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The Charge Carried by a Layer Formed by an Aggregation of Polyelectrolytes in a Solution Containing a Salt

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A layer formed by the aggregation of polyelectrolyte molecules is charged according to the ionic dissociation of the layer in a simple salt solution. The charge carried by the layer is estimated on a basis of solutions of the Poisson-Boltzmann equation. It has been found that this charge is independent of the concentration, n_s, of a salt, in spite of the permanence of the layer to counter ions when the density, n_g, of charged groups in the polyelectrolyte molecules is much higher than the concentration n_s. As the result, the charge may be given as a function of three parameters (temperature, density n_g, and thickness of the layer) except for n_s. Moreover, it has been found that the distribution of counter ions within the layer and their distribution in the vicinity of the layer may be independent of n_s and that these distributions of counter ions may agree with that in a salt-free solution.

An electric field is formed around a polyelectrolyte molecule in an aqueous solution because of the ionic dissociation of the polyelectrolyte molecule. This formed electric field restricts the diffusion of counter ions due to thermal motion and a repulsive force between the counter ions. In general, it is known that the charge density of a polyion in a solution may be independent of the concentration of a salt.[1)]

Guéron and Weisbuch noted, on a basis of calculations using the Poisson-Boltzmann equation, that counter ions exist with quite high densities in the immediate vicinity of the surface of highly charged polyelectrolyte molecules.[2)] Moreover, they found that the distribution of counter ions in the vicinity of these polyelectrolyte molecules is insensitive to the concentration, n_s, of a salt, as has been noted by Stigter,[3)] and that this distribution is not strongly dependent on the shapes of the polyelectrolyte molecules.[2)]

Plates, cylinders, and spheres, the surfaces of which hold constant surface-charge densities, were introduced as models of polyelctrolytes in order to ascertain these properties of counter-ion distributions.[2)] In the layer-model system of a polyelectrolyte solution,[4)] layers formed by the aggregations of polyelectrolyte molecules were immersed in a solvent instead of plates, which hold a constant surface-charge density. This layer model was capable of giving a quantitative estimation of the charged characteristics of a polyion in a salt-free solution. Counter ions in the layer-model system distribute continuously from the inside of the layers of polyelectrolytes to the outside of the layers, since the layers are permeable to counter ions. The purpose of this investigation was to show that the charge carried by such layers of polyelectrolytes may be independent of the salt concentration. If a salt is added to a layer-model system, it is doubtful whether the charge of the layers would be influenced by the salt, owing to an effect related to the permeance of the layers which may not occur on charged surfaces of constant surface-charge density. If the layer model is capable of having a nature found in the relation between the charge density of polyion and the concentration of a salt (as described above), the charge of the polyelectrolyte layers should not be affected by a salt added to a layer-model system.

Engström and Wennerström used the Gouy-Chapman solution in order to estimate the density of counter ions in the immediate vicinity of charged plates which maintain a constant surface-charge density and which immerse in a simple salt solution; they showed that this density of cunter ions is independent of the concentration of a salt, and that it agrees with the counter-ion density in a salt-free solution.[5)] Similarly, by using the Gouy-Chapman solution in this study it has been shown that the distribution of counter ions in the vicinity of the surface of the layers may be independent of n_s under the condition that any effect dependent on the distance between the layers can be ignored. Also, this counter-ion distribution may agree with that in a salt-free solution. In accordance with the above condition, the layer-model system described in this paper is composed of one layer of polyelectrolytes immersed in a simple salt solution. It is shown here that any charge carried by the layer can be independent of n_s.

In addition, the charged circumstance of the layer can be represented as the total charge contained in an imaginary cylinder. This imaginary cylinder is perpendicular to the surface of the layer and has a unit cross section. Also, the both ends of the imaginary cylinder are at the center of the layer and on the surface of the layer, respectively. A system composed of a layer can be an electric equivalent to a system composed of a charged plate of a conductor substituted for the layer, if the charge per unit area on the surface of the plate is equal to the total charge in an imaginary cylinder as is described above. On the basis of this situation, the total charge in the imaginary cylinder was regarded as being the surface-charge density on a polyelectrolyte layer in a previous paper,[4)] although this surface-charge density was imaginary. The charged circumstance of the layer differs, in fact, from the charged circumstance of the dielectric in an electric field in which the dielectric induces a charge on its surface and from the charged circumstance of a charged conductor in which a charge accumulates on its surface. In this paper, the total charge in the imaginary cylinder will be called the layer-charge density (LCD), in order to avoid any confusion between these charged circumstances.

Model

Structure of a Layer Model. The layer-model system used in order to estimate the charged characteristics of polyions in a salt-free solution consisted of many layers formed by aggregations of polyelectrolyte molecules and arranged in a solvent.[4)] When these layers are immersed in a simple salt solution, it is difficult to estimate the charge carried by the layers (i.e., LCD), the distribution of counter ions, etc., by considering any effect dependent on the distance between the layers and by solving the Poisson-Boltzmann equation. In this paper, a certain condition, which corresponds to the dilute concentration of polyelectrolytes, is assumed in order to avoide this difficulty, i.e., it is assumed that the electrostatic interaction between layers of polyelectrolytes is negligible. The estimations of the LCD, of the electric field, and of the counter-ion distribution under this condition are the objects of this investigation. Consequently, the layer-model system used in this paper consists of one layer of polyelectrolytes (Fig. 1); this layer is immersed in a simple salt solution. The thickness of the layer is Δx and the density of the charged groups packed in the layer is n_g. The concentration of a salt in the solution, in which the layer is immersed, is n_s. In addition, even in the layer-model system which is salt-free, though the distance between neighboring layers of polyelectrolytes is of the order 10^2 Å, the electrostatic interaction between the layers hardly affects the LCD in the system when this LCD is of the order 10^{-2} C·m^{-2}.[4)]

Electrostatic Potential. Though it is assumed that the absolute value of the charge of a counter ion is the same as that of a co-ion, the electrostatic potential ψ in the layer-model system (as is shown in Fig. 1) can be described by the following Poisson-Boltzmann equation: within a layer of polyelectolytes ($-\Delta x/2 < x < \Delta x/2$) it is

$$\frac{d^2\psi_1}{dx^2} = -\frac{1}{\varepsilon}\{-z'en_g - zen_s\exp[ze\psi_1/kT] + zen_s\exp[-ze\psi_1/kT]\}, \tag{1}$$

while outside the layer ($\Delta x/2 \leqq x$) it is

$$\frac{d^2\psi_2}{dx^2} = \frac{2zen_s}{\varepsilon}\sinh[ze\psi_2/kT]. \tag{2}$$

In the above, ε is the dielectric constant of a solvent, $-z'e$ is the charge of a charged group, ze is the charge of a counter ion, $-ze$ is the charge of a co-ion, k is Boltzmann's constant, and T is the absolute temperature. In addition, it is assumed that the dielectric constant within the layer is the same as that of a solvent.

For boundary conditions

$$\psi_1\left(\frac{\Delta x}{2}\right) = \psi_2\left(\frac{\Delta x}{2}\right) \text{ and } -\varepsilon\left.\frac{d\psi_1}{dx}\right|_{x=\Delta x/2} = -\sigma,$$

the approximate solution of Eq. 1 can be obtained as follows:[4,6)]

$$\begin{aligned}\psi_1(x) = &-\frac{kT}{ze}\cdot\operatorname{arcsinh} f \\ &+\frac{kT}{2ze}\cdot\left\{\sqrt{2}\,\Lambda\sigma + \frac{ze\psi_2(\Delta x/2)}{kT} + \operatorname{arcsinh} f\right\}\cdot\exp\left[-\mu\left(\frac{\Delta x}{2} - x\right)\right] \\ &+\frac{kT}{2ze}\cdot\left\{-\sqrt{2}\,\Lambda\sigma + \frac{ze\psi_2(\Delta x/2)}{kT} + \operatorname{arcsinh} f\right\}\cdot\exp\left[\mu\left(\frac{\Delta x}{2} - x\right)\right],\end{aligned} \tag{3}$$

where $\Lambda^2 \equiv z/(2z'kT\varepsilon n_g)$, $\mu^2 \equiv zz'e^2n_g/(\varepsilon kT)$, and $f \equiv z'n_g/(2zn_s)$. Also, $-\sigma$ is the layer-charge density (LCD). By considering the continuity of the electric field in the layer, it can be described as

$$-\sigma = \int_0^{\Delta x/2}\{-z'en_g - 2\,zen_s\sinh[ze\psi_1/kT]\}\,dx.$$

On the other hand, the Gouy-Chapman solution given for the following boundary conditions is used as a solution of Eq. 2:

$$\psi_2(\infty) = 0,\ -\varepsilon\left.\frac{d\psi_2}{dx}\right|_{x=\infty} = 0,\ -\varepsilon\left.\frac{d\psi_2}{dx}\right|_{x=\Delta x/2} = -\sigma.$$

The Formulation of the LCD. A formula which represents the LCD, $-\sigma$, in a simple salt solution can be formed by substituting the Gouy-Chapman solution into $\psi_2(\Delta x/2)$ in Eq. 3 and by considering the following condition in conectin with the continuity of the electric field $-\varepsilon\, d\psi_1/dx$ in the layer:

$$-\varepsilon\left.\frac{d\psi_1}{dx}\right|_{x=0} = 0. \tag{4}$$

As a result, the obtained formula is

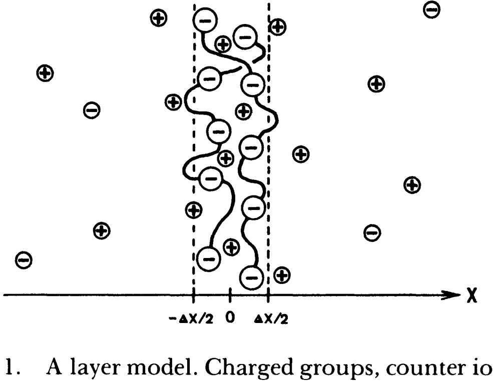

Fig. 1. A layer model. Charged groups, counter ions, and co-ions are represented by ~(−)~, (+), and (−), respectively.

$$\Lambda\sigma\cdot\left[\ln\left\{\left(\sqrt{\frac{1}{4}+\left(\frac{zn_s}{z'n_g}\right)^2}+\frac{1}{2}\right)^{-1/2}\cdot\left(\sqrt{\frac{1}{4}\Lambda^2\sigma^2+\frac{zn_s}{z'n_g}}+\frac{1}{2}\Lambda\sigma\right)\right\}\right]^{-1}=-\sqrt{2}\ \tanh\left[\mu\frac{\Delta x}{2}\right]. \qquad (5)$$

Thus, the LCD is given by Eq. 5 as a function of four parameters (T, n_g, n_s, Δx).

If the existance of co-ions in the layer can be ignored, the $-zen_s\cdot\exp[ze\psi_1/kT]$ term disappears in Eq. 1 and, as a result, the $(zn_s/z'n_g)^2$ term disappears in Eq. 5. Moreover, if the existance of co-ions on the surface of the layer can be ignored, the $zn_s/z'n_g$ term also disappears in Eq. 5. It has been suggested that, if co-ions can be sufficiently excluded in the vicinity of the layer, the LCD may be independent of n_s.

In addition, an approximation to Eq. 5 can be given when $zn_s/z'n_g$ is small. It is possible that the $zn_s/z'n_g$ ratio is sufficiently small, because the value of n_g is of the order of 10^{28} m^{-3},[4] if a polyacrylate molecule is considered as an example. For a small $zn_s/z'n_g$ ratio, the magnitude of $\Lambda\sigma$, in accordance with the sign of the right-hand side of Eq. 5, must satisfy $\Lambda\sigma<1$. In accordance with the magnitude of this right-hand side, $\Lambda\sigma$ can be close to 1. By considering this magnitude of $\Lambda\sigma$ and the sign of $\Lambda\sigma$, the following approximation for $-\sigma$ is found when $zn_s/z'n_g$ is sufficiently small:

$$-\sigma=-\sigma_0+\Delta\sigma(n_s), \qquad (6)$$

where $-\sigma_0$ is the LCD in a salt-free solution[4] and it is

$$-\sigma_0=-\frac{Y}{2\Lambda}\{(2+Y)-\sqrt{Y(Y+4)}\},$$

In Eq. 6, $\Delta\sigma(n_s)$ is defined as

$$\Delta\sigma(n_s)\equiv\frac{2kT\varepsilon}{\sigma_0}\sqrt{\frac{Y}{Y+4}}\cdot n_s\,.$$

In the above formulae, Y is defined as

$$Y\equiv 2\sqrt{2}\ \tanh[\mu\Delta x/2].$$

Results and Discussion

Layer-Charge Density (LCD). LCD in a simple salt solution can be given as a function of four parameters (T, n_g, n_s, Δx). It can be shown, however, that this LCD becomes a function of three parameters (T, n_g, Δx) if the $zn_s/z'n_g$ ratio is sufficiently small.

When $zn_s/z'n_g$ is small, Eq. 6 becomes an approximation of Eq. 5, and the relationship between $-\sigma$ and n_s can be well understood in Eq. 6. For the conditions used in order to estimate the charge density of polyion in a salt-free, dilute solution of a polyelectrolyte (the T, n_g and Δx parameters are 298 K, 1.7×10^{28} m^{-3}, and 3 Å, respectively, and both z and z' are 1),[4] the $\Delta\sigma(n_s)/\sigma_0$ ratio is of the order of 10^{-2} if n_s is 10^{-1} mol·dm^{-3}. This ratio is much smaller than 1. Thus, the second term in the right-hand side of Eq. 6 reduces, when $zn_s/z'n_g$ is small. As is shown in Fig. 2, the LCD $-\sigma$ may become independent of n_s, even though the layer is permeable to counter ions. Moreover, this LCD, which is independent of n_s, may agree with that in a salt-free solution, as can be seen from Eq. 6. In addition, if n_g is small, $-\sigma$ is liable to be influenced by n_s, as can be seen in Fig. 2.

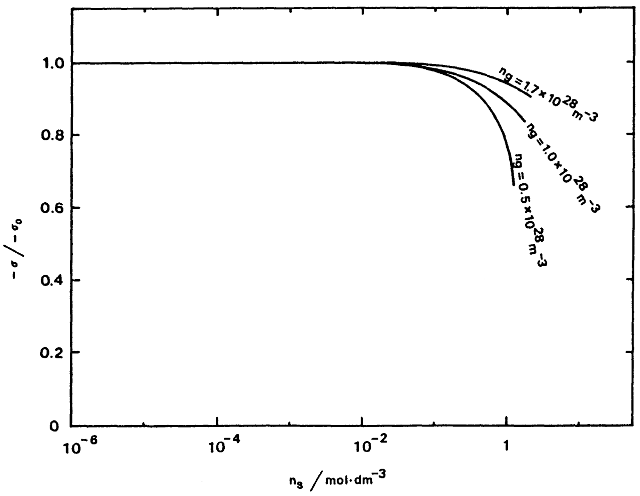

Fig. 2. The dependence of $-\sigma/\sigma_0$ on n_s at 298 K on the basis Eq. 6. The $-\sigma/\sigma_0$ ratio is values calculated for $\Delta x=3$ Å.

On the other hand, when the distribution of co-ions within the layer and in the vicinity of the layer can be ignored, the $zn_s/z'n_g$ and $(zn_s/z'n_g)^2$ terms disappear in Eq. 5; then, LCD agrees with that in a salt-free solution. This result shows that when $z'n_g$ is much larger than zn_s, co-ions are sufficiently excluded within the layer and in the vicinity of the layer.

Ultimately, it is inferred that the independence of the charge density of polyions from the concentration of a salt occurs owing to the quite high density of charged groups contained in the polyions (then, co-ions are sufficiently excluded in the vicinity of the polyions).

Electric Field. The electric field, $-\varepsilon\mathrm{d}\psi/\mathrm{d}x$, on the surface of the layer is proportional to $-\sigma$. Since $-\sigma$ for the small value of $zn_s/z'n_g$ is independent of n_s, for such a value of $zn_s/z'n_g$ the electric field on the surface is independent of n_s. Moreover, it can be shown that the electric field in the vicinity of the layer is insensitive to n_s if n_s is sufficiently small. The electric field in the vicinity of the layer is given by

$$-\varepsilon\frac{\mathrm{d}\psi_2}{\mathrm{d}x}=\varepsilon E_0+\varepsilon E(n_s), \qquad (7)$$

where εE_0 is the electric field occurring in a salt-free solution[4] and it is

$$\varepsilon E_0=\frac{-\sigma_0}{1-\frac{\Lambda\sigma_0}{\sqrt{2}}\cdot\mu\left(\frac{\Delta x}{2}-x\right)}$$

In Eq. 7, $\varepsilon E(n_s)$ is defined as

$$\varepsilon E(n_s) \equiv \varepsilon E_0 \cdot \Biggl[- \frac{\Delta\sigma/\sigma_0}{1-\frac{\Lambda\sigma_0}{\sqrt{2}}\mu\left(\frac{\Delta x}{2}-x\right)} + \frac{\sqrt{2}}{f\Lambda\sigma_0}\cdot\frac{\mu\left(\frac{\Delta x}{2}-x\right)}{\left\{1-\frac{\Lambda\sigma_0}{\sqrt{2}}\mu\left(\frac{\Delta x}{2}-x\right)\right\}^2}\cdot\Biggl\{1-\sqrt{2}\Lambda\sigma_0\mu\left(\frac{\Delta x}{2}-x\right) + \frac{1}{3}\left(\sqrt{2}\Lambda\sigma_0\mu\left(\frac{\Delta x}{2}-x\right)\right)^2 - \frac{1}{24}\left(\sqrt{2}\Lambda\sigma_0\mu\left(\frac{\Delta x}{2}-x\right)\right)^3\Biggr\}\Biggr].$$

In the Guoy-Chapman solution, the coefficient κ defined as

$$\kappa^2 \equiv \frac{2z^2e^2n_s}{\varepsilon kT},$$

is contained. Equation 7 is obtained by considering n_s and $\kappa\cdot(\Delta x/2-x)$ to be small and by approximating $-\varepsilon d\psi/dx$ given by the Gouy-Chapman solution. The ratio of the second term to the first term in the right-hand side of Eq. 7, $|E(n_s)/E_0|$, is much smaller than 1 in the vicinity of the layer, as is found from the dependence of $\{E_0+E(n_s)\}/E_0$ on x in Fig. 3. As a result, it is found that the electric field in the vicinity of the layer may be independent of n_s, and that it may agree with the electric field in a salt-free solution. Moreover, the dependence of $\{E_0+E(n_s)\}/E_0$ on x in Fig. 3 suggests that the extent of the electric field insensitive to n_s expands more if n_s decreases more.

In addition, the electric field within the layer is given by the following formula obtained by using Eq. 3 and by considering Eq. 4:

$$-\varepsilon\frac{d\psi_1}{dx} = -\frac{\sigma}{2}\left\{\left(1+\frac{2\sqrt{2}}{Y}\right)\cdot\exp\left[-\mu\left(\frac{\Delta x}{2}-x\right)\right] + \left(1-\frac{2\sqrt{2}}{Y}\right)\cdot\exp\left[\mu\left(\frac{\Delta x}{2}-x\right)\right]\right\}.$$

As is noted by this formula, the dependence of this electric field on n_s is the same as the dependence of $-\sigma$ on n_s. If $zn_s/z'n_g$ is sufficiently small, $-\varepsilon d\psi_1/dx$ may be independent of n_s and may agree with the electric field in a salt-free solution (as can be noted according to Ref. 4).

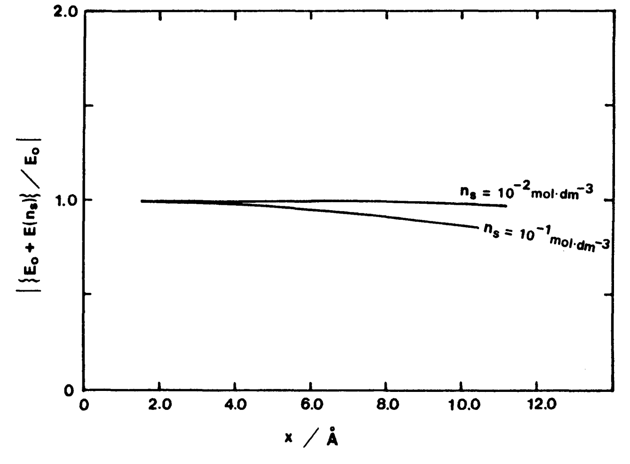

Fig. 3. The dependence of $\{E+E(n_s)\}/E_0$ on x at 298 K on the basis of Eq. 7. The $\{E+E(n_s)\}/E_0$ ratio is values calculated for $n_g=1.7\times10^{28}$ m^{-3} and $\Delta x=3$ Å.

The Distribution of Counter Ions. The property of the electric field in the vicinity of the layer suggests that the distribution of ions in the vicinity of the layer is insensitive to n_s and that the extent of the ion-distribution insensitive to n_s expands in accordance with a reduction in n_s. The relationship between the counter-ion distribution and n_s in the vicinity of the layer may be represented by

$$n_2(x) = n_0(x) + n_0(x)\cdot\Biggl[- \frac{2\Delta\sigma/\sigma_0}{1-\frac{\Lambda\sigma_0}{\sqrt{2}}\mu\left(\frac{\Delta x}{2}-x\right)} + \frac{2}{f\Lambda^2\sigma_0^2}\cdot\frac{1}{\left\{1-\frac{\Lambda\sigma_0}{\sqrt{2}}\mu\left(\frac{\Delta x}{2}-x\right)\right\}^2}\cdot\Biggl\{1-\sqrt{2}\Lambda\sigma_0\mu\left(\frac{\Delta x}{2}-x\right) + \frac{1}{2}\left(\sqrt{2}\Lambda\sigma_0\mu\left(\frac{\Delta x}{2}-x\right)\right)^2 - \frac{1}{6}\left(\sqrt{2}\Lambda\sigma_0\mu\left(\frac{\Delta x}{2}-x\right)\right)^3 + \frac{1}{48}\left(\sqrt{2}\Lambda\sigma_0\mu\left(\frac{\Delta x}{2}-x\right)\right)^4\Biggr\}\Biggr], \tag{8}$$

where $n_2(x)$ is the density of counter ions, and $n_0(x)$ is the density of counter ions in a salt-free solution,4) i.e.:

$$n_0(x) = \frac{\sigma_0{}^2}{2kT\varepsilon\left\{1-\frac{\Lambda\sigma_0}{\sqrt{2}}\cdot\mu\left(\frac{\Delta x}{2}-x\right)\right\}^2}.$$

In addition, Eq. 8 is obtained by considering n_s and $\kappa\cdot(\Delta x/2-x)$ to be small and by approximating the counter-ion density given by the Gouy-Chapman solution. It is noted in Fig. 4 (depicted in accordance with Eq. 8) that the density of counter ions in the vicinity of the layer, $n_2(x)$, may be insensitive to n_s if n_s is less than 0.1 mol·dm^{-3} ($zn_s/z'n_g$ is less than 10^{-2}). The insensitivity of $n_2(x)$ to n_s is similar to the property of the counter-ion distribution in the vicinity of the charged surfaces of plates, cylinders, and spheres.2,3) The behavior of $n_2(x)$ (Fig. 4) suggests that the extent of the distribution of counter ions insensitive to n_s expands in accordance with a reduction in n_s. Furthermore, when n_s is so small that the second term in the right-hand side of Eq. 8 can be ignored, the density $n_2(x)$ may agree with the counter-ion density in a salt-free solution. This result is similar to that regarding the charged-plates model of Engström and Wennerström.5)

On the other hand, the density of co-ions in the vicinity of the layer is given by

$$n_s{}^2/n_2(x).$$

This formula does not include terms independent of n_s. The formula shows that the density of co-ions is quite small when $zn_s/z'n_g \ll 1$ is satisfied. As a result, the co-ion distribution in the vicinity of the layer may be ignored, although this distribution depends on n_s. Therefore, it is deduced that the insensitivity of the electric field to n_s is attributable to only the property of the counter-ion distribution in the vicinity of the layer.

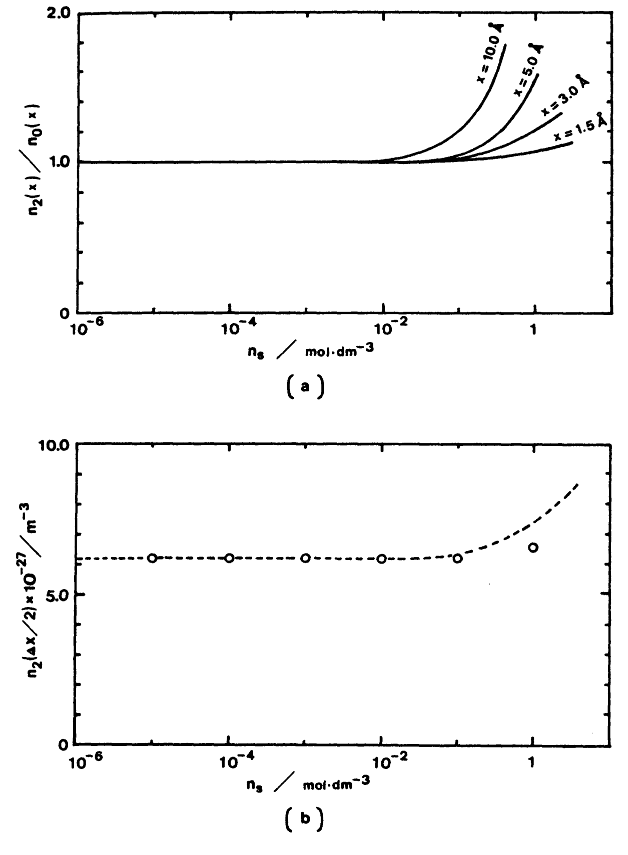

Fig. 4. The dependence of $n_2(x)$ on n_s at 298K on the basis of Eq. 8. The $n_2(x)/n_0(x)$ ratio is values calculated for $n_g=1.7\times1.0^{28}$ m^{-3} and $\Delta x=3$ Å. The circles represent the $n_2(\Delta x/2)$ counter-ion density on the surface of the layer. The broken line represents the counter-ion density in the immediate vicinity of a charged plate and its surfaces hold a constant surface-charge density 0.190 C·m^{-2} (which equals to a value given by the layer model under the above condition when $n_s=0$).

In addition, in Fig. 4 the behavior of counter-ion distribution in the immediate vicinity of a charged plate, which holds a constant surface-charge density (0.190 C·m^{-2}), agrees well with the behavior of n_2 $(\Delta x/2)$ (which is n_2 (x) on the surface of the layer) depicted by the circles. The insensitivity of the LCD to n_s is reconfirmed by means of an agreement between these circles and the broken line in Fig. 4.

The density of counter ions within the layer, n_1 (x), is given by using Eq. 3 and by considering Eq. 4; it is represented as

$$n_1(x)=\frac{z'n_g}{z}\cdot\left(\sqrt{\frac{1}{4}+\left(\frac{zn_s}{z'n_g}\right)^2}+\frac{1}{2}\right)\cdot\exp\left[-\frac{\Lambda\sigma}{\sqrt{2}}\left\{\left(1+\frac{2\sqrt{2}}{Y}\right)\cdot\exp\left[-\mu\left(\frac{\Delta x}{2}-x\right)\right]-\left(1-\frac{2\sqrt{2}}{Y}\right)\cdot\exp\left[\mu\left(\frac{\Delta x}{2}-x\right)\right]\right\}\right].$$

The density n_1 (x) described by this formula may be as insensitive as n_2 (x), expressed by Eq. 8, if $zn_s/z'n_g$ is sufficiently small. Under the condition that satisfies $zn_s/z'n_g\ll1$, the density n_1 (x) may agree with the counter-ion density in a salt-free solution (as can be noted according to Ref. 4). Ultimately, it is found that the counter-ion distribution within the layer and in the vicinity of the layer may agree with that in a salt-free solution not only when n_s is zero, but also when it is small.

Conclusion

The LCD in a layer model system containing a salt is given as a function of three parameters $(T, n_g, \Delta x)$ when $zn_s/z'n_g$ is sufficiently small, even though a layer of polyelectrolytes is immersed in a simple salt solution. Thus, in spite of the permeance of the layer to counter ions, it has been determined that the LCD in this system may be quite insensitive to n_s, though the system satisfies $zn_s/z'n_g\ll1$. It may be inferred that the independence of the polyion-charge density from the concentration of a salt is attributable to the much higher density of charged groups than the concentratin of the salt. In addition, under the condition that the existance of co-ions in the layer can not be ignored (i.e., $zn_s/z'n_g$ is not small) the LCD in the layer model system may depend on four parameters $(T, n_g, n_s, \Delta x)$.

The independence of the LCD from n_s in the layer model system is attributable to the insensitivity of counter-ion distribution to n_s. When $zn_s/z'n_g$ is small, the counter-ion distribution in the vicinity of the layer may become quite insensitive to n_s. This result indicates an insensitivity similar to that found from the behavior of the counter-ion distribution in the vicinity of the charged surfaces of the plates, of the cylinders, and of the spheres which hold a constant surface-charge density. Moreover, it has been found that a counter-ion distribution which shows a behavior independent of n_s may agree with the counter-ion distribution in a salt-free solution. If a polyelectrolyte molecule satisfies $zn_s/z'n_g\ll1$, it is inferred that the cunter-ion distribution in the vicinity of its polyion may be identified with that in a salt-free solution, although n_s is not zero.

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