Macromolecules **1980**, *13*, 1549–1553 **1549**

Potentiometric Titration of Copolymers of Maleic Acid. 1. A Simple Theory

Akira Minakata* and Kazuko Matsumura

Department of Physics, Hamamatsu University School of Medicine, Hamamatsu 431-31, Japan

Shigeo Sasaki

Department of Physics, Faculty of Science, Nagoya University, Nagoya 464, Japan

Hiroshi Ohnuma

Department of Polymer Science, College of Science, Osaka University, Toyonaka 560, Japan. *Received February 13, 1980*

ABSTRACT: An expression is derived to analyze the potentiometric titration behavior of alternating copolymers of maleic acid. Copolymers are represented by a linear lattice having shorter and longer intervals between ionizable groups. Electrostatic interactions between ionizable groups are divided into two types. The nearest- and second-neighbor interactions corresponding to the shorter and longer intervals are directly incorporated into the partition function which determines the activities of un-ionized and ionized groups, similar to Lifson's theory. The remaining interactions as well as the shielding effect due to small ions are expressed by a potential term. Then the above two terms are combined to obtain the final expression of the titration, i.e., pK_{app} vs. degree of ionization, α. The expression predicts the overall titration profile: that is, with increasing ionization, pK_{app} increases gradually, jumps at about $\alpha = 0.5$, and again increases gradually. The calculated curve agrees roughly with the experimental curve of poly(maleic acid-*co*-ethyl vinyl ether). Comparison with other theories is made.

Introduction

Analysis of the potentiometric titration of linear polyelectrolytes in terms of a smeared-charge model has been carried out by Kotin and Nagasawa[1] by numerical integration of the Poisson–Boltzmann equation. This method, however, cannot be applied directly to the copolymers of maleic acid because of strong local electrostatic interaction between the two carboxyl groups of maleic acid. Local interaction has usually been treated as the nearest-neighbor interaction in a linear lattice system. For example, Lifson[2] derived an expression of the potentiometric titration of a polyacid in terms of the nearest-neighbor interaction between ionized sites. In his equation, long-range interaction was expressed by adding a potential term. However, he did not give explicit expressions for this term, leading to ambiguity in estimating the contribution of the potential term.

Schultz and Strauss[3] have used a modification of Lifson's theory for potentiometric titration of a poly(diprotic acid). They assumed two intrinsic dissociation constants $K_1{}^0$ and $K_2{}^0$ empirically and analyzed first and second dissociation steps separately. However, existence of the two dissociation constants is a result of the nearest-neighbor interaction if a polyelectrolyte molecule has a single species of ionizable groups. Therefore it is desirable to analyze the whole titration profile in terms of the neighbor interaction.

In this paper, an alternative equation is derived to describe the potentiometric titration of a linear poly(diprotic acid). Two types of neighbor interactions are introduced in the theory; one is the nearest-neighbor interaction between two carboxyl groups in the same monomer unit, and the other the second-neighbor interaction between two adjacent groups in two successive diprotic acid groups. Long-range interaction expressed by a potential term in Lifson's theory[2] is defined as the remaining electrostatic interactions. The result is applied to the copolymer of maleic acid and ethyl vinyl ether.

Potentiometric Titration Equation

According to Lifson,[2] the pH of a solution of a polyacid is expressed as

$$\mathrm{pH} = \mathrm{p}K_0 + \log a - 0.4343e\psi/kT \qquad (1)$$

with

$$\mathrm{p}K_0 = 0.4343(\mu_{\mathrm{H}}{}^\circ + \mu_-{}^\circ - \mu_0{}^\circ)/kT$$
$$a = a_-/a_0 \qquad (2)$$

where $\mu_{\mathrm{H}}{}^\circ$, $\mu_-{}^\circ$, and $\mu_0{}^\circ$ are the standard chemical potentials of a hydrogen ion, an ionized group, and an un-ionized group of the polyacid, a_- and a_0 are the activities of the ionized and un-ionized groups, respectively, and ψ is the electrostatic potential of the polyacid due to the long-range electrostatic interaction between H$^+$ ion and other ionized groups on the polyacid. In eq 1, the nearest-neighbor interaction is incorporated into the term log a; otherwise this term can be replaced by the usual expression log $[\alpha/(1 - \alpha)]$, corresponding to random mixing of the ionized and un-ionized groups.

It is convenient to define a partition function of a polyion to calculate the term log a. For a linear equidistant lattice polymer, the form of the partition function has been given by Lifson[2]

$$\Xi = \sum_{\epsilon=0,-} \Big(\prod_{i=1}^{p-1} a_{\epsilon_i} u_{\epsilon_i,\epsilon_{i+1}}\Big) a_{\epsilon_p} \qquad (3)$$

where

$$a_{\epsilon_i} = \exp[(\mu_{\epsilon_i} - \mu_{\epsilon_i}{}^\circ)/kT]$$
$$u_{\epsilon_i,\epsilon_{i+1}} = \exp(-E_{\epsilon_i,\epsilon_{i+1}}/kT) \qquad (4)$$

In eq 3 and 4, the subscript ϵ_i stands for – if the ith site is ionized and for 0 if it is un-ionized, a_{ϵ_i} is the activity of site i, which is either a_- or a_0, and $E_{\epsilon_i,\epsilon_{i+1}}$ is the nearest-neighbor interaction energy between the ith and $(i + 1)$th sites.

In the case of an alternating copolymer of maleic acid, at least two types of neighbor interactions should be considered: one is the true nearest-neighbor interaction between the intramonomeric unit $E_{\epsilon_{2i-1},\epsilon_{2i}}$, and the other the second-nearest-neighbor interaction between adjacent monomeric units $E'_{\epsilon_{2i},\epsilon_{2i+1}}$. In this case, the number of sites

0024-9297/80/2213-1549$01.00/0

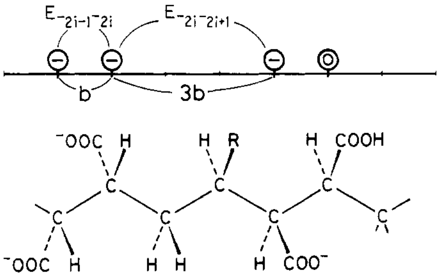

Figure 1. Schematic representation of a linear lattice used as the molecular model of the copolymer of maleic acid. This corresponds to the projection of the all-trans chain to the polymer axis, as drawn below.

is assumed to be $2N$; i.e., $p = 2N$, where N is the degree of polymerization. The assumption of random mixing of the ionized and un-ionized groups is incorrect because the strong nearest-neighbor interaction results in the two-step dissociation process.

Similar to eq 3, the partition function can be written as

$$\Xi = \sum_{\epsilon=0,-} \left(\prod_{i=1}^{N-1} a_{\epsilon_{2i-1}} u_{\epsilon_{2i-1},\epsilon_{2i}} a_{\epsilon_{2i}} u_{\epsilon_{2i},\epsilon_{2i+1}}\right) a_{\epsilon_{2N-1}} u_{\epsilon_{2N-1},\epsilon_{2N}} a_{\epsilon_{2N}} \quad (5)$$

where

$$u_{\epsilon_{2i-1},\epsilon_{2i}} = \exp(-E_{\epsilon_{2i-1},\epsilon_{2i}}/kT)$$
$$u_{\epsilon_{2i},\epsilon_{2i+1}} = \exp(-E'_{\epsilon_{2i},\epsilon_{2i+1}}/kT) \quad (6)$$

are defined in the same way as in eq 4. With the aid of the matrix method, we can rewrite eq 5 as

$$\Xi = (1,1)(\mathrm{MM'})^{N-1}\mathrm{M}\begin{bmatrix} a_- \\ a_0 \end{bmatrix} \quad (7)$$

where

$$\mathrm{M} = \begin{bmatrix} u_{--}a_- & u_{0-}a_- \\ u_{-0}a_0 & u_{00}a_0 \end{bmatrix}$$
$$\mathrm{M'} = \begin{bmatrix} u'_{--}a_- & u'_{0-}a_- \\ u'_{-0}a_0 & u'_{00}a_0 \end{bmatrix} \quad (8)$$

For sufficiently large values of N, the degree of ionization α is approximated as

$$\alpha = \frac{a_-}{2\lambda_1}\frac{\partial\lambda_1}{\partial a_-} \quad (9)$$

where λ_1 is the largest eigenvalue of the matrix **MM′**. Similarly

$$1 - \alpha = \frac{a_0}{2\lambda_1}\frac{\partial\lambda_1}{\partial a_0} \quad (10)$$

Equations 9 and 10 give the relation between α and a as a function of other parameters defined in eq 6. For simplicity, we assume that the polymer chain is extended like a linear lattice with interval b. Namely, the distance between sites $2i$ and $2i + 1$ is assumed to be $3b$, i.e., 3 times the distance between sites $2i - 1$ and $2i$, as represented schematically in Figure 1. Under this condition, the values of the parameters can be estimated as follows:

$$u_{--} = u^3 \qquad u'_{--} = u \qquad u = \exp(-e^2/3bDkT)$$
$$u_{00} = u'_{00} = u_{-0} = u'_{-0} = u_{0-} = u'_{0-} = 1 \quad (11)$$

Then, combining eq 9 and 10, we have

$$x^4 - vx^3 - [v(u + u^{-1}) + 2]x^2 - vx + 1 = 0 \quad (12)$$

where

$$x = u^2 a$$
$$v = u^{-2}(R + R^{-1} - 2) \quad (13)$$
$$R = \alpha/(1 - \alpha)$$

Hence the term log a is given by solving eq 12 with respect to x by assuming a suitable value for u. As special cases, the following simple relations are obtained by eq 12:

$$x \to u^2 R \qquad \text{for } \alpha \to 0$$
$$x = 1 \qquad \text{for } \alpha = 1/2 \quad (14)$$
$$x \to u^{-2} R \qquad \text{for } \alpha \to 1$$

To analyze the titration curve, it is convenient to rewrite eq 1 as

$$\mathrm{pH} - \log R = \mathrm{p}K_0 + \log x - 2\log u - \log R - 0.4343e\psi/kT \quad (15)$$

The left-hand side of eq 15 is the apparent pK value, pK_{app}. The value pK_0 can be determined by extrapolating $\alpha \to 0$, as expressed by eq 14, and the term log x is given by solution of eq 12.

The next process is the calculation of the potential term, $0.4343e\psi/kT$. Ionization of a particular site i on the polyion is a statistical process and is expressed by the probability of ionization $p(i)$ as a function of α. This quantity is also affected by the distribution of ionized sites on the polyion. Namely, the dissociation of site i is affected by the neighboring ionized sites. This effect is described in terms of the mutual dissociation probability of two separate sites i and j, $p(i, j)$. Therefore, contribution of the dissociation of site j to the potential at the position of site i is given by

$$\psi_{ij} = -\frac{e}{D}\frac{\exp(-\kappa r_{ij})}{r_{ij}}\frac{p(i, j)}{p(i)} \quad (16)$$

where D is the dielectric constant of the medium, κ the Debye–Hückel parameter, and r_{ij} the distance between site i and site j. Here, the Debye–Hückel approximation is used. Then the average potential ψ is written as

$$\psi = \sum_{j \neq i, i\pm1} \psi_{ij} \quad (17)$$

According to the assumption that the distance between sites $2i$ and $2i + 1$ is 3 times the distance between sites $2i - 1$ and $2i$, eq 17 is expressed as

$$\psi = -2\sum_{j=1}^{\infty}\frac{e}{D}\frac{\exp(-4j\kappa b)}{4jb}\frac{p(2i, 2i + 2j)}{p(2i)} - \sum_{j=1}^{\infty}\frac{e}{D}\frac{\exp[-(4j + 1)\kappa b]}{(4j + 1)b}\frac{p(2i, 2i - 2j - 1)}{p(2i)} - \sum_{j=1}^{\infty}\frac{e}{D}\frac{\exp[-(4j + 3)\kappa b]}{(4j + 3)b}\frac{p(2i, 2i + 2j + 1)}{p(2i)} \quad (18)$$

where the summation can be extended to infinity for sufficiently large N. As already mentioned, the nearest- and second-neighbor interactions are taken into account explicitly in calculating the term log a, so that their contribution to the potential is eliminated in eq 17 and 18.

From the partition function, eq 7, the mutual dissociation probabilities are derived according to the ordinary method of the statistical mechanics, as follows:

$$p(2i, 2i + 2j) = \alpha\left[\alpha + \left(\frac{\lambda_2}{\lambda_1}\right)^j(1 - \alpha)\right] \quad (19\text{-}1)$$

$$p(2i, 2i - 2j - 1) = \alpha\left[\alpha + \frac{1}{\lambda_1}\left(\frac{\lambda_2}{\lambda_1}\right)^j (1 - \alpha)F(\lambda_1)\right] \tag{19-2}$$

$$p(2i, 2i + 2j + 1) = \alpha\left[\alpha + \frac{1}{\lambda_1}\left(\frac{\lambda_2}{\lambda_1}\right)^j (1 - \alpha)F(\lambda_2)\right] \tag{19-3}$$

where

$$F(\lambda) = \frac{\lambda - (u^4a_- + a_0)a_-}{u^3a_- + a_0}u^3a_- - \frac{\lambda - (a_- + a_0)a_0}{ua_- + a_0}ua_- + (u^4a_- - a_0)a_- \tag{20}$$

Then, eq 18 is expressed in terms of the components of the matrices **M** and **M′**, and the eigenvalues of **MM′** as

$$\psi = \frac{e\alpha}{2Db} \ln\,[1 - \exp(4\kappa b)] + \frac{e(1 - \alpha)}{2Db} \ln\left[1 - \frac{\lambda_2}{\lambda_1} \exp(-4\kappa b)\right] + \frac{e\alpha}{Db} \exp(-\kappa b) + \frac{e\alpha}{3Db} \exp(-3\kappa b) + \frac{e\alpha}{2Db} \ln\left[\tanh\left(\frac{\kappa b}{2}\right)\right] + \frac{e}{Db}\,\frac{(1 - \alpha)}{\lambda_1}F(\lambda_1)\left\{\exp(-\kappa b) + \left(\frac{\lambda_1}{\lambda_2}\right)^{1/4}\left[\frac{1}{4} \ln\left(\frac{1 - w}{1 + w}\right) - \frac{1}{2} \tan^{-1} w\right]\right\} + \frac{e}{Db}\,\frac{(1 - \alpha)}{\lambda_1}F(\lambda_2)\left\{\frac{1}{3} \exp(-3\kappa b) + \left(\frac{\lambda_1}{\lambda_2}\right)^{3/4}\left[\frac{1}{4} \ln\left(\frac{1 - w}{1 + w}\right) + \frac{1}{2} \tan^{-1} w\right]\right\} \tag{21}$$

where

$$w = \left(\frac{\lambda_2}{\lambda_1}\right)^{1/4} \exp(-\kappa b)$$

Details of the derivation of eq 19-1 to 19-3 and 21 are given in the Appendix.

Results and Discussion

Figure 2 shows an example of the curve fitting to the experimental values of poly(maleic acid-*co*-ethyl vinyl ether) (PMAEVE) by changing the values of u which is a function of the interval b. The steep rise in pK_{app} at about $\alpha = 0.5$ is mainly caused by the term log x in eq 15. This means that the jump in pK_{app} at $\alpha = 0.5$ is due mostly to the neighbor interaction between carboxyl groups. On the other hand, the potential term increases rather uniformly with increasing α, as shown in Figure 3.

A good agreement was obtained between the calculated and experimental curves for $\alpha > 0.5$ by using the value of $u = 0.22$, corresponding to the interval $b = 1.57$ Å. Below $\alpha = 0.5$, however, the experimental values of pK_{app} increase more gradually than do the theoretical values. The experimental curve cannot be reproduced by a single value of u, although a somewhat larger value (e.g., $u = 0.3$) seems more appropriate. Two reasons may be considered for the disagreement in this region. One is the effect of the conformational change with increasing ionization. Some copolymers of maleic acid, such as poly(maleic acid-*co*-styrene), are known to exhibit a compact coil–extended coil conformational change for $\alpha < 0.5$.[4,5] Although PMAEVE is usually understood not to show such a conformational change,[3,6] an inelastic light scattering study suggested such a possibility.[7] In addition, the overall conformation of a weak polyacid is more or less changed with ionization.

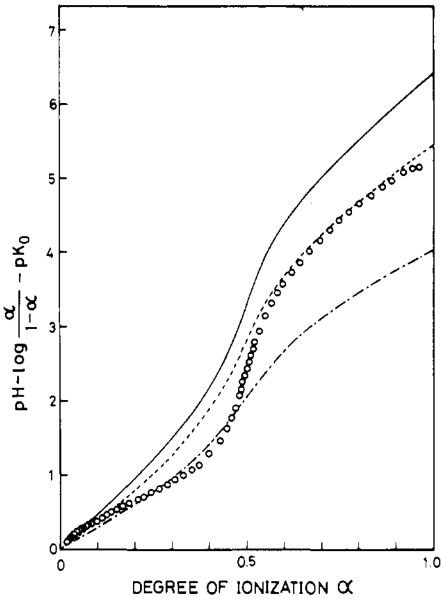

Figure 2. Comparison of the experimental values of $pK_{app} - pK_0$ of PMAEVE (○) with the calculated values as a function of the degree of ionization, α. Values of the parameter u are (—) 0.18, (- - -) 0.22, and (-·-) 0.3.

Therefore the gradual conformational change may be responsible for the small deviation. The other reason is that only the nearest- and second-neighbor interactions are incorporated into the theory and that the distances from a site to both neighbors are fixed to be b and $3b$ for all regions of the ionization. Other factors such as hydrogen bonding between carboxyl groups may contribute to the transition of the pK_{app} values. These assumptions are too simple to describe the local molecular structure. However, partial modifications of these assumptions, such as the removal of the second-neighbor interaction, do not alter so much the overall titration profile, as shown in Figure 3.

The present theory predicts the qualitative feature of the ionization and the mutual interaction between two ionizable groups in close proximity, without setting the value of pK_2^0. Namely, by assigning an appropriate value of the interval b, the calculated value of pK_{app} increases gradually for $\alpha < 0.5$, jumps at $\alpha = 0.5$, and then increases gradually. Some quantitative disagreement may be ascribed primarily to the conformational change of the polyion as well as to the effect of hydrogen bonding between carboxyl groups. A modified theory is developed to include the neighbor interactions up to third neighbor successively as well as the dipole–dipole interaction between ion pairs formed by the binding of the counterions. This theory agrees well with the experiments on the stereoregular poly(acrylic acids).[8] Application of the modified theory to the copolymers of maleic acid is now in progress.[9]

Schultz and Strauss[3] ascribed the difference in the increase in pK_{app} between $\alpha < 0.5$ and $\alpha > 0.5$ to the change in the dielectric constant of water in the vicinity of the charged site. This effect also seems contribute to the titration behaviors of the poly(diprotic acid) to some extent. However, the decrease in the dielectric constant of water is a result of the ionization of the polyion which determines the titration behavior primarily, although it seems plausible to expect some feedback effect due to lowering the dielectric constant.

The potentiometric titration behavior of the copolymers of maleic acid is a typical case where the short-range electrostatic interaction has a dominant role. This is not

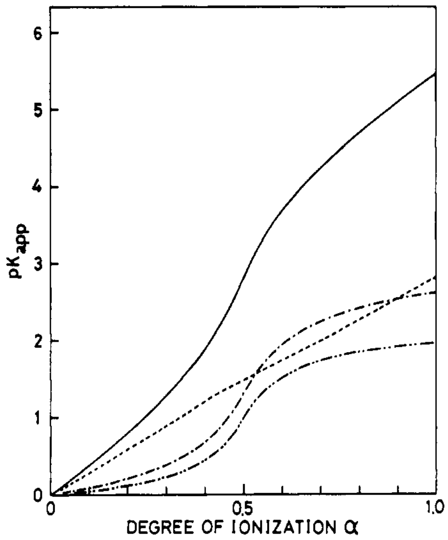

Figure 3. Comparison of the neighbor interaction term with the potential term as a function of α ($u = 0.22$): (—) total $\mathrm{p}K_{\mathrm{app}}$ value; (-−-) contribution of the neighbor interaction term; (---) contribution of the potential term; (--−--) contribution of the neighbor interaction term for the case where the second-neighbor interaction is absent.

easily understood in terms of the smeared-charged rod model. To clarify the local interaction in these copolymers, it is necessary to consider the three-dimensional arrangement of ionizable groups more exactly.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 358108).

Appendix

Here, eq 19–21 are derived from the partition function eq 7. According to statistical mechanics, the probabilities of dissociation of the sites $2i$ and $2i - 1$ are given by

$$p(2i) = \Xi^{-1}(1, 1)\mathbf{X}^{N-i-1}\bar{\mathbf{M}}\mathbf{M}'\mathbf{X}^{i-1}\mathbf{M}'' \qquad \text{(A-1)}$$

$$p(2i - 1) = \Xi^{-1}(1, 1)\mathbf{X}^{N-i-1}\mathbf{M}\bar{\mathbf{M}}'\mathbf{X}^{i-1}\mathbf{M}'' \qquad \text{(A-2)}$$

where

$$\begin{gathered} \mathrm{X} = \mathrm{MM}' \\ \mathrm{M}'' = \mathrm{M}\begin{bmatrix} a_- \\ a_0 \end{bmatrix} \\ \bar{\mathbf{M}} = \begin{bmatrix} u^3a_- & a_- \\ 0 & 0 \end{bmatrix} \\ \bar{\mathbf{M}}' = \begin{bmatrix} ua_- & a \\ 0 & 0 \end{bmatrix} \end{gathered} \qquad \text{(A-3)}$$

With the aid of the diagonalization of matrix **X**

$$\begin{gathered} \mathrm{T}^{-1}\mathrm{XT} = \Lambda = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} \\ |T| = 1 \end{gathered} \qquad \text{(A-4)}$$

these expressions are transformed as

$$\begin{aligned} p(2i) &= \Xi^{-1}(1, 1)\mathbf{T}\Lambda^{N-i-1}\mathbf{T}^{-1}\bar{\mathbf{M}}\mathbf{M}'\mathbf{T}\Lambda^{i-1}\mathbf{T}^{-1}\mathbf{M}'' \\ &= t_{11}t_{22} \end{aligned} \qquad \text{(A-5)}$$

$$\begin{aligned} p(2i - 1) &= \Xi^{-1}(1, 1)\mathbf{T}\Lambda^{N-i-1}\mathbf{T}^{-1}\mathbf{M}\bar{\mathbf{M}}'\mathbf{T}\Lambda^{i-1}\mathbf{T}^{-1}\mathbf{M}'' \\ &= \frac{1}{\lambda_1}(t_{11}ua_- + t_{21}a_-)(t_{22}u^3a_- - t_{12}a_0) \end{aligned} \qquad \text{(A-6)}$$

where t_{rs} is the (r, s) component of the matrix **T**.

Since the probabilities $p(2i)$ and $p(2i - 1)$ are the same on the basis of the physical meaning of the dissociation and the structural symmetry in the present molecular model, relation A-7 holds and can be proved mathematically.

$$t_{11}t_{22} = \frac{1}{\lambda_1}(t_{11}ua_- + t_{21}a_-)(t_{22}u^3a_- - t_{12}a_0) = \alpha \qquad \text{(A-7)}$$

Similarly, the following mutual dissociation probabilities may be written:

$$p(2i, 2i + 2j) = \Xi^{-1}(1, 1)\mathbf{X}^{N-i-j-1}\bar{\mathbf{M}}\mathbf{M}'\mathbf{X}^{j-1}\bar{\mathbf{M}}\mathbf{M}'\mathbf{X}^{i-1}\mathbf{M}'' \qquad \text{(A-8)}$$

$$p(2i, 2i - 2j - 1) = \Xi^{-1}(1, 1)\mathbf{X}^{N-i-1}\bar{\mathbf{M}}\mathbf{M}'\mathbf{X}^{j-1}\mathbf{M}\bar{\mathbf{M}}'\mathbf{X}^{i-j-1}\mathbf{M}'' \qquad \text{(A-9)}$$

$$p(2i, 2i + 2j + 1) = \Xi^{-1}(1, 1)\mathbf{X}^{N-i-j-2}\mathbf{M}\bar{\mathbf{M}}'\mathbf{X}^{j}\bar{\mathbf{M}}\mathbf{M}'\mathbf{X}^{i-1}\mathbf{M}'' \qquad \text{(A-10)}$$

Equations A-8 to A-10 can be transformed by using relations A-3 to A-6

$$p(2i, 2i + 2j) = \alpha\left[\alpha + (1 - \alpha)\left(\frac{\lambda_2}{\lambda_1}\right)^j\right] \qquad \text{(19-1)}$$

$$p(2i, 2i - 2j - 1) = \alpha^2 + \frac{\alpha(1 - \alpha)}{\lambda_1}\left(\frac{\lambda_2}{\lambda_1}\right)^j\left[(u^4a_- - a_0)a_- + \frac{t_{21}}{t_{11}}u^3a_-^{\,2} - \frac{t_{11}}{t_{21}}ua_-a_0\right] \qquad \text{(A-9}'\text{)}$$

$$p(2i, 2i + 2j + 1) = \alpha^2 + \frac{\alpha(1 - \alpha)}{\lambda_1}\left(\frac{\lambda_2}{\lambda_1}\right)^j\left[(u^4a_- - a_0)a_- + \frac{t_{22}}{t_{12}}u^3a_-^{\,2} - \frac{t_{12}}{t_{22}}ua_-a_0\right] \qquad \text{(A-10}'\text{)}$$

By using the following relations which can be derived from eq A-4

$$\begin{gathered} \frac{t_{21}}{t_{11}} = \frac{\lambda_1 - (u^4a_- + a_0)a_-}{(u^3a_- + a_0)a_-} \\ \frac{t_{11}}{t_{21}} = \frac{\lambda_1 - (a_- + a_0)a_0}{(ua_- + a_0)a_0} \\ \frac{t_{22}}{t_{12}} = \frac{\lambda_2 - (u^4a_- + a_0)a_-}{(u^3a_- + a_0)a_-} \\ \frac{t_{12}}{t_{22}} = \frac{\lambda_2 - (a_- + a_0)a_0}{(ua_- + a_0)a_0} \end{gathered} \qquad \text{(A-11)}$$

we have expressions 19-2 and 19-3.

Summation of the Debye–Hückel potential terms is carried out as follows. Equation 18 is expressed by introducing the following six summation terms as

$$\begin{aligned} \psi = -\frac{2e\kappa}{D}[2\alpha S_1 + 2(1 - \alpha)S_2 + \alpha S_3 + (1 - \alpha) \times \\ (F(\lambda_1)/\lambda_1)S_4 + \alpha S_5 + (1 - \alpha)(F(\lambda_2)/\lambda_1)S_6] \end{aligned} \qquad \text{(A-12)}$$

where

$$S_1 = \sum_{j=1}^{\infty}\frac{\exp(-4j\kappa b)}{4j\kappa b} = \sum_{j=1}^{\infty}\frac{\exp(-4jc)}{4jc} \qquad \text{(A-13)}$$

$$S_2 = \sum_{j=1}^{\infty} \left(\frac{\lambda_2}{\lambda_1}\right)^j \frac{\exp(-4jc)}{4jc} \qquad \text{(A-14)}$$

$$S_3 = \sum_{j=1}^{\infty} \frac{\exp[-(4j+1)c]}{(4j+1)c} \qquad \text{(A-15)}$$

$$S_4 = \sum_{j=1}^{\infty} \left(\frac{\lambda_2}{\lambda_1}\right)^j \frac{\exp[-(4j+1)c]}{(4j+1)c} \qquad \text{(A-16)}$$

$$S_5 = \sum_{j=1}^{\infty} \frac{\exp[-(4j+3)c]}{(4j+3)c} \qquad \text{(A-17)}$$

$$S_6 = \sum_{j=1}^{\infty} \left(\frac{\lambda_2}{\lambda_1}\right)^j \frac{\exp[-(4j+3)c]}{(4j+3)c} \qquad \text{(A-18)}$$

The sum S_1 is simply calculated as

$$S_1 = \sum_{j=1}^{\infty} \int_1^{\infty} \exp(-4jct)\, dt = \int_1^{\infty} [\sum_{j=1}^{\infty} \exp(-4jct)]\, dt$$
$$= \int_1^{\infty} \frac{\exp(-4ct)}{1-\exp(-4ct)}\, dt = -\frac{1}{4c} \ln\,[1-\exp(-4c)] \qquad \text{(A-13')}$$

Similarly

$$S_3 = \sum_{j=1}^{\infty} \int_1^{\infty} \exp[-(4j+1)c]\, dt = \int_1^{\infty} \frac{\exp(-5ct)}{1-\exp(-4ct)}\, dt$$
$$= \frac{1}{c} \int_0^{\exp(-c)} \frac{y^4}{1-y^4}\, dy$$
$$= \frac{1}{c}\left[-\exp(-c) - \frac{1}{4} \ln|\tanh(c/2)| + \frac{1}{2} \tan^{-1}(\exp(-c))\right] \qquad \text{(A-15')}$$

$$S_5 = \sum_{j=1}^{\infty} \int_1^{\infty} \exp[-(4j+3)c]\, dt$$
$$= \frac{1}{c}\left[\frac{1}{3}\exp(-3c) + \frac{1}{4} \ln|\tanh(c/2)| + \frac{1}{2} \tan^{-1}(\exp(-c))\right] \qquad \text{(A-17')}$$

The sum S_2 is rewritten as

$$S_2 = \sum_{j=1}^{\infty} \exp(-jz) \int_1^{\infty} \exp(-4jct)\, dt = \int_1^{\infty} \sum_{j=1}^{\infty} \exp[-4ct + z)j]\, dt$$

where $\exp(-z) = \lambda_1/\lambda_2$. Then we have

$$S_2 = \int_1^{\infty} \frac{\exp[-(4ct+z)]}{1-\exp[-(4ct+z)]}\, dt = \frac{1}{4c} \int_{4c+z}^{\infty} \frac{\exp(-\xi)}{1-\exp(-\xi)}\, d\xi$$
$$= -\frac{1}{4c} \ln\,[1-(\lambda_2/\lambda_1)\exp(-4c)] \qquad \text{(A-14')}$$

Similarly, S_4 and S_6 are expressed as

$$S_4 = \sum_{j=1}^{\infty} \exp(-jz) \int_1^{\infty} \exp[-(4j+1)ct]\, dt$$
$$= \int_1^{\infty} \frac{\exp[-(5ct+z)]}{1-\exp[-(4ct+z)]}\, dt = \frac{1}{c}\exp(z/4) \int_0^{w} \frac{y^4}{1-y^4}\, dy$$
$$= -\frac{1}{c}\exp(-c) - \frac{1}{c}\exp(z/4)\left[\frac{1}{4} \ln\left|\frac{1-w}{1+w}\right| - \frac{1}{2}\tan^{-1} w\right] \qquad \text{(A-16')}$$

where $w = \exp[-(c + z/4)] = (\lambda_2/\lambda_1)^{1/4} \exp(-c)$ and

$$S_6 = \sum_{j=1}^{\infty} \exp(-jz) \int_1^{\infty} \exp[-(4j+3)ct]\, dt$$
$$= \frac{1}{c}\exp(3z/4) \int_0^{w} \frac{y^6}{1-y^4}\, dy$$
$$= -\frac{1}{3c}\exp(-3c) - \frac{1}{c}\exp(3z/4)\left[\frac{1}{4} \ln\left|\frac{1-w}{1+w}\right| + \frac{1}{2}\tan^{-1} w\right] \qquad \text{(A-18')}$$

Then, substituting eq A-13′ to A-18′ into eq A-12, we have eq 21.

References and Notes

(1) Kotin, L.; Nagasawa, M. *J. Chem. Phys.* **1962**, *36*, 873.
(2) Lifson, S. *J. Chem. Phys.* **1957**, *26*, 727.
(3) Schultz, A. W.; Strauss, U. P. *J. Phys. Chem.* **1972**, *76*, 1767.
(4) Sugai, S.; Ohno, N.; Nitta, K. *Macromolecules* **1974**, *7*, 961.
(5) Sasaki, S.; Minakata, A. *Rep. Prog. Polym. Phys. Jpn.* **1976**, *19*, 65.
(6) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1970**, *74*, 2842.
(7) Meullenet, J. P.; Schmitt, A.; Candau, S. *Chem. Phys. Lett.* **1978**, *55*, 523.
(8) Sasaki, S.; Minakata, A. *Biophys. Chem.*, in press.
(9) Sasaki, S.; Ohnuma, H.; Minakata, A., to be submitted for publication.