The Independence of the Counter-Ion Density and the Electric Field from Polyelectrolyte Model Configurations on the Model Surfaces

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(Received September 5, 1989)

The polyelectrolyte models of two different configurations are used in order to show that the counter-ion density and the electric field on the surface of a polyelectrolyte model can not be strongly sensitive to the configuration of the model. These models are a layer and a cylinder in which charged groups are packed. Counter-ion densities and electric fields, which appear in water on the surfaces of the layer and the cylinder because of ionic dissociation, are estimated on the basis of the Poisson–Boltzmann equation. Their estimations show that both the counter-ion density and the electric field on the surface of the cylinder are approximately equal to those on the surface of the layer.

Polyelectrolytes should be generally surrounded by counter-ion atmospheres in a solution. Some knowledge of the properties of counter-ion atmospheres have been obtained by using polyelectrolyte models, polyelectrolyte solution model-systems consisting of these models, and the electrostatic potentials of the model systems described by the Poisson–Boltzmann equation.[1,2]

Analytically rigorous solutions of the Poisson–Boltzmann equation give both one-dimensional[1] and cylindrically symmetric[3] solutions; they can be used in investigations of two types of solution model systems, namely, the systems of polylectrolyte layers[4] and those of polyelectrolyte cylinders.[5,6] If the analytically rigorous solutions of the Poisson–Boltzmann equation are employed to investigate the systems, they must be salt free, and in both the layers and the cylinders the charged groups must be packed in uniform densities.

By applying the analytically rigorous solutions to the model systems, it can be determined whether or not the counter-ion density and the strength of the electric field, estimated using the Poisson–Boltzmann equation, are influenced by the model configuration. It is the purpose of this investigation to ascertain if they are indeed insensitive to the model configuration.

Polyelectrolyte molecules have a variety of configurations. If the insensitivity mentioned here is established, it is anticipated, from aspects of the estimations based on the Poisson–Boltzmann equation, that this variety does not influence either the counter-ion density in the vicinity of the surfaces of polyelectrolyte molecules or the strength of the electric field on the surfaces.

Guéron and Weisbuch[7] concluded from their results that the counter-ion densities in the immediate vicinity of polyelectrolytes are not strongly dependent on the configurations of the polyelectrolytes. They used charged plates, charged cylinders, and charged spheres, all of which carry uniform surface charge densities, as polyelectrolyte models. By using the Poisson–Boltzmann equation, they estimated the counter-ion densities in the immediate vicinity of the surfaces of these models. In this paper, the strength of the electric field on the surface of a polyelectrolyte model is also estimated using the Poisson–Boltzmann equation; it is not a certain value used as a boundary condition in order to solve this equation.

Formulae

The Poisson–Boltzmann equations used to describe the electrostatic potential ψ in salt-free solution-model systems at a certain temperature T are as follows: within a layer and a cylinder in which charged groups are packed with a density of n_g, it is:

$$\nabla^2\psi = -\frac{1}{\varepsilon}\left\{-z'en_g + zen_0\exp\left[-\frac{ze\psi}{kT}\right]\right\}, \tag{1}$$

while outside the layer and the cylinder, it is:

$$\nabla^2\psi = -\frac{zen_0}{\varepsilon}\exp\left[-\frac{ze\psi}{kT}\right]. \tag{2}$$

In the above, ze is the charge of a counter ion, $-z'e$ is the charge of a charged group, n_0 is a normalization constant, and k is Boltzmann's constant. In Eq. 1, it is assumed that both the dielectric constant in the layer and that in the cylinder are equal to the dielectric constant, ε, of water.

If the center of a layer of thickness $2d$ is designated as the origin, and if the x-axis is perpendicular to the surface of the layer, then the counter-ion density n_L is given by an approximate solution for Eq. 1 and an analytically rigorous solution of Eq. 2 as follows:[4] within the layer, it is:

$$n_L(x) = \frac{z'}{z}n_g\exp\left[\left(\frac{\Lambda\sigma_L}{\sqrt{2}} + \ln\Lambda\,\sigma_L\right)\cdot\exp[\mu(d-x)] - \left(\frac{\Lambda\sigma_L}{\sqrt{2}} - \ln\Lambda\,\sigma_L\right)\cdot\exp[-\mu(d-x)]\right], \tag{3}$$

while outside the layer, it is:

$$n_L(x) = \frac{\sigma_L{}^2}{2\varepsilon kT}\left\{1-\frac{1}{\sqrt{2}}A\sigma_L\mu(d-x)\right\}^{-2}. \qquad (4)$$

In the above, $A^2 \equiv z/2z'\varepsilon kTn_g$, $\mu^2 \equiv zz'e^2n_g/\varepsilon kT$, and

$$-\sigma_L \equiv \varepsilon\left.\frac{d\psi}{dx}\right|_{x=-d} = -\varepsilon\left.\frac{d\psi}{dx}\right|_{x=d}.$$

In addition, the solution of Eq. 2 used in deriving Eq. 4 must satisfy the following boundary condition:

$$\psi(\pm\infty) = 0, \text{ and } \left.\frac{d\psi}{dx}\right|_{x=\pm\infty} = 0.$$

Also, the solutions to Eq. 1 and to Eq. 2 must link continuously both at $x=-d$ and at $x=d$, while the derived functions of these solutions must link continuously both at $x=-d$ and at $x=d$. The value of σ_L can be calculated using the following formula:[4]

$$A\sigma_L = -\sqrt{2}\tanh[\mu d]\cdot\ln A\sigma_L. \qquad (5)$$

This formula can be derived by considering the following condition:

$$\left.\frac{d\psi}{dx}\right|_{x=0} = 0.$$

Although the value of σ_L calculated using Eq. 5 has previously been called the surface charge density,[4] it is the strength of the electric field estimated by the Poisson–Boltzmann equation; it actually represents its strength on the surface of a layer.

Alternatively, if the distance from the axis of a cylinder with a radius of a is denoted by r, then the counter-ion density n_c is given by an approximate solution for Eq. 1 and an analytically rigorous solution of Eq. 2 as follows:[6] within the cylinder, it is:

$$n_c(r) = \frac{z'}{z}n_g\exp\left[-\frac{ze\sigma_c}{\varepsilon kT}\cdot\frac{1}{\mu I_1(\mu a)}\cdot I_0(\mu r)\right], \qquad (6)$$

while outside the cylinder, it is:

$$n_c(r) = \frac{2\varepsilon kT}{(ze)^2r^2}\cdot\left(1-\frac{zea\sigma_c}{2\varepsilon kT}\right)^2\cdot\left\{1-\left(1-\frac{zea\sigma_c}{2\varepsilon kT}\right)\cdot\ln\frac{r}{a}\right\}^{-2}. \qquad (7)$$

In the above:

$$-\sigma_C \equiv -\varepsilon\left.\frac{d\psi}{dr}\right|_{r=a}.$$

In Eq. 6, $I_0(\mu r)$ and $I_1(\mu r)$ are modified Bessel functions.

In addition, the solution to Eq. 2 used in deriving Eq. 7 must satisfy the following boundary condition:

$$-\varepsilon\left.\frac{d\psi}{dr}\right|_{r=\infty} = 0.$$

Also, the solutions to Eq. 1 and to Eq. 2 must link continuously at $r=a$, while the derived functions of the solutions must link continuously at $r=a$. The value of σ_c can be calculated by means of the following formula:[6]

$$-\frac{ze\sigma_c}{\varepsilon kT}\cdot\frac{I_0(\mu a)}{\mu I_1(\mu a)} = \ln\frac{\mu^2a^2}{2}\left(\frac{zea\sigma_c}{2\varepsilon kT}-1\right)^{-2}. \qquad (8)$$

This formula can be derived by considering the following condition:

$$-\left.\frac{d\psi}{dr}\right|_{r=0} = 0.$$

The value of σ_c calculated by Eq. 8 represents the strength of the electric field on the surface of a cylinder.

Results and Discussion

Counter-Ion Densities on the Surfaces of Models. The counter-ion density, $n_c(a)$, on the surface of a cylinder can be calculated by using Eq. 7. Thus, the dependence of $n_c(a)$ on a can be found to be as is seen in Fig. 1. The value of σ_c used in calculating $n_c(a)$ can be obtained by numerically solving Eq. 8.

The counter-ion density, $n_L(d)$, on the surface of a layer can be calculated by using Eq. 4. The value of σ_L used in calculating $n_L(d)$ can be obtained by numerically solving Eq. 5. The points in Fig. 1 represent the dependence of $n_L(d)$ on d.

A counter-ion density estimated by Eq. 7 is

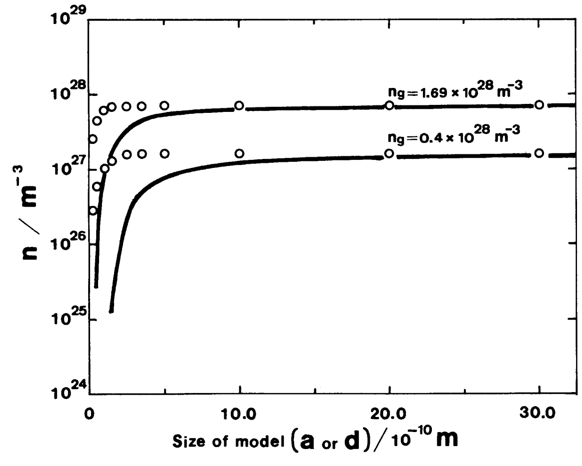

Fig. 1. The counter-ion densities, n, on the surfaces of the models at 298 K. The solid lines represent the counter-ion densities on the surfaces of the cylinders, i.e., $n_c(a)$. The circles represent the counter-ion densities on the surfaces of the layers, i.e., $n_L(d)$. Both the values of $n_c(a)$ and $n_L(d)$ are calculated at $ze=z'e=1.6\times10^{-19}$ C.

dependent upon a. However, as a increases, the counter-ion density approaches a function independent of a, as is shown in Fig. 1. When n_g is large, it rapidly approaches a function independent of a, according to the increase in a. If a is larger than $10\times\mu^{-1}$, then n_c (a) becomes almost independent of a. In Fig. 1, the value of $10\times\mu^{-1}$ at $n_g=1.69\times10^{28}$ m^{-3} is equal to 8.2×10^{-10} m and the value of $10\times\mu^{-1}$ at $n_g=0.4\times10^{28}$ m^{-3} is equal to 1.7×10^{-9} m. As may be seen in Fig. 1, the values given by the function independent of a are almost equal to the counter-ion density on the surface of a layer.

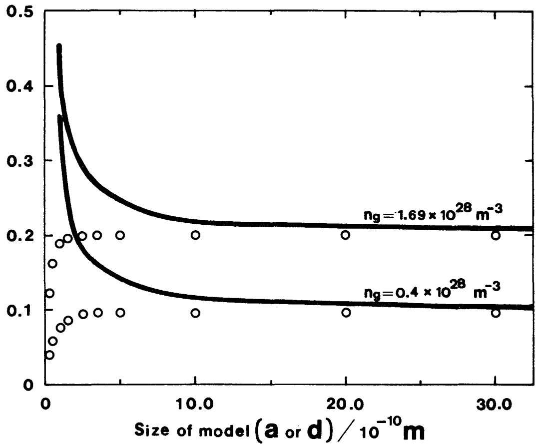

Fig. 2. The strength of the electric field, σ, on the surfaces of the models at 298 K. The solid lines represent the strength of the electric field on the surfaces of the cylinders, i.e., σ_c calculated using Eq. 8. The circles represent the strength of the electric field on the surfaces of the layers, i.e., σ_L calculated using Eq. 5. Both the values of σ_c and σ_L are calculated at $ze=z'e=1.6\times10^{-19}$ C.

The results shown in Fig. 1 are similar to those which Guéron and Weisbuch[7] obtained by using charged plates, charged cylinders, and charged spheres. When a is large, the counter-ion density in the vicinity of a cylinder with a packing density, n_g, of charged groups approaches that in the vicinity of a layer with the same packing density, n_g. As a result, it is possible that the difference between the configurations of a cylinder and a layer causes hardly any difference between the counter-ion densities on their surfaces. Thus, it can be suggested that the counter-ion density in the vicinity of the surface of a polyelectrolyte is not strongly dependent on the configuration of the region occupied by the charged groups and chains of the polyelectrolyte.

The Strength of the Electric Field on the Surface of a Model. In this investigation, the electric field on the surface of a model is defined as the electric field appearing in an ionic dispersed state described by the Poisson–Boltzmann equation. The strength of the electric field on the surface of the model is determined in accordance with the degree of the ionic dissociation of the model in the ionic dispersed state. The behavior of this electric field is similar to that of a counter-ion density on the surface of the model. As is shown in Fig. 2, as a increases, the strength of the electric field, σ_c, calculated using Eq. 8 closely approaches the σ_L value calculated using Eq. 5. When a is large, even though n_g is not a large value, σ_c is almost equal to σ_L.

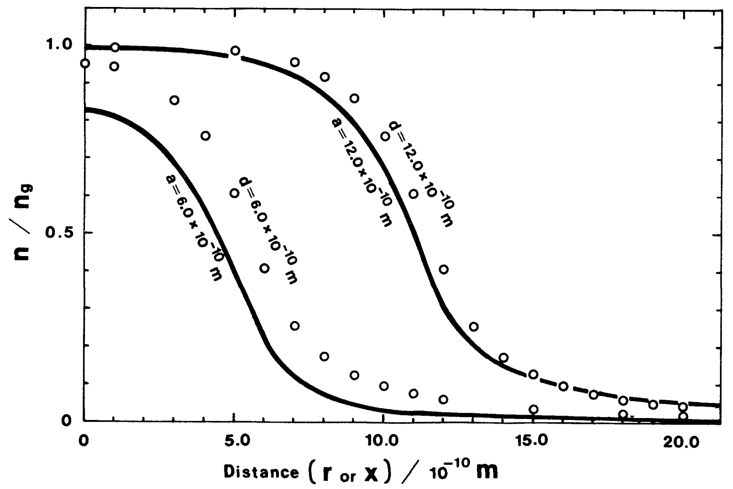

Fig. 3. The distribution of counter ions within and outside the models with $n_g=0.4\times10^{28}$ m^{-3} at 298 K. The solid lines represent the distribution of counter ions within and around the cylinders, i.e., $n_c(r)/n_g$ calculated on a basis of Eqs. 6 and 7. The circles represent the distribution of counter ions within and outside the layers, i.e., $n_L(x)/n_g$ calculated on a basis of Eqs. 3 and 4. Both the values of $n_c(r)/n_g$ and $n_L(x)/n_g$ are calculated at $ze=z'e=1.6\times10^{-19}$ C.

The behavior of σ_c at a small value of a has been discussed in a previous paper.[6]

As is shown in Fig. 3, if a layer has sufficient thickness, then the $zn_L(x)/z'n_g$ within the layer has a value close to 1, but in the vicinity of the layer surface it is much smaller than 1 (Fig. 3 shows its behavior at $ze=z'e=1.6\times10^{-19}$ C). Similarly, the $zn_c(r)/z'n_g$ within a cylinder of a large radius has a value nearly close to 1, but in the vicinity of the cylinder surface it is much smaller than 1 (Fig. 3 shows its behavior at $ze=z'e=1.6\times10^{-19}$ C). Therefore, it can be inferred that the charged groups which contribute significantly to the strength of the electric field on each of the surfaces of the layer and the cylinder are located close to their surfaces.

The strength of an electric field, according to Gauss' law, can be related to a counter-ion density n as follows:

$$\int_S(-\nabla\psi)_n \mathrm{d}S = \frac{1}{\varepsilon}\int_V\Big\{-z'en_g + zen\Big\}\,\mathrm{d}V, \tag{9}$$

where $(-\nabla\psi)_n$ is the component of $-\nabla\psi$ perpendicular to a surface element dS and where dV is a volume element in a volume $\boldsymbol{V}$ defined by a closed surface $\boldsymbol{S}$.

By using a suitable closed surface $\boldsymbol{S}$ on which the following relation can be considered:

$$(-\nabla\psi)_n\Big|_{r=a} = -\frac{\sigma_c}{\varepsilon},$$

the following formula can be derived from Eq. 9:

$$-\sigma_c = -z'en_g\int_0^{a-\delta}\Big\{1-\frac{zn_c(r)}{z'n_g}\Big\}\frac{r}{a}\,dr - z'en_g\int_{a-\delta}^{a}\Big\{1-\frac{zn_c(r)}{z'n_g}\Big\}\frac{r}{a}\,dr\,, \tag{10}$$

where δ is an arbitrary value satisfying the following relation:

$$0 > \delta/a > 1 \text{ and}\left|1-\frac{zn_c(a-\delta)}{z'n_g}\right| \ll 1.$$

When a is large, the value of the definite integral over the interval which belongs in the vicinity of $r=a$ may contribute significantly to the magnitude of $-\sigma_c$ because a function $zn_c(r)/z'n_g$ may behave as is seen in Fig. 3. The behavior of the function shown in Fig. 3 is that at $ze=z'e=1.6\times10^{-19}$C.

By applying a suitable closed surface S on which the following relation can be considered:

$$(-\nabla\psi)_n\Big|_{x=d} = -\frac{\sigma_L}{\varepsilon}\,,$$

the following formula can be derived from Eq. 9:

$$-\sigma_L = -z'en_g\int_0^{d-\delta}\Big\{1-\frac{zn_L(x)}{z'n_g}\Big\}\,\mathrm{d}x - z'en_g\int_{d-\delta}^{d}\Big\{1-\frac{zn_L(x)}{z'n_g}\Big\}\,\mathrm{d}x\,, \tag{11}$$

where δ is an arbitrary value satisfying the following relation:

$$0 < \delta/d < 1 \text{ and}\left|1-\frac{zn_L(d-\delta)}{z'n_g}\right| \ll 1.$$

The value of the definite intergral over the interval which belongs in the vicinity of $x=d$ may contribute significantly to the magnitude of $-\sigma_L$, because of the behavior of $zn_L(x)/z'n_g$ shown in Fig. 3, when d is large.

The function $n_L(x)$ described by Eq. 3 can be modified by considering Eq. 5 as follows:

$$n_L(x) = \frac{z'}{z}\,n_g\exp\left[-\frac{ze\sigma_L}{\varepsilon kT}\cdot\frac{\cosh[\mu x]}{\mu\sinh[\mu d]}\right].$$

Hence, an approximate expression of $n_L(x)$ at large values of μx and μd is:

$$n_L(x) = \frac{z'}{z}\,n_g\exp\left[-\frac{ze\sigma_L}{\varepsilon kT}\cdot\frac{1}{\mu}\exp[-\mu(d-x)]\right]. \tag{12}$$

Similarly the function $n_c(r)$ described by Eq. 6 has the following approximate expression at large values of μr and μa:

$$n_c(r) = \frac{z'}{z}\,n_g\exp\left[-\frac{ze\sigma_c}{\varepsilon kT}\cdot\frac{1}{\mu}\sqrt{\frac{a}{r}}\exp[-\mu(a-r)]\right]. \tag{13}$$

Equations 12 and 13 suggest that $n_c(r)$ at large values of μr and μa may approach $n_L(x)$ at large values of μx and μd in the vicinity of $r=a$.

The definite integral at the second term on the right-hand side of Eq. 10 can be approximately carried out by applying an approximate formula to a definite integral. As a result, if the interval which belongs in the vicinity of $r=a$ is $[a-\delta, a]$ when a is large, the following approximate formula can be obtained by considering Eq. 13:

$$\begin{aligned}\int_{a-\delta}^{a}\Big\{1-\frac{zn_c(r)}{z'n_g}\Big\}\frac{r}{a}\,\mathrm{d}r = \Bigg[1 &- \frac{1}{6}\exp[-\sqrt{2}\Lambda\sigma_c]\\ &-\frac{2}{3}\exp[-\sqrt{2}\Lambda\sigma_c t^{1/2}] - \frac{1}{6}\exp[-\sqrt{2}\Lambda\,\sigma_c t]\\ &+\frac{1}{2}\frac{\delta}{a}\Big\{-1+\frac{2}{3}\Big(1+\frac{\Lambda\sigma_c}{\sqrt{2}}t^{1/2}\Big)\exp[-\sqrt{2}\Lambda\sigma_c t^{1/2}]\\ &+\frac{1}{3}\Big(1+\frac{\Lambda\sigma_c}{\sqrt{2}}t\Big)\exp[-\sqrt{2}\Lambda\sigma_c t]\Big\}\Bigg]\cdot\delta,\end{aligned} \tag{14}$$

where:

$$t = \exp[-\mu\,\delta].$$

In order to derive Eq. 14, $\delta/a \ll 1$ has been considered.

If the interval which belongs in the vicinity of $x=d$ is $[d-\delta, d]$ when d is large, the definite integral at the second term on the right-hand side of Eq. 11 can be approximately carried out by considering Eq. 12 and by applying an approximate formula to a definite integral as follows:

$$\int_{d-\delta}^{d}\left\{1-\frac{zn_{\mathrm{L}}(x)}{z'n_{\mathrm{g}}}\right\}\mathrm{d}x=\left\{1-\frac{1}{6}\exp[-\sqrt{2}\Lambda\sigma_{\mathrm{L}}]-\frac{2}{3}\exp[-\sqrt{2}\Lambda\sigma_{\mathrm{L}}t^{1/2}]-\frac{1}{6}\exp[-\sqrt{2}\Lambda\sigma_{\mathrm{L}}t]\right\}\cdot\delta. \tag{15}$$

The comparison of Eq. 14 with Eq. 15 suggests that, as a increases, the value of definite integral at the second term on the right-hand side of Eq. 10 can approach that at the second term on the right-hand side of Eq. 11. The value of the definite integral evaluated by Eq. 14, according to the counter-ion distribution seen in Fig. 3, should contribute significantly to the magnitude of $-\sigma_c$ via Eq. 10 when a is large. Thus, the approach of σ_c to σ_L at a large value of a is attributable to the distribution of counter ions.

In addition, if T is constant, then the σ_c derived from Eq. 8 is a function $\sigma_c(a, n_g)$ of a and n_g. If $n_{g1} \neq n_{g2}$, then it is not possible that as a increases, the value of $\sigma_c(a, n_{g1})$ approaches the value of $\sigma_c(a, n_{g2})$. As may be seen in Fig. 2, the difference between the value of $\sigma_c(a, n_{g1})$ at $n_{g1}=1.69\times10\ \mathrm{m}^{28}\ \mathrm{m}^{-3}$ and the value of $\sigma_c\ (a, n_{g2})$ at $n_{g2}=0.4\times10^{28}\ \mathrm{m}^{-3}$ becomes constant as a increases. The difference between the value of $\sigma_c(a_1, n_g)$ at $a_1=3.0\times10^{-10}$ m and the value of $\sigma_c(a_2, n_g)$ at $a_2=12.0\times10^{-10}$ m is almost constant, as may be seen in Fig. 4, if n_g is large. It is not possible that the value of $\sigma_c(a_1, n_g)$ is almost equal to the value of $\sigma_c(a_2, n_g)$ because of a large value of n_g (for example, $n_g=3\times10^{28}\ \mathrm{m}^{-3}$) if a_1 and a_2 are not large and if a_1 is not equal to a_2. Alternatively, the σ_L derived from Eq. 5 is a function, $\sigma_L(d, n_g)$, of d and n_g if T is constant. The property of $\sigma_L(d, n_g)$ differs from that of $\sigma_c(a, n_g)$. Even though d_1 is not equal to d_2, the value of $\sigma_L(d_1, n_g)$ agrees well with the value of $\sigma_L(d_2, n_g)$ when d_1 and d_2 are not small. As may be seen in Fig. 4, the value of $\sigma_L(d_1, n_g)$ at $d_1=12.0\times10^{-10}$ m agrees well with the value of $\sigma_L(d_2, n_g)$ at $d_2=3.0\times10^{-10}$ m. (In addition, the behavior of σ_c at a small value of n_g has been discussed in a previous paper.[6])

The results in Fig. 2 suggest that the difference between the configurations of polyelectrolyte molecules does not influence the strength of the electric field on the surfaces of polyelectrolyte molecules if they have an equal packing density of charged groups and if they are sufficiently large. The results shown in Fig. 4 suggest that, when an association consists of small polyelectrolyte molecules, the strength of the electric field on the surface of the association can not be equal to that on the surface of one of the polyelectrolyte molecules, even though the value of n_g in the polyelectrolyte molecules and the value of n_g in the association increase upon the control to the pH value of a solution in which the polyelectrolyte molecules and the association are dispersed.

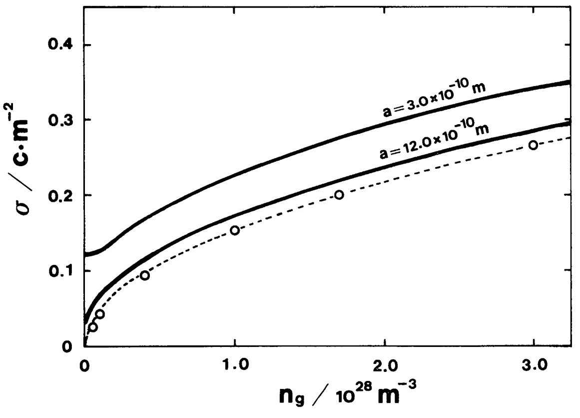

Fig. 4. The relationship between n_g and the strength of the electric field, σ, on the surfaces of the models at 298 K. The solid lines represent σ_c calculated using Eq. 8. The broken line represents σ_L calculated at $d=12.0\times10^{-10}$ m by using Eq. 5. The circles represent σ_L calculated at $d=3.0\times10^{-10}$ m by using Eq. 5. Both the values of σ_c and σ_L are calculated at $ze=z'e=1.6\times10^{-19}$ C.

Appendix

An approximate formula to a definite integral is given as follows:

$$\int_{b}^{a} f(x)\,\mathrm{d}x=\frac{b-a}{6}\left\{f(a)+f(b)+4f\left(\frac{a+b}{2}\right)\right\}.$$

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