop a high-performance battery [7], to consider

the theory using the E-ICPB solution with the g-FBV equation will be important in the future.

5. Conclusion

In summary, we have proposed an expanded ion-conserving Poisson-Boltzmann theory in an extremely high voltage region in which the screening effect becomes incomplete, and by this theory, we have first succeeded in predicting potentials and ion concentrations between parallel electrodes at the extremely high voltages precisely. Further, we have succeeded in providing precise bulk electric fields and appropriate zeta potentials.

CRediT authorship contribution statement

Hideyuki Sugioka: Conceptualization, Methodology, Formal analysis, Writing – original draft, Investigation, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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