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A Consideration of the Charge Density of Polyelectrolytes Based on a Layer Model in Solution

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In a model system where layers formed by aggregations of polyelectrolyte molecules are mutually parallel in a solvent, the surface-charge density of the layers is estimated by solving the one-dimensional Poisson-Boltzmann equation. The surface-charge density at a over temperature, T, can be determined depending on the number, n_g, of charged groups per unit of the volume in a layer of polyelectrolytes and on the thickness, Δx, of the layer, if the distance between layers of polyelectrolyts is sufficiently large. This surface-charge density is evaluated by assuming that n_g is given by the reciprocal of the cubed mean length between neighboring charged groups in a polyelectrolyte molecule and that Δx is of the order of an ion diameter, possibly including the hydration sheath. The surface-charge density given by the layer model agrees well with that semiempirically given by a rod-like polyelectrolyte model. Also, the ratio of the total charge of a layer to the total charge of the charged groups in the layer agrees well with the degree of the ionic dissociation of ionene polymers in a salt-free solution.

Polyelectrolytes in aqueous solutions form a strong electric field which attracts counter ions, because the molecules of the polyelectrolytes have ionizable groups with high densities. Because of the strong electric field, counter ions may condense in the charged macromolecules, and counter ions condensed in polyions may affect the charge density of the polyions. In order to interpret some properties of polyelectrolyte solutions as exhibited in the phenomenon of osmotic pressure, it is important to know the charge density of polyions. The phenomenon of the condensation of counter ions due to polyions is well-known,[1] although the charge density of polyions after the condensation of counter ions has not yet been obtained obviously on a priori grounds. Lately, Manning deduced that the condensation of counter ions on polyions composed of wormlike chains depended on the charge (of charged groups) per unit of length in a chain of polyelectrolytes.[2] If the solution of the Poisson-Boltzmann equation can be obtained in a system consisting of not freely mobile charges and freely mobile ions, the charge density of the polyion should be given. Manning noted that the statistical-mechanical phase integral for an infinite line-charge model diverges for all values of a uniform linear-charge density greater than the critical value, and he was able to estimate the condensation of counter ions on a polyion,[2] although he did not solve the Poisson-Boltzmann equation.

The purpose of the investigation in this paper is to determine the polyion-charge density by solving the Poisson-Boltzmann equation. Although the Poisson-Boltzmann equation is not readily solved, an analytically rigorous solution of the one-dimensional Poisson-Boltzmann equation for two parallel charged plates in a solution containing only counter ions has been given by Engström and Wennerström.[3]

The polyelectrolyte solution model treated in this investigation is a system in which the layers formed by aggregations of polyelectrolyte molecules are immersed in a solvent and in which the layers are parallel to each other. The charge density of the polyions in this investigation is taken as the surface-charge density on these layers; this surface-charge density is obtained by using an analytically rigorous solution given by Engström and Wennerström. The magnitute of the surface-charge density in this paper is determined from the electrostatic interaction between a polyion and counter ions. Knowledge with respect to its magnitude determined by means of the contribution of the electrostatic interaction would be useful in ascertaining the dominant factor which determines polyion-charge density. Thus, it would be valuable to estimate the surface-charge density attributable to the electrostatic contribution, although the surface-charge density in the rod-like polyelectrolyte model of Lifson and Katchalsky[4] can be estimated by using an experimentally given osmotic coefficient.

The density, n_g, of charged groups of polyelectrolytes taken into the model used in this paper is the number of charged groups per unit of volume in an aggregation of polyelectrolytes. A net-like polyelectrolyte, an ion-permeable membrane (which contains ionizable groups in its structure), etc. can be regarded as aggregations of the chains of polyelectrolytes. Therefore, their surface-charge density in water may be readily estimated if the surface-charge density of an aggregation of polyelectrolytes can be determined as a function of n_g. In addition, the thickness of a layer formed by the aggregation of polyelectrolytes must be determined in order to estimate the surface-charge density. It is considered, becuase of the size of the charged groups, that this layer thickness should have a minimum value which is not zero. The surface-charge density of a layer is estimated by assuming the minimum thickness of a layer and a sufficiently large distance between layers. As a result, it is found that the ratio of this surface-charge density to the charges attributed to charged groups in the layer is comparable with the degree of the ionic dissociation of ionene polymers.[5)]

Model

Structure of a Layer Model. A model which represents polyelectrolyte solutions as charged plates immersed in a simple salt solution has been used in order to describe the properties of polyelectrolyte solutions.[6)] In this investigation, instead of the charged plates, layers consisting of polyelectrolytes are placed in a solvent, and layers of a salt-free solution interleave the layers of polyelectrolytes, as is shown in Fig. 1. This polyelectrolyte-solution model of the layer structure may be described as follows:

1) A model system is comprised of many layers consisting of layers of polyelectrolytes and layers of the solution, and these layers are parallel to each other.

2) The distances between the layers of polyelectrolytes equal $2a$.

3) All the layers of polyelectrolytes are Δx thick.

4) The number of charged groups per unit of volume in all layers of polyelectrolytes is n_g.

Electrostatic Potential. The electrostatic potential, ψ, in this layer model is described by the one-dimensional Poisson-Boltzmann equation. In accordance with the assumption of a salt-free solution, the Poisson-Boltzmann equation (SI units) within the layer of polyelectrolyte (Region 1 : $0 \leqq x \leqq \Delta x/2$) is:

$$\frac{d^2\psi_1}{dx^2} = -\frac{1}{\varepsilon}\cdot\{-z'e\,n_g + zen_0 \exp[-ze\psi_1/kT]\}, \quad (1)$$

while outside the layer of polyelectrolytes (Region 2: $\Delta x/2 \leqq x \leqq 2a+\Delta x/2$) it is:

$$\frac{d^2\psi_2}{dx^2} = -\frac{z\,en_0}{\varepsilon}\cdot \exp[-ze\psi_2/kT], \quad (2)$$

where ze is the charge of a counter ion, $-z'e$ is the charge of a charged group, n_0 is a normalization constant, ε is the dielectric constant of the pure solvent, k is Boltzmann's constant, and T is the absolute temperature. In addition, it has been assumed that the dielectric constant within a layer of polyelectrolytes is the same as that outside.

The boundary conditions for Eq. 2 are:

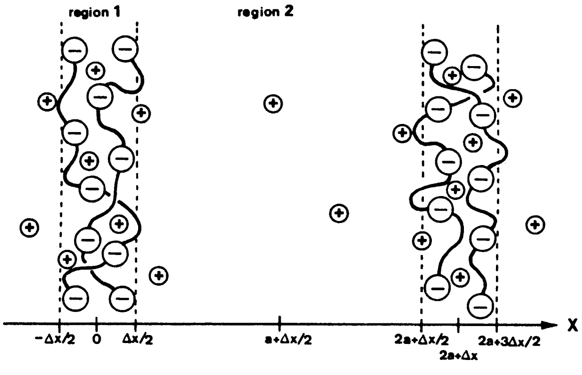

Fig. 1. Layer model of polyelectrolyte solution. Charged groups and counter ions are represented by (−) and (+) respectively.

$$\psi_2(a+\Delta x/2) = 0\,, \quad -\left.\frac{d\psi_2}{dx}\right|_{x=a+\Delta x/2} = 0\,,$$

and:

$$-\left.\frac{d\psi_2}{dx}\right|_{x=\Delta x/2} = \left.\frac{d\psi_2}{dx}\right|_{x=2a+\Delta x/2} = -\frac{\sigma}{\varepsilon}\,, \quad (3)$$

where $-\sigma$ is the surface-charge density on a polyelectrolyte layer.

A rigorous solution for Eq. 2 can be obtained analytically by integrating Eq. 2 twice in a manner similar to that in which a rigorous solution for two parallel charged plates was given by Engström and Wennerström.[3)] As a result, the electrostatic potential in the Region 2 ($\Delta x/2 \leqq x \leqq a+\Delta x/2$) is given as follows:

$$\psi_2 = \frac{2kT}{ze}\cdot \ln\{\cos\frac{s}{a}\cdot((a+\frac{\Delta x}{2}) - x)\}\,, \quad (4)$$

where $s \equiv a\cdot\left(\frac{n_0 z^2 e^2}{2kT\varepsilon}\right)^{1/2}$

On the basis of Eq. 3 and the first derivative of Eq. 4, the dimensionless parameter s can also be represented as:

$$s \tan s = \frac{\sigma z e a}{2kT\varepsilon}\,, \quad (5)$$

and for a sufficiently large value of the right side of Eq. 5, s approaches $\pi/2$; then the above formula becomes:

$$\tan s = \frac{\sigma z e a}{\pi k T \varepsilon}\,. \quad (6)$$

On the other hand, it is difficult to solve Eq. 1 analytically and rigorously. On the basis of a perturbation method used by Lifson in order to obtain an approximate analytical solution for the electrostatic potential of spherical polyelectrolytes,[7)] an approximate solution of Eq. 1 can, however, be obtained.

A first approximation, v, to ψ_1 in this perturbation method means that the total charge density is zero everywhere; v must satisfy:

$$\frac{d^2 v}{dx^2} = 0\,, \quad (7)$$

Moreover, in order to satisfy Eq. 1 v should be:

$$v = -\frac{kT}{ze}\ln f\,, \quad (8)$$

where:

$$f \equiv \frac{z'n_g}{zn_0}\,.$$

A correction function, w, for v is defined as satisfying the following equation:

$$\psi_1 = v + w. \quad (9)$$

If Taylor's expansion is carried out as follows:

$$\exp[-\frac{ze\,\psi_1}{kT}] = \exp[-\frac{ze}{kT}v] - \frac{ze}{kT}\cdot \exp[-\frac{ze}{kT}v]\cdot w + \cdots\,,$$

when Eq. 9 is substituted into Eq. 1, by considering Eqs. 7 and 8 the following differential equation for w is obtained:

$$\frac{d^2 w}{dx^2} = \mu^2 w, \tag{10}$$

where $\mu^2 \equiv zz'e^2 n_g/\varepsilon kT$. An approximation of w is given by solving Eq. 10.

The continuity of the electrostatic potential at $x=\Delta x/2$ and the continuity of the electrostatic field at $x=\Delta x/2$ require the following conditions, based on Eqs. 3 and 4:

$$\psi_1\left(\frac{\Delta x}{2}\right) = \frac{kT}{ze} \cdot \ln(\cos^2 s) \tag{11}$$

$$-\left.\frac{d\psi_1}{dx}\right|_{x=\Delta x/2} = -\frac{\sigma}{\varepsilon}.$$

The electrostatic potential, ψ_1, which is obtained by substituting the solution of w from Eq. 10 into Eq. 9 and which satisfies the above conditions, is given as follows:

$$\psi_1 = -\frac{kT}{ze} \cdot \ln f + \frac{kT}{ze} \cdot \left\{\frac{1}{2}(\ln(\cos^2 s) + \ln f) + \frac{\Lambda\sigma}{\sqrt{2}}\right\} \cdot \exp\left[-\mu\left(\frac{\Delta x}{2} - x\right)\right] + \frac{kT}{ze} \cdot \left\{\frac{1}{2}(\ln(\cos^2 s) + \ln f) - \frac{\Lambda\sigma}{\sqrt{2}}\right\} \cdot \exp\left[\mu\left(\frac{\Delta x}{2} - x\right)\right], \tag{12}$$

where $\Lambda^2 \equiv z/(2z'kT\varepsilon n_g)$.

Surface-Charge Density. The demand of electrostatic field continuity in Region 1 ($-\Delta x/2 < x < \Delta x/2$) imposes a restriction on the exponential coefficients in Eq. 12. The demand is:

$$-\left.\frac{d\psi_1}{dx}\right|_{x=0} = 0, \tag{13}$$

because the sign of the electrostatic field at $x>0$ differs from that at $x<0$ in the region close to $x=0$ if the distribution of counter ions on the right side of a layer equals that on the left side of the layer. Equation 13 requires that the exponential coefficients in Eq. 12 satisfy the following equation:

$$\ln f = \sqrt{2}\Lambda\sigma \cdot \{\tanh[\mu\Delta x/2]\}^{-1} - \ln\cos^2 s. \tag{14}$$

The continuity of counter-ion distribution in all regions of the system leads to a formula independent of Eq. 14 on the basis of the electrostatic potential at $x=\Delta x/2$, the second derivative of the potential, and the definition of f. By considering Eq. 11, the density of counter ions $n(x)$ at $x=\Delta x/2$ is:

$$n(\Delta x/2) = n_0 \cdot \exp\left[-\frac{ze\psi_1(\Delta x/2)}{kT}\right] = \frac{n_0}{\cos^2 s}. \tag{15}$$

On the other hand, by considering Eq. 5, the second derivative of $\psi_2(x)$ given by Eq. 4 yields:

$$n(\Delta x/2) = \frac{\sigma^2}{2kT\varepsilon} + \frac{2kT\varepsilon s^2}{(zea)^2}. \tag{16}$$

If the magnitude of a is of the order of 10^2 Å and the magnitude σ is of the order of 10^{-2} C·m^{-2}, even though the magnitude of s is the maximum $\pi/2$, the second term on the right side of Eq. 16 is much smaller than the first term. Hence, under the condition that the second term can be neglected, the following equation is obtained:

$$n(\Delta x/2) = \frac{\sigma^2}{2kT\varepsilon}. \tag{17}$$

By substituting Eq. 17 into Eq. 15, the following formula is obtained:

$$n_0 = \frac{\sigma^2}{2kT\varepsilon} \cdot \cos^2 s. \tag{18}$$

When, Eq. 18 is substituted into the definition of f,

$$\ln f = -2\ln\Lambda\sigma - \ln\cos^2 s. \tag{19}$$

By equating Eq. 14 with Eq. 19, we obtain the following formula for the surface-charge density of the layer of polyelectrolytes:

$$\frac{\Lambda\sigma}{\ln\Lambda\sigma} = -\sqrt{2}\tanh[\mu\Delta x/2]. \tag{20}$$

In addition, in accordance with the sign on the right side of Eq. 20 and its magnitude, the magnitude of $\Lambda\sigma$ is close to 1 and must satisfy $\Lambda\sigma<1$. Therefore, $\ln\Lambda\sigma$ may be represented approximately as follows:

$$\ln\Lambda\sigma = -2(1 - \sqrt{\Lambda\sigma}).$$

On the basis of this approximation and Eq. 20, the surface-charge density can be described as:

$$-\sigma = -\frac{Y}{2\Lambda}\{(Y+2) - \sqrt{(Y+4)Y}\}, \tag{21}$$

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

Parameters in $-\sigma$. Both the surface-charge density, $-\sigma$, given by Eq. 20 and that given approximately by Eq. 21 depend on only three parameters: n_g, Δx, and T, when Eq. 17 is satisfied. f depends on four parameters: n_g, Δx, a, and T, as may be seen in both Eq. 14 and Eq. 19 because s depends on four parameters: n_g, Δx, a, and T, as may be seen in Eq. 5. Hence, the electrostatic potential, the electrostatic field, and the density of counter ions at a certain position x depend on four parameters: n_g, Δx, a, and T.

In order to estimate $-\sigma$, the n_g and Δx parameters must be determined. It is considered that the density n_g must be equivalent to the density of charged groups in a polyion dispersed in a solution, if we are to describe the charged circumstance of the polyion according to the layer model, and it is assumed that, while the distance, b, between neighboring charged groups in a polyion dispersed in a salt-free solution is held constant, charged groups in polyelectrolyte molecules are packed in a layer of polyelectrolytes. Thus, n_g is given as follows:

$$n_g = 1/b^3. \tag{22}$$

The density n_g given by Eq. 22 is regarded as the density approximately equivalent to the density of charged groups in a polyion. In addition, Fujii has found[5)] that the distance between neighboring charged groups (obtained by substituting the degree of ionic dissociation, ξ^{-1}, of polyions found experimentally in a sufficiently dilute salt-free solution of ionene polymers into the formula given by Manning: $\xi^{-1}=(e^2/\varepsilon kTb)^{-1}$ (CGS-esu)) is approximately equal to the mean distance between neighboring charged groups in the polyion chain, which is regarded as a freely rotating methylene chain. Therefore, the density n_g, obtained on the basis of Eq. 22 by assuming that the distance, b, between neighboring charged groups in a flexible polyelectrolyte can be taken as the mean distance between neighboring ionizable groups in a freely rotating methylene chain, is used to calculate $-\sigma$ when a polyelectrolyte solution described by the layer model is a sufficiently dilute salt-free solution.

The thickness, Δx, of a layer is another parameter affecting $-\sigma$ and must be determined in order to calculate $-\sigma$. This thickness, Δx, should have a minimum which is not zero because of the size of the charged groups. The most dilute condition in the layer model system corresponds to the condition that Δx is at its minimum and the distance between layers is infinite. Therefore, it is considered that $-\sigma$, compared with the charge density of a polyion in a sufficiently dilute salt-free solution, should be calculated under the condition that Δx is at its minimum; in order to calculate this surface-charge density, $-\sigma$, it is assumed that Δx is at its minimum and that Δx is of the order of an ion diameter, possibly including the hydration sheath, when the polyelectrolyte is flexible.

Results and Discussion

Surface-Charge Density. The electrostatic potential, the electrostatic field, and the density of counter ions in the layer model treated here depend on these parameters: n_g, Δx, a, and T.

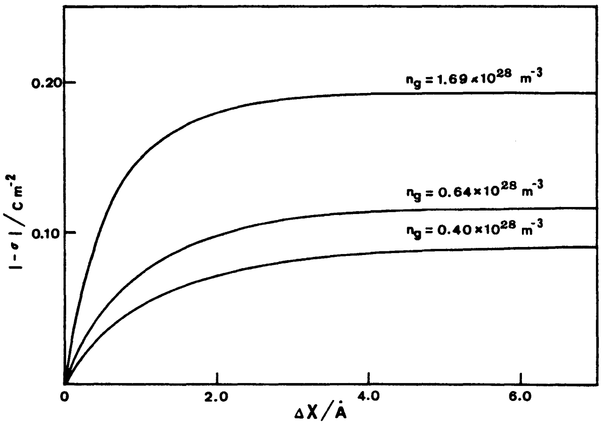

Fig. 2. The dependence of $-\sigma$ on Δx at 298 K on the basis of Eq. 21. The physical meaning of $-\sigma$ is incomplete at the magnitude of Δx which is smaller than a minimum thickness.

The surface-charge density $-\sigma$ depends on these parameters: n_g, Δx, and T, when the magnitude of a is larger than the order of 10^2 Å. Moreover, when the magnitude of Δx is larger than several angstroms, the $-\sigma$ value given by Eq. 21 becomes independent of, Δx, as is shown in Fig. 2. This independence from Δx is hardly affected by the magnitute of n_g, and it is interesting that the magnitude of Δx at which the independence begins to appear nearly equals the order of an ion diameter, possibly including the hydration sheath. The behavior of $-\sigma$, which become independent of Δx, suggests that, although several polyelectrolytes are associated with one another, the charge density of polyions may be invariable in a sufficiently dilute solution.

Electrostatic Potential. The dependence of the electrostatic potential on a may be seen from the following formulae, which are obtained from Eq. 4 and Eq. 12 by considering Eqs. 6 and 19, when a is sufficiently large: at $0\leqq x<\Delta x/2$ (in a layer of polyelectrolytes):

$$\psi_1(x) = -\frac{2kT}{ze}\cdot\ln\left(\frac{\sqrt{2}}{\pi}\mu a\right) - \frac{kT}{ze}\cdot\left\{\left(\frac{\Lambda\sigma}{\sqrt{2}}+\ln\Lambda\sigma\right)\cdot\exp\left[\mu\left(\frac{\Delta x}{2}-x\right)\right] - \left(\frac{\Lambda\sigma}{\sqrt{2}}-\ln\Lambda\sigma\right)\cdot\exp\left[-\mu\left(\frac{\Delta x}{2}-x\right)\right]\right\} \quad (23)$$

and at $\Delta x/2\leqq x$ (in the vicinity of the layer surface where $\{\pi(x-\Delta x/2)/2a\}^2\ll 1$ is satisfied):

$$\psi_2(x) = -\frac{2kT}{ze}\cdot\ln\left(\frac{\sqrt{2}}{\pi}\Lambda\sigma\mu a\right) + \frac{2kT}{ze}\cdot \ln\left\{1+\frac{1}{\sqrt{2}}\Lambda\sigma\mu\left(x-\frac{\Delta x}{2}\right)\right\}. \quad (24)$$

The increase in the absolute value of the potential in accordance with the increase in a, as noted by Engströn and Wennerström,[3)] is shown in Eqs. 23 and 24. Equations 23 and 24, however, indicate that the difference in potential $\psi(x_1)-\psi(x_2)$ between the x_1 and x_2 positions which satisfies $\{\pi(x-\Delta x/2)/2a\}^2\ll 1$ is independent of a.

Electric Field. As is suggested by the property of the potential mentioned above, when a is sufficiently large the electrostatic field $-\varepsilon\mathrm{d}\psi/\mathrm{d}x$ at a position which satisfies $\{\pi(x-\Delta x/2)/2a\}^2\ll 1$ is independent of a, as is shown in the following formulae:
at $0\leqq x<\Delta x/2$ (in a layer of polyelectrolytes):

$$-\varepsilon\cdot\frac{\mathrm{d}\psi_1}{\mathrm{d}x} = \frac{-1}{\sqrt{2}\Lambda}\cdot\left\{\frac{\Lambda\sigma}{\sqrt{2}}+\ln\Lambda\sigma\right\}\cdot\exp\left[\mu\left(\frac{\Delta x}{2}-x\right)\right] - \frac{1}{\sqrt{2}\Lambda}\cdot\left\{\frac{\Lambda\sigma}{\sqrt{2}}-\ln\Lambda\sigma\right\}\cdot\exp\left[-\mu\left(\frac{\Delta x}{2}-x\right)\right], \quad (25)$$

and at $\Delta x/2\leqq x$ (where $\{\pi(x-\Delta x/2)/2a\}^2\ll 1$ is satisfied):

$$-\varepsilon\cdot\frac{\mathrm{d}\psi_2}{\mathrm{d}x} = -\sigma\cdot\left\{1+\frac{1}{\sqrt{2}}\cdot\Lambda\sigma\mu\left(x-\frac{\Delta x}{2}\right)\right\}^{-1}. \quad (26)$$

The property of this electrostatic field suggests that the number of counter ions which are distributed within a closed surface covering a polyion and close to the polyion itself is independent of the concentration of polyelectrolytes in a sufficiently dilute salt-free solution.

Density of Counter Ions. As is suggested by the property of the electrostatic field mentioned above, when a is sufficiently large the density of counter ions $n(x)$ at a position which satisfies $\{\pi(x-\Delta x/2)/2a\}^2 \ll 1$ is independent of a, and $n(x)$ is given by the following formulae: at $0 \leqq x < \Delta x/2$ (in a layer of polyelectrolytes):

$$n(x) = \frac{z'}{z} \cdot n_g \cdot \exp[\{\frac{\Lambda\sigma}{\sqrt{2}} + \ln \Lambda\sigma\} \cdot \exp[\mu(\frac{\Delta x}{2} - x)] - \{\frac{\Lambda\sigma}{\sqrt{2}} - \ln \Lambda\sigma\} \cdot \exp[-\mu(\frac{\Delta x}{2} - x)]], \quad (27)$$

and at $\Delta x/2 \leqq x$ (where $\{\pi(x-\Delta x/2)/2a\}^2 \ll 1$ is satisfied):

$$n(x) = \frac{1}{\sqrt{2}} \cdot \Lambda\sigma\mu \cdot (\frac{\sigma}{e}) \cdot \{1 + \frac{1}{\sqrt{2}} \cdot \Lambda\sigma\mu \cdot (x - \frac{\Delta x}{2})\}^{-2}. \quad (28)$$

Equation 27 is given by substituting Eq. 23 into $n_0 \cdot \exp[-ze\psi/kT]$ and by considering Eqs. 6 and 18. Similarly, Eq. 28 is obtained by substituting Eq. 24 into $n_0 \cdot \exp[-ze\psi/kT]$. The property of $n(x)$ mentioned here suggests that the density of counter ions close to a polyion is independent of the concentration of polyelectrolytes in a sufficiently dilute salt-free solution.

Evaluation of $-\sigma$. The surface-charge density $-\sigma$ and the $\sigma/(en_g\Delta x/2)$ ratio, calculated under the conditions that Δx is the minimum thickness and a is sufficiently large, agree well with the polyion-charge density[8)] (given by the rod-like model of a polyelectrolyte) and the degree of ionic dissociation[5)] of a polyelectrolyte (found experimentally in a sufficiently dilute salt-free solution) respectively, as may be seen in Tables 1 and 2. These results suggest that the layer model is a good approximate description of a polyelectrolyte solution. Also, the charged-groups packing density n_g assumed in the Model and the determination of Δx mentioned in the Model both seem reasonable when a sufficiently dilute salt-free solution of flexible polyelectrolytes is described according to the layer model. As a result, although the layer model is a one-dimensional model system, it seem that this model can lead to a quantitative description of the charged circumstance of a polyion.

Table 1. $-\sigma_{rod}$ and $-\sigma$ for Polyacrylate at 298 K

$\alpha^{a)}$	r / Å	$\lambda_{effectve}$	$-\sigma_{rod}{}^{c)}$ / $C \cdot m^{-2}$	$-\sigma^{d)}$ / $C \cdot m^{-2}$
0.8	6	4	−0.24	−0.17
0.3	6	2.4	−0.14	−0.10
0.1	6	1.25	−0.07	−0.05
1	6	3.0[b)]	−0.18	−0.19

a) Degree of ionization b) $\lambda_{effective}$ for the vinylic polyelectrolytes at sufficiently high degrees of ionization is found to be about twice the magnitude calculated for the wholly stretched chain.[8)] This value of λ is represented as:

$$\lambda_{stretched} = \alpha e^2/\varepsilon k\,Tl\,(\text{CGS-esu}),$$

where l is the distance between neighboring charged groups. For polyacrylate, $l \fallingdotseq 4.9$ Å and so $\lambda_{stretched}=1.5$. c) Values reduced to SI units d) Values calculated by means of Eq. 21 (the mean distance between neighboring -COOH's in the polyacrylate molectule is taken as 3.9 Å and considering the degree of ionization: $n_g=\alpha/(3.9)^3/\text{Å}^{-3}$.)

Table 2. The Degree of the Ionic Dissociation[5)] of Ionene Bromide and the Change Density on a Layer of This Polyelectrolyte at 298 K

Polyelectrolyte	$b^{a)}$ / Å	$\xi^{-1\,b)}$	$\sigma^{c)}$ / $C \cdot m^{-2}$	σ / $en_g\Delta x/2$
3.3-ionene bromide	3.9	0.576	0.189	0.47
4.4-ionene bromide	4.5	0.628	0.149	0.56
6.6-ionene bromide	5.4	0.745	0.109	0.71
8.8-ionene bromide	6.3	0.876	0.081	0.84

a) The mean distance between neighboring ionizable groups in a freely rotating methylene chain. b) The measured degree of ionic dissociation.[5)] c) The values given by Eq. 21.

The values of $-\sigma$ and σ shown in Tables 1 and 2 were calculated by determining n_g from Eq. 22 and by using Eq. 21, at 298 K. It is assumed that the minimum thickness of a layer of polyelectrolytes is 3 Å,[3)] regarded as the order of an ion diameter, possibly including its hydration sheath. $-\sigma_{rod}$ in Table 1 is the surface-charge density given by the rod-like model of a polyelectrolyte. $-\sigma_{rod}$ is obtained by using the dimensionless parameter λ[8)] in CGS-esu as follows:

$$-\sigma_{rod} = -(\varepsilon kT/2\pi re) \cdot \lambda,$$

where r is the radius of the rod-like model. λ may be calculated[4)] on the basis of the osmotic coefficient of a salt-free polyelectrolyte solution. The λ calculated as described here is $\lambda_{effective}$[8)] in Table 1. The $\sigma/(en_g\Delta x/2)$ ratio, shown in Table 2, represents the charged rate of a layer of polyelectrolytes, because σ is the total charge within a cylinder of unit cross section; it ends at $x=0$ and $x=\Delta x/2$ and is parallel to the x-axis.

In the layer model, counter ions permeate into a layer of polyelectrolytes. Consequently, the condensation of counter ions implies that counter ions are condensed between charged groups. The counter ions located between charged groups contribute to the relaxation of the positive electrostatic energy and to the relaxation of tension induced in a methylene chain by the repulsion between charged groups. If it is noted that the $\sigma/(en_g\Delta x/2)$ ratio agrees well with the degree of dissociation ξ^{-1} given experimentally, it may be considered that the counter ions mentioned above are located between the charged groups, even though a polyelectrolyte solution is a sufficiently dilute salt-free solution.

Conclusion

The layer model of a polyelectrolyte solution treated here has a structure in which layers of polyelectrolytes are arranged in a parallel manner in a solvent. The electrostatic potential, the electrostatic field, and the density of counter ions within and outside the layers are determined on the basis of solutions of the one-dimensional Poisson-Botzmann equation; they depend on the thickness, Δx, of the layers; the distance, $2a$, between the layers; the density, n_g, of charged groups in the layers; and the absolute temperature T. When a is sufficiently large, the electrostatic field and the density of counter ions within a layer of polyelectrolytes become independent of a. Outside the layer also, the electrostatic field and the density of counter ions become independent of a at positions which satisfy $\{\pi(x-\Delta x/2)/2a\}^2 \ll 1$. These results suggest not only that the charge density of a polyion is independent of the concentration of polyelectrolytes in a sufficiently dilute salt-free solution, but also that the distribution of counter ions close to a polyion is independent of thier concentration.

The surface-charge density $-\sigma$ on a layer of polyelectrolytes in the layer model depends only on Δx, n_g, and T, as determined from the properties of the electrostatic field when a is sufficiently large. The surface-charge density $-\sigma$ given by Eq. 21 for polyacrylate when a is sufficiently large is comparable to the $-\sigma_{\text{rod}}$ value semiempirically givien by the rod-like model of polyelectrolytes. Also, the charged rate, $\sigma/(en_g\Delta x/2)$, of layers of polyelectrolytes calculated by using the σ value given by Eq. 21 agrees with degree of dissociation of counter ions in salt-free solutions of ionene bromides at an infinite dilution. In addition, it has been assumed that the methylene chain of polyelectrolyte rotates freely and that n_g is given by the reciprocal of the cubed mean length between neighboring ionizable groups in the chain in calculating $-\sigma$ and $\sigma/(en_g\Delta x/2)$; also, it has been assumed that Δx is of the order of an ion diameter, possibly including the hydration sheath.

The surface-charge density $-\sigma$ comparable to $-\sigma_{\text{rod}}$ and the $\sigma/(en_g\Delta x/2)$ ratio comparable to the degree of the ionic dissociation of the ionene polymer suggest that, although the layer model is one-dimensional, the charged circumstance of a polyion may be quantitatively described according to the layer model. Therefore, it may be concluded that the layer model can lead to a quantitative estimation of the charged circumstance of a polyion, while $-\sigma$ in the layer model can be determined from Δx, n_g, and T when the solution of polyelectrolytes is salt-free and is sufficiently dilute.

Appendix

The mean distance, $(\overline{d^2})^{1/2}$, between the neighboring ionizable groups in a freely rotating methylene chain is given by the following formula:

$$\overline{d^2} = n\,l^2 \cdot \left\{\frac{1-\cos\theta}{1+\cos\theta} + \frac{2-\cos\theta}{n} \cdot \frac{1-(-\cos\theta)^n}{(1+\cos\theta)^2}\right\},$$

where n is the number of bonds between neighboring ionizable groups, l is the bond length, and θ is the bond angle. $\overline{d^2}$ is calculated by assuming that both C–C and C–N bond lengths are 1.5 Å, while both C–C–C and C–C–N bond angles are 109.5°.

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