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THE DEVELOPMENT OF AN EQUATION FOR THE POTENTIOMETRIC TITRATION OF LINEAR POLYELECTROLYTES USING A SITE MODEL

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An equation for the potentiometric titration of linear polyelectrolytes is derived by considering neighbor interactions of ionizable groups and the association equilibria between ionized groups and counterions. The first, second, ... and lth neighbor interactions are directly introduced into the equation, and additional neighbor interactions together with interactions between the ionizable groups and simple salt ions are taken into account as perturbed electrostatic potentials. It is observed that the approximation which includes the second or third neighbor interaction is sufficient for description of the potentiometric titration. Good agreement between predictions of the present theory and experiment is obtained for isotactic and syndiotactic poly(acrylic acids).

1. Introduction

Polyelectrolyte solutions exhibit various interesting phenomena which are different from those encountered in solutions of nonionic polymers. These phenomena are due to electrostatic interactions between (1) ionized groups of the polymer molecule and between (2) ionized groups and small ions in the bulk of the solution.

Various thermodynamic properties of polyelectrolyte solutions can be explained in a limited way by the overall electrostatic potential of a rodlike or a randomly coiled polyion [1]. With a smeared charge model, Kotin and Nagasawa obtained the overall electrostatic potential of the polyion by numerical integration of the Poisson-Boltzmann equation to describe the ion binding and potentiometric titration behavior of weak polyacids [2]. The potentiometric titration behavior of some protein molecules as well as synthetic polyelectrolytes were explained in terms of the surface potential of the rod or spherical macroion through numerical analysis of the non-linear Poisson-Boltzmann equation [3–5]. However, the description afforded by the overall potential is often insufficient for a detailed analysis of the observed titration behavior. In the case of polyampholytes, theories based on the smeared charge model yield estimates in poor agreement with the experimental results [4]. Even in the case of weak polyacids, where the titration curves of an alternating copolymer of maleic acid and poly(maleic acid) exhibit the two step dissociation of carboxyl groups, this approach predicts a greater effect on the difference in the two dissociation constants with the addition of salts than is observed [6–8]. In order to describe such behavior, localized interaction of ionizable groups need to be taken into account in the development of a more useful theoretical model for the interpretation of potentiometric titrations.

With this in mind Marcus [9] derived an equation to describe the potentiometric titration behavior of polyelectrolyte solutions by including nearest neighbor interaction. This was accomplished with a statistical mechanical approach employing a model similar to the Ising model of ferromagnetism [10]. His approach, however, did not include the interaction between distant ionized groups. Harris and Rice [11], and Lifson [12] extended his treatment to include such long range interaction by adding an electrostatic potential term. However, explicit expressions for the added term were not provided and this led to ambiguity in estimating the contribution of this term.

In the present study, an improved equation to describe the potentiometric titration of a linear polyelectrolyte is derived by considering the effects of neighbor interaction and counterion binding. To clarify the role of neighbor and long range interactions introduced in Lifson's theory [12], the neighbor interactions are taken into account for three cases; in the first approximation nearest neighbor interaction is considered, in the second the nearest and second neighbor interactions are considered, and in the third the nearest, second and third neighbor interactions are taken into account. The counterion binding is treated as an association equilibrium between the ionized group and the mobile ions. In each case, the remaining long range interactions are expressed in the form of a perturbed electrostatic potential. Comparison of the contribution of these approximations to the end result shows that the second and third approximations are sufficient for the examination of potentiometric titrations of linear polyelectrolytes. Application of the present theory to the titration data of isotactic and syndiotactic poly(acrylic acids) results in good agreement with experiment.

2. Theory

In this section, an equation is presented for the potentiometric titration of a weak polyacid. A "Site model" is used as the theoretical base for its development. Because of the discreteness of the distribution of the ionizable groups of the polymer, the following can be assumed: 1) The electrical repulsion of the ionized groups extends the polymer chain, so that it assumes the shape of a rod along which the ionizable groups are distributed. 2) The ionizable groups are arranged in a three-dimensional pattern defined by the actual conformation of the polymer chain with each ionizable group considered a point charge. 3) With this "Site model" for the polyelectrolyte each ionizable group on the polymer chain is influenced by the electrical interaction of the other ionizable groups on the chain and by the counter ion in the bulk of the solution. 4) Each ionizable group is at equilibrium with the hydrogen ion, H^+, and the monovalent metal cation, M^+, in the bulk of the solution, and it loses net charge when H^+ is bound, whereas it forms a dipole when M^+ is bound. In the latter case, a small separation between the ionized group and the ion is expected due to their hydration layers, resulting in the dipole whose moment depends on the thickness of the hydration layers. 5) The electric field in the bulk of the solution that emanates from the ionized sites along the polymer chain is essentially the same as from the smeared charged rod of a polyion. The distribution of the small ions in the bulk of the solution is therefore believed to be described by the Poisson-Boltzmann equation of the system having cylindrical symmetry. 6) Dipole–dipole interaction as well as coulombic interaction between ions are taken into consideration. Ion–dipole interaction, however, is neglected, since the direction of the dipole is, in most cases, believed to be approximately perpendicular to the rod of the polymer skeleton, so that the interaction of this type may vanish when averaged over all directions. The dielectric constant of the medium around the ionized group as well as the ions is assumed to be the same as that of the solvent, D. 7) All the ionizable groups have the same chemical structure, and are equivalent so that there is no distinction between them from a statistical mechanical sense.

2.1. General expressions

Each ionizable group of a polyion is capable of assuming three states, ionized, unionized and cation-bound. The equilibria are expressed as

$$\mu_0 = \mu_{H^+} + \mu_- \tag{1}$$

$$\mu_m = \mu_{M^+} + \mu_- \tag{2}$$

where μ_0, μ_m and μ_- are the chemical potentials of the unionized, cation-bound and ionized groups, respectively, and μ_{H^+} and μ_{M^+} are the chemical potentials of the hydrogen ion and the metal cation, respectively. By letting a_0, a_m and a_- correspond to their respective activities, eqs. (1) and (2) are expressed in the following way,

$$\mathrm{pH} = \mathrm{pK}_0 + \log(a_-/a_0), \qquad (3)$$

$$\mathrm{pM} = \mathrm{pM}_0 + \log(a_-/a_\mathrm{m}), \qquad (4)$$

where

$$\mathrm{pK}_0 = 0.4343\ (\mu^0_{\mathrm{H}^+} + \mu^0_- - \mu^0_\mathrm{m})/kT.$$

and

$$\mathrm{pM}_0 = 0.4343\ (\mu^0_{\mathrm{M}^+} + \mu^0_- - \mu^0_0)/kT,$$

Here the superscript 0 designates the chemical potential of the standard state.

To describe the dissociation of the ionizable groups, it is convenient to evaluate the grand partition function, Ξ_p, for a macroion whose charged groups interact with each other and with the small ions in the bulk of the solution. The grand partition function, as defined by the standard methods of statistical mechanics, is

$$\Xi_\mathrm{p} = \sum_{\epsilon_1 = 0,\mathrm{m},-} \cdots \sum_{\epsilon_i = 0,\mathrm{m},-} \cdots \sum_{\epsilon_\mathrm{p} = 0,\mathrm{m},-} \exp\left[\sum_i \left\{(\mu_{\epsilon_i} - \mu^0_{\epsilon_i})/kT - \sum_j \tfrac{1}{2} E_{\epsilon_i,\epsilon_j}/kT - E^\mathrm{s}_{\epsilon_i}/kT\right\}\right], \qquad (5)$$

where the subscripts 0, m and – refer as before to the unionized, metal bound and ionized groups, respectively, and $E_{\epsilon_i,\epsilon_j}$ and $E^\mathrm{s}_{\epsilon_i}$ represent the interaction energies between the i-th group in the ϵ_i state and the j-th group in the ϵ_j state, and that between the i-th group in the ϵ_i-state and all the small ions in the bulk of the solution, respectively. According to assumption (6), $E_{\epsilon_i,\epsilon_j}$ is due to coulombic and dipole–dipole interactions, and the following conditions are satisfied

$$E_{\epsilon_i,\epsilon_j} \neq 0 \text{ if } \epsilon_i = - \text{ and } \epsilon_j = -, \text{ or } \epsilon_i = \mathrm{m} \text{ and } \epsilon_j = \mathrm{m}; \quad = 0 \text{ otherwise}, \qquad (6)$$

and

$$E^\mathrm{s}_{\epsilon_i} \neq 0 \text{ if } \epsilon_i = -; \quad = 0 \text{ otherwise}. \qquad (7)$$

2.2. *The interaction between the ionized group and small ions in the bulk of the solution*

The electric field due to the polyion is cylindrically symmetrical about the axis of the polyion rod. The distribution of small ions in the bulk of the solution can thus be approximately described by the Poisson-Boltzmann equation expressed employing cylindrical coordinates. The interaction energy between the i-th ionized group and small ions in the bulk of the solution can be expressed as

$$E^\mathrm{s}_{-i} = -\int_a^R 2\pi r\,\mathrm{d}r \int_{-\infty}^{\infty} \mathrm{d}z \left\{\frac{D}{4\pi}\frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r}\psi(r)\right\} \times \frac{e_0}{D}\frac{1}{\sqrt{r^2+z^2}}, \qquad (8)$$

where $\psi(r)$ is the electric potential at r, e_0 the charge of an ionized group, a the radius of the polyion rod and R the distance between the center of the polyion and the boundary where the conditions, $\partial\psi/\partial r|_R = 0$ and $\psi(R) = 0$ are satisfied. Integration with respect to r in eq. (8) yields

$$E^\mathrm{s}_{-i} = \frac{e_0}{D}\frac{1}{a}\frac{\partial\psi}{\partial r}\bigg|_a \int_{-\infty}^{\infty} \frac{\mathrm{d}z}{\sqrt{a^2+z^2}} + e_0\psi(a). \qquad (9)$$

The averaged charge density of the surface of the polyion rod can be substituted for $(1/2\pi)\ \partial\psi/\partial r|_a$ in eq. (9) and

$$E^\mathrm{s}_{-i} = -\frac{e_0}{D}\rho \int_{-\infty}^{\infty} \frac{\mathrm{d}z}{\sqrt{a^2+z^2}} + e_0\psi(a), \qquad (10)$$

where ρ, the charge density per unit length of the polyion, is proportional to the degree of ionization, α. Though the integration of eq. (10) with respect to z diverges to infinity, this interaction energy terms can be compensated by the interaction energy between the i-th ionized group and another long distant ionized group, as shown in the next section.

2.3. *An approximation for long range interaction*

Since the solution of eq. (5) in a rigorous manner is very difficult and since the interaction energies, $E_{-i,-j}$, and $E_{\mathrm{m}i,\mathrm{m}j}$, decrease rapidly with distance between the

i-th and j-th groups, it is convenient to introduce an approximation for the interaction between distant groups. Namely, the $E_{\epsilon_i,\epsilon_j}$ term is introduced directly into the expression for the grand-partition function when $|i-j| \leqslant l$ where the value of l represents the degree of approximation. Remaining terms for $|i-j| > l$ are regarded as perturbation terms and are expressed by a modified electrostatic potential.

The term $\frac{1}{2}\sum_{|j-i|>l} E_{\epsilon_i,\epsilon_j}$ for $|i-j| > l$, is replaced by the averaged interaction energy expressed as

$$\Phi^{(l)}_{\epsilon_i} = \sum_{|j-i|>l} \frac{P_{\mathrm{I}}(\epsilon_i, \epsilon_j)}{P_{\mathrm{I}}(\epsilon_i)} E_{\epsilon_i,\epsilon_j}, \tag{11}$$

where $P_{\mathrm{I}}(\epsilon_i, \epsilon_j)$ is the mutual probability for the i-th and j-th groups being in states ϵ_i and ϵ_j simultaneously, and $P_{\mathrm{I}}(\epsilon_i)$ is the probability for the i-th group being in state ϵ_i. With this approach eq. (5) is reduced to

$$\Xi^{(l)}_p = \sum_{\epsilon_1=0,\mathrm{m},-} \cdots \sum_{\epsilon_p=0,\mathrm{m},-} \exp\left[\sum_i (\mu^{(l)}_{\epsilon_i} - \mu^0_{\epsilon_i})/kT - \sum_{1\leqslant h\leqslant l} E_{\epsilon_i,\epsilon_{i+h}}/kT\right], \tag{12}$$

where the following abbreviations are used

$$\mu^{(l)}_{-_i} = \mu_{-_i} - \Phi^{(l)}_{-_i} - E^{\mathrm{s}}_{-_i}, \quad \mu^{(l)}_{0_i} = \mu_{0_i}, \qquad \mu^{(l)}_{\mathrm{m}_i} = \mu_{\mathrm{m}_i} - \Phi^{(l)}_{\mathrm{m}_i}. \tag{13}$$

In the perturbation terms the coulombic and dipole—dipole interactions are taken into account, so that

$$\Phi^{(l)}_{-_i} = \sum_{|j-i|>l} \frac{P_{\mathrm{I}}(-_i, -_j)}{P_{\mathrm{I}}(-_i)} \frac{e_0^2}{Dr_{i,j}}, \tag{14-1}$$

$$\Phi^{(l)}_{\mathrm{m}_i} = \sum_{|j-i|>l} \frac{P_{\mathrm{I}}(\mathrm{m}_i, \mathrm{m}_j)}{P_{\mathrm{I}}(\mathrm{m}_i)} \frac{(e_0 d)^2}{Dr_{i,j}{}^3}, \tag{14-2}$$

where d is the distance between the bound cation and the ionized group.

Now, if the value $|j-i|$ is larger than a sufficiently large number, N, the following situations are encountered.

$$P_{\mathrm{I}}(-_i, -_j)/P_{\mathrm{I}}(-_i) = \alpha \tag{16}$$

and

$$r_{i,j} = b|j-i|, \tag{17}$$

where b is the average distance between ionizable groups along the axis of the polyion rod. The summation for values of $|j-i|$ larger than N can be written as

$$\sum_{|j-i|>N} \frac{P_{\mathrm{I}}(-_i, -_j)}{P_{\mathrm{I}}(-_i)} \frac{e_0^2}{Dr_{i,j}} = 2\sum_{n=1}^{\infty} \alpha \frac{e_0^2}{Db(N+n)}, \tag{18}$$

The integration term in eq. (10) is expressed as

$$2\frac{e_0}{D}\int_{Nb}^{\infty} \frac{\alpha e_0}{b}\frac{\mathrm{d}z}{z} = 2\frac{\alpha e_0^2}{Db}\sum_{n=0}^{\infty}\int_{(N+n)b}^{(N+n+1)b} \frac{\mathrm{d}z}{z} \approx 2\sum_{n=1}^{\infty} \alpha \frac{e_0^2}{Db(N+n)}, \tag{19}$$

when $Nb \gg a$. In this equation the integrand $\sqrt{a^2+z^2}$ in eq. (10) is replaced by $|z|$, since $\sqrt{a^2+z^2}$ is nearly equal to $|z| \gg a$. The divergent terms in eq. (10) and eq. (14) compensate each other and eq. (13) can be expressed as

$$\mu^{(l)}_{-_i} = \mu_{-_i} - \Phi^{(l)}_{-} + \alpha \cdot \frac{e_0^2}{Db}\int_{-Nb}^{Nb} \frac{\mathrm{d}z}{\sqrt{z^2+a^2}} - e_0\psi(a), \tag{20}$$

where

$$\Phi^{(l)}_{-} = 2\sum_{|j-i|>l}^{N} \frac{P_{\mathrm{I}}(-_i, -_j)}{P_{\mathrm{I}}(-_i)} \frac{e_0^2}{r_{i,j}}.$$

In the above calculation of the grand partition function, the replacement of $E_{-_i,-_j}$ by the potential term $[P_{\mathrm{I}}(-_i, -_j)/P_{\mathrm{I}}(-_i)]\ E_{-_i,-_j}$ in eqs. (11), (12) and (14) indicates that the long range interactions provide some contributions to the grand partition function and that they increase the energy of the ionized i-th state by

$$\mu_{-_i} - \mu^{(l)}_{-} = \Phi^{(l)}_{-} - \alpha\frac{e_0^2}{Db}\int_{-Nb}^{Nb} \frac{\mathrm{d}z}{\sqrt{z^2+a^2}} + e_0\psi(a).$$

The precision of this treatment depends on the contribution of the long range interactions relative to that of the neighbor interactions. A comparison of n ($n = 1$, 2, 3) approximations conducted as described above is presented in a later section.

2.4. Equation for the potentiometric titration

To obtain the relation between the apparent dissociation constant of a polyelectrolyte, $\mathrm{pK_{app}}$, and the activity ratio in eq. (3) and eq. (4), respectively, let us first assume that the degree of polymerization of the macromolecule is sufficiently large so that end-effects are negligible. Then eqs. (1) and (2) can be rewritten as

$$\mu_{\mathrm{H}^+} + e_0\psi^{(l)} = \mu_0 - \mu_-^{(l)} \tag{1$'$}$$

and

$$\mu_{\mathrm{M}^+} + e_0\psi^{(l)} - \Phi_{\mathrm{m}}^{(l)} = \mu_{\mathrm{m}}^{(l)} - \mu_-^{(l)} \tag{2$'$}$$

where

$$\begin{cases} \mu_-^{(l)} = \mu_- - e_0\psi^{(l)}, & \text{(21-1)} \\ \mu_{\mathrm{m}}^{(l)} = \mu_{\mathrm{m}} - \Phi_{\mathrm{m}}^{(l)} & \text{(21-2)} \end{cases}$$

and

$$\begin{cases} e_0\psi^{(l)} = \Phi_-^{(l)} - \dfrac{2\alpha e_0^2}{Db}\ln\left(\dfrac{Nb + \sqrt{N^2b^2 + a^2}}{a}\right) & \\ \quad + e_0\psi(a) & \text{(22-1)} \\ \Phi_{\mathrm{m}}^{(l)} \equiv \Phi_{\mathrm{m}_i}^{(l)}. & \text{(22-2)} \end{cases}$$

Also eqs. (3) and (4) can be rewritten as

$$\mathrm{pH} = \mathrm{pK}_0 + \log a_-^{(l)}/a_0 + 0.4343\, e_0\psi^{(l)}/kT, \tag{3$'$}$$

$$\begin{aligned} \mathrm{pM} = \mathrm{pM}_0 &+ \log(a_-^{(l)}/a_{\mathrm{m}}^{(l)}) \\ &+ 0.4343\,(e_0\psi^{(l)} - \Phi_{\mathrm{m}}^{(l)})/kT, \end{aligned} \tag{4$'$}$$

where

$$a_-^{(l)} = a_-\exp(-e_0\psi^{(l)}/kT), \tag{23}$$

$$a_{\mathrm{m}}^{(l)} = a_{\mathrm{m}}\exp(-\Phi_{\mathrm{m}}^{(l)}/kT). \tag{24}$$

Eq. (3)′ which is similar to Lifson's expression [12] clarifies the physical meaning of $e_0\psi$ and eq. (22-1) can be used to obtain $e_0\psi$ explicitly as well.

The following abbreviations have been introduced for convenience into the grand partition function given by eq. (12).

$$\begin{aligned} \Xi_p^{(l)} = \sum_{\epsilon_1}\cdots\sum_{\epsilon_i}\cdots\sum_{\epsilon_p}&\left(a_{\epsilon_1}^{(l)}\prod_{1\leqslant h\leqslant l}u_{\epsilon_{1,1+h}}\right)\cdots \\ &\left(a_{\epsilon_i}^{(l)}\prod_{1\leqslant h<l}u_{\epsilon_{i,i+h}}\right)\cdots a_{\epsilon_{p-1}}^{(l)}u_{\epsilon_{p-1},\epsilon_p}a_{\epsilon_p}^{(l)}, \end{aligned} \tag{25}$$

where the summation of ϵ_i is the same as in eq. (12) and

$$a_{\epsilon i}^{(l)} = \exp[(\mu_{\epsilon i}^{(l)} - \mu_{\epsilon i}^{0})/kT], \tag{26}$$

$$u_{\epsilon i,\epsilon i+h} = \exp(-E_{\epsilon i,\epsilon i+h}/kT). \tag{27}$$

By using matrix representation, eq. (25) can be rewritten in a shortened form

$$\Xi_p^{(l)} = \boldsymbol{b}^{(l)}\prod_{i=l+1}^{p}M_i^{(l)}\boldsymbol{a}_l^{(l)}, \tag{28}$$

where

$$\prod_{i=l+1}^{p}M_i = M_p\cdots M_{l+1}$$

and $\boldsymbol{a}_l^{(l)}$ is a column vector whose elements are sets of the states of the $(p - l + 1)$-th ... and the p-th sites written as

$$\begin{aligned} (\boldsymbol{a}_l^{(l)})_{\epsilon_{p-l+1},\cdots,\epsilon_p} &= a_{\epsilon_{p-l+1}} \\ &\times\prod_{1\leqslant h\leqslant l}u_{\epsilon_1,\epsilon_{1+h}}\cdots a_{\epsilon_{p-1},\epsilon_p}a_{\epsilon_p}. \end{aligned} \tag{29}$$

Here $\boldsymbol{b}^{(l)}$ is the row vector whose elements are all unity, and $\boldsymbol{M}_i$ is the i-th matrix operator which generates the statistical sum in eq. (25) as follows: The matrix $M_{l+1}^{(l)}$ operates on the vector $\boldsymbol{a}_l^{(l)}$ to generate a new vector $\boldsymbol{a}_{l+1}^{(l)}$ whose elements are expressed as

$$\begin{aligned} (\boldsymbol{a}_{l+1}^{(l)})_{\epsilon_{p-l},\cdots,\epsilon_{p-1}} &= \sum_{\epsilon_p}a_{\epsilon_{p-l}} \\ &\times\prod_{1\leqslant h<l}u_{\epsilon_{p-l},\epsilon_{p-l+h}}\cdots a_{\epsilon_{p-1}}u_{\epsilon_{p-1},\epsilon_p}a_{\epsilon_p}. \end{aligned} \tag{30}$$

The result of $M_{i+1}^{(l)}$ operating on the vector $\boldsymbol{a}_i^{(l)}$ is $\boldsymbol{a}_{i+1}^{(l)}$ whose elements are

$$\begin{aligned} &(\boldsymbol{a}_{i+1}^{(l)})_{\epsilon_{p-i},\cdots,\epsilon_{p-i+l-1}} \\ &\quad= \sum_{\epsilon_p}\cdots\sum_{\epsilon_{p-i+l}}a_{\epsilon_{p-i}}\prod_{1\leqslant h\leqslant l}u_{\epsilon_{p-i},\epsilon_{p-i+h}}\cdots a_{\epsilon_p} \end{aligned} \tag{31}$$

and $\boldsymbol{a}_p^{(l)}$ can be obtained through this progressive procedure. The grand partition function, $\Xi_p^{(l)}$, expressed by eq. (25) can be obtained by summing up all elements of $\boldsymbol{a}_p^{(l)}$. This is done by combining vectors, $\boldsymbol{a}_p^{(l)}$ and $\boldsymbol{b}_p^{(l)}$ as shown in eq. (28).

If the ionizable groups are arranged regularly; for example, if they are equidistant on the polymer chain, then the matrices $\boldsymbol{M}_i$ are equivalent and eq. (28) can be written as

$$\Xi_p^{(l)} = \boldsymbol{b}^{(l)}(\boldsymbol{M}^{(l)})^{p-l}\boldsymbol{a}_l^{(l)}. \tag{32}$$

This equation can be transformed as follows:

$$\Xi_p^{(l)} = \boldsymbol{b}^{(l)}\boldsymbol{T}^{(l)}(\boldsymbol{\lambda}^{(l)})^{p-l}\ \boldsymbol{T}^{(l)\ -1}\boldsymbol{a}_l^{(l)}, \tag{33}$$

where $\boldsymbol{T}^{(l)}$ and $\boldsymbol{\lambda}^{(l)}$ satisfy the following relation

$$\boldsymbol{M}^{(l)}\boldsymbol{T}^{(l)} = \boldsymbol{T}^{(l)}\boldsymbol{\lambda}^{(l)}, \tag{34}$$

$\boldsymbol{\lambda}^{(l)}$ being a diagonal matrix. Since P is very large, the grand partition function can be expressed in terms of the maximum eigenvalues. The explicit expressions of $\boldsymbol{a}_l^{(l)}$ and $\boldsymbol{M}^{(l)}$ in the above case are shown in Appendix I.

The expressions of the probabilities, $P_{\mathrm{I}}(\epsilon_i)$ and $P_{\mathrm{I}}(\epsilon_j, \epsilon_{j+k})$ are derived from the grand partition function as

$$P_{\mathrm{I}}(\epsilon_j) = (\Xi_p^{(l)})^{-1}\boldsymbol{b}^{(l)} \times \prod_{i=j+1}^{p} \boldsymbol{M}_i^{(l)}\boldsymbol{N}_j^{(l)}(\epsilon_j) \prod_{i=l+1}^{j-1} \boldsymbol{M}_i^{(l)}\boldsymbol{a}_l^{(l)}, \tag{35}$$

and

$$P_{\mathrm{I}}(\epsilon_j, \epsilon_{j+k}) = (\Xi_{\mathrm{p}}^{(l)})^{-1}\boldsymbol{b}^{(l)} \times \prod_{i=j+k+1}^{p} \boldsymbol{M}_i^{(l)}\boldsymbol{N}_{j+k}^{(l)}(\epsilon_{j+k}) \times \prod_{i=j+1}^{j+k-1} \boldsymbol{M}_i^{(l)}\boldsymbol{N}_j^{(l)}(\epsilon_j) \prod_{i=l+1}^{j-1} \boldsymbol{M}_i^{(l)}\boldsymbol{a}_l^{(l)}, \tag{36}$$

where $\boldsymbol{N}_j^{(l)}(\epsilon_j)$ is a matrix, the elements of which are the same as those of $\boldsymbol{M}_j^{(l)}$, except for the replacement of a_ϵ with 0 when $\epsilon \neq \epsilon_j$. In the case of the equidistant distribution of the ionizable groups, eqs. (35) and (36) can be rewritten as

$$P_{\mathrm{I}}(\epsilon_j) = (\Xi_p^{(l)})^{-1}\boldsymbol{b}^{(l)}(\boldsymbol{M}^{(l)})^{p-j-1} \times \boldsymbol{N}^{(l)}(\epsilon)(\boldsymbol{M}^{(l)})^{j-l}\boldsymbol{a}_l^{(l)} \tag{37}$$

and

$$P_{\mathrm{I}}(\epsilon_j, \epsilon_{j+k}) = (\Xi_p^{(l)})^{-1}\boldsymbol{b}^{(l)}(\boldsymbol{M}^{(l)})^{p-j-k-1}\boldsymbol{N}^{(l)}(\epsilon) \times (\boldsymbol{M}^{(l)})^{k-1}\boldsymbol{N}^{(l)}(\epsilon)(\boldsymbol{M}^{(l)})^{j-l-1}\boldsymbol{a}_l^{(l)}. \tag{38}$$

Also the degree of ionization, α, can be expressed as

$$\alpha = \frac{\nu}{P} = \frac{kT}{P}\frac{\partial \Xi_p}{\partial \mu_-} = \frac{1}{P}\frac{a_-}{\Xi_p}\frac{\partial \Xi_p}{\partial a_-}, \tag{39}$$

where ν is the number of the ionized site. The differentiation of eq. (39) with respect to a_- yields the relation

$$\frac{\partial \Xi_p^{(l)}}{\partial a_-^{(l)}} = \boldsymbol{b}^{(l)}\frac{\partial}{\partial a_-^{(l)}}(\boldsymbol{M}^{(l)})^{p-l}\boldsymbol{a}_l^{(l)}. \tag{40}$$

The right-hand side of this equation can be approximated as

$$\begin{aligned}\frac{1}{P}\frac{a_-}{\Xi_p^{(l)}}\frac{\partial}{\partial a_-^{(l)}}\boldsymbol{b}^{(l)}(\boldsymbol{M}^{(l)})^{p-l}\boldsymbol{a}_l^{(l)} &\approx (\Xi_p^{(l)})^{-1}\boldsymbol{b}^{(l)}(\boldsymbol{M}^{(l)})^{p-j-1} \times \left(a_-\frac{\partial}{\partial a_-}\boldsymbol{M}^{(l)}\right)(\boldsymbol{M}^{(l)})^{j-l}\boldsymbol{a}_l^{(l)} \\ &= (\Xi_p^{(l)})^{-1}\boldsymbol{b}^{(l)}(\boldsymbol{M}^{(l)})^{p-j-l}\boldsymbol{N}^{(l)}(-)(\boldsymbol{M}^{(l)})^{j-l}\boldsymbol{a}_l^{(l)}.\end{aligned} \tag{41}$$

Eqs. (37) and (41) give

$$\alpha = P_{\mathrm{I}}(-_j). \tag{42}$$

A similar equation with respect to the degree of ion-binding, β, can also be obtained

$$\beta = P_{\mathrm{I}}(m_j). \tag{43}$$

If the dipole–dipole interaction is neglected, the ratio of the fraction of unionized sites (β_0) to the degree of ion-binding (β) can be generally related to the activities a_0 and a_m, as:

$$\beta_0/\beta = a_0/a_{\mathrm{m}} \tag{44}$$

This result is obtained as follows: Let us use another expression of the grand partition function,

$$\Xi_p = \prod_{i=1}^{p}(u^{\mathrm{s}}_{-i}a_{-i}\hat{u}_i + a_{0_i} + a_{\mathrm{m}_i}), \tag{45}$$

where

$$u^{\mathrm{s}}_{-i} = \exp(-E^{\mathrm{s}}_i/kT) \tag{46}$$

and $\hat{u}_i$ is the interaction operator which operates on $a_{\epsilon i+j}$ from the left hand side and generates the interaction term

$$\hat{u}_i a_{\epsilon i+j} = \begin{cases} a_{-i+j}\exp(-E_{-i,-i+j}/kT)\hat{u}_i & \text{for } \epsilon_{i+j} = - \\ a_{\epsilon i+j}\hat{u}_i & \text{otherwise} \end{cases}$$

$$\hat{u}_i \prod_j^p a_{\epsilon i+j} = \prod_{j=1}^p a_{\epsilon i+j} \exp(-E_{-i,\epsilon i+j}). \tag{47}$$

From the grand partition function (45), $P_{\mathrm{I}}(0_j)$ and $P_{\mathrm{I}}(\mathrm{m}_j)$ are derived corresponding to eq. (35) as

$$P_{\mathrm{I}}(0_j) = \frac{1}{\Xi_p}\prod_{i=1}^{j-1}(u^{\mathrm{s}}_{-i}a_{-i}\hat{u}_i + a_{0_i} + a_{\mathrm{m}_i})a_{0_j} \times \prod_{i=j+1}^{p}(u^{\mathrm{s}}_{-i}a_{-i}\hat{u}_i + a_{0_i} + a_{\mathrm{m}_i}), \tag{48}$$

$$P_{\mathrm{I}}(\mathrm{m}_j) = \frac{1}{\Xi_p}\prod_{i=1}^{j-1}(u^{\mathrm{s}}_{-i}a_{-i}\hat{u}_i + a_{0_i} + a_{\mathrm{m}_i}) \times a_{m_j}\prod_{i=j+1}^{p}(u^{\mathrm{s}}_{-i}a_{-i}\hat{u}_i + a_{0_i} + a_{\mathrm{m}_i}). \tag{49}$$

From these equations we can derive the relation,

$$\beta_0/\beta = P_{\mathrm{I}}(0_j)/P_{\mathrm{I}}(\mathrm{m}_j) = a_0/a_{\mathrm{m}}$$

if no difference exists between the ionizable groups. The above equation is transformed to

$$\beta = (1-\alpha)\,a_{\mathrm{m}}/(a_0 + a_{\mathrm{m}}) \tag{50}$$

instead of eq. (44).

The potential at the surface of the polyion, $\psi(a)$, is obtained by solving the following Poisson-Boltzmann equation for the bulk solution,

$$\nabla^2\psi = -(4\pi e_0/D)[C_+\exp(-e_0\psi/kT) - C_-\exp(e_0\psi/kT)] \tag{51}$$

$$\partial\psi/\partial r|_{r=a} = 2e_0\alpha/Dab, \tag{52}$$

$$\partial\psi/\partial r|_{r=R} = \psi|_{r=R} = 0, \tag{53}$$

where

$$C_+ = \frac{(\alpha C_{\mathrm{p}} + C_{\mathrm{s}})}{1000}N_{\mathrm{A}}F_+, \quad C_- = \frac{C_{\mathrm{s}}}{1000}N_{\mathrm{A}}F_-,$$

$$F_\pm = (R^2 - a^2)\bigg/\int_a^R \exp(\mp e_0\psi/kT)\,2r\,\mathrm{d}r. \tag{54}$$

In eqs. (51)–(54), N_{A} is the Avogadro number, C_{p} and C_{s} are the equivalent molar concentrations of the macroion and added salt, respectively, and C_+ is related to pM as shown

$$\mathrm{pM} = -\log C_+.$$

According to the cell model proposed by Katchalsky et al. [13], R in eqs. (53) and (54) is given by the relation

$$\frac{1}{b\pi R^2} = \frac{C_{\mathrm{p}}}{1000}N_{\mathrm{A}}.$$

3. Results

3.1. Titration curve of a linear lattice polyelectrolyte.

Numerical calculation is carried out by the procedure shown in fig. 1. First, a suitable value of the activity ratio, $a_-^{(l)}/a_0$ is chosen and initial values of ϕ ($= (e_0\psi^{(l)} - \Phi_{\mathrm{m}}^{(l)})/kT$) and C_+ are tentatively assigned as $\phi_0 = 0$ and $C_{+,0} = C_s$. Next, from eq. (4)′, the activity ratio, $a_{\mathrm{m}}^{(l)}/a$ is given by

$$a_{\mathrm{m}}^{(l)}/a_0 = C_{+,0}(a_-^{(l)}/a_0)\exp(\phi_0)(10)^{-\mathrm{pM}_0}. \tag{55}$$

Then, α, β, $P_{\mathrm{I}}(\epsilon_j, \epsilon_{j+k})$, Φ_- and Φ_{m} can be obtained as function of ϕ_0 and $C_{+,0}$, according to the expressions presented in section 2.

Values of C_+ and $\psi(a)$ are given numerically in terms of α and C_{s}, as follows. The solution of eq. (51) can be easily obtained by the Runge-Kutta-Gill method if C_+ and C_- are given. By an iteration method, suitable values of C_+ and C_- satisfying eq. (54) can be obtained when the values of C_{p} and C_{s} are given. Thus C_+, C_- and $\psi(a)$ can be defined numerically as functions of α and C_{s}.

According to eqs. (1)′–(4)′, the second approximation of ϕ, ϕ_1 is given by

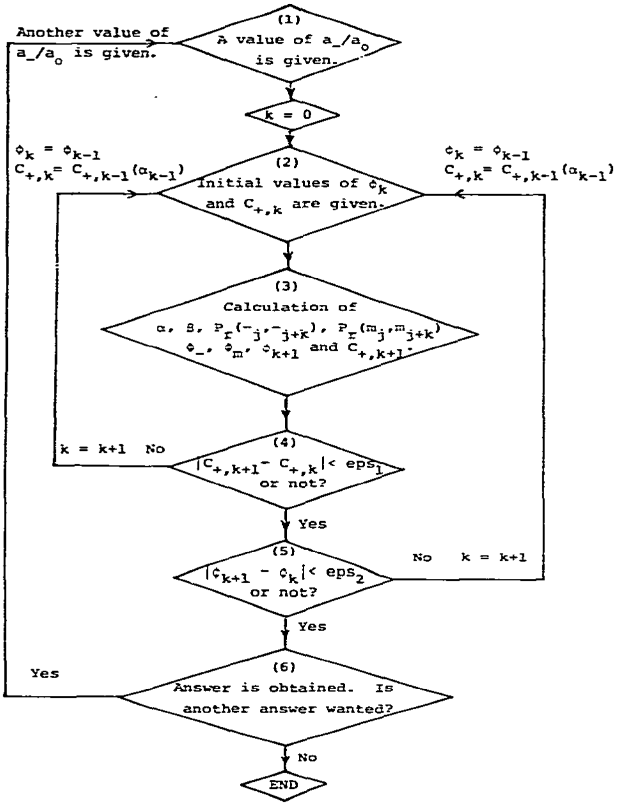

Fig. 1. Flow chart of the computation. Values of eps_1 and eps_2 give the allowable errors of the computation.

$$\phi_1 = (kT)^{-1}\left[\Phi^{(l)}_{-,0} - \frac{\alpha_0 e_0^2}{Db}\ln\left(\frac{Nb + \sqrt{N^2b^2 + a^2}}{a}\right) + e_0\psi_0(a) - \Phi^{(l)}_{m,0}\right], \tag{56}$$

where subscript 0 stands for the values obtained by the first step of the calculation as mentioned above. The next step of the calculation is carried out by using the values of ϕ_1 and $C_{+,1}$ (= $C_{+,1}(\alpha_0)$) for ϕ_0(= 0) and C_s, respectively. This process is repeated until the differences $|\phi_{k+1} - \phi_k|$ and $|C_{+,k+1} - C_{+,k}|$ become smaller than certain values which are indices of correctness.

The calculation was performed for various values of C_p and C_s at fixed values of $N = 100$, $T = 25°C$ and $D = 80$. The polyion was assumed to be represented by a linear lattice as described in section 2. At first, an equidistant array of ionizable groups was assumed with an interval b of 2.5 Å; later this assumption was refined by assigning values deduced from the most probable conformation of PAA. The radius of the rod, a, and the average distance between the ionized group and the bound cation, d, were used as adjustable parameters; their best values were found to be 10 Å and 5 Å, respectively.

If the dipole–dipole interaction between cation-bound sites is negligible, i.e., $\Phi_m = 0$, the calculation procedure can be simplified as follows. Instead of the ratio $a_-^{(l)}/a_0$, a new conditional value $a_-^{(l)}/(a_0 + a_m)$ is chosen, and α, $P_r(-_j, -_{j+k})$ and Φ_- are calculated, leading to the values of the ratio $a_m/(a_0 + a_m)$ as

$$a_m/(a_0 + a_m) = C_+[a_-^{(l)}/(a_0 + a_m)] \times \exp(e_0\psi^{(l)}/kT)(10)^{-\mathrm{pM}_0}. \tag{55$'$}$$

Thus the degree of the counterion binding, β, is obtained by use of eq. (50) as

$$\beta = \frac{a_m}{a_0 + a_m}(1 - \alpha),$$

and eq. (3)$'$ is rewritten as

$$\mathrm{pH} = \log\frac{a_-^{(l)}}{a_0 + a_m} - \log\left(1 - \frac{a_m}{a_0 + a_m}\right) + 0.4343\frac{e_0\psi^{(l)}}{kT} + \mathrm{pK}_0\ .$$

Typical examples of the calculation are shown in figs. 2 and 3, where $\Delta\mathrm{pK}_a = \mathrm{pH} - \log[\alpha_{\mathrm{app}}/(1 - \alpha_{\mathrm{app}})]$ and $\alpha_{\mathrm{app}}' = \alpha + \beta$. The calculation is carried out at $C_s = 10$ mN and at infinite dilution ($C_p \to 0$). The error of $\Delta\mathrm{pK}_a$ due to the computer calculation does not exceed 0.01 in each case. Fig. 2 shows a case where almost no cation is bound to the ionized group ($\mathrm{pM}_0 = -50$), whereas figs. 3 show a case where cation binding exists to some extent ($\mathrm{pM}_0 = -1.5$). The curves of the degree of the cation binding, β, versus the apparent degree of dissociation, α_{app}, are shown in fig. 4. In any case, the second and the third approximations give almost the same curve, although the curve for the first approximation is slightly different from the others, as shown in figs. 2–4. This fact indicates that the second or the third approximation is needed to describe the potentiometric titration behavior and the cation binding of polyelectrolyte solutions.

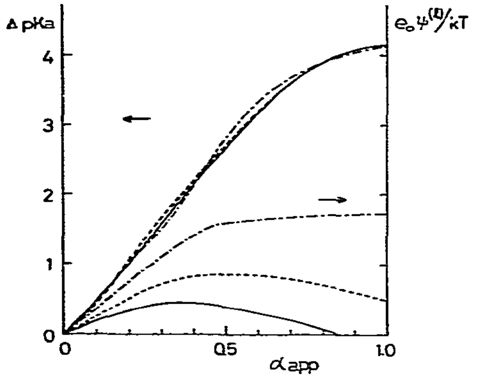

Fig. 2. Calculated apparent dissociation constant, ΔpK_a, and contribution of the long range interaction, $e_0\psi^{(l)}/kT$, to ΔpK_a as function of apparent degree of ionization, α_{app}, for the case of no counterion binding. —·—·—, first approximation; ------, second approximation; ———, third approximation. The following parameters are used in the calculation: $C_p \to 0$, $C_s = 10$ mN, $T = 25°C$, $D = 80$, $N = 100$ and $pM_0 = -50$.

Contribution of the long range interaction $e_0\psi/kT$ to ΔpK_a is indicated in fig. 2. The values of $e_0\psi/kT$ increase at first with α_{app}. Then, due to the shielding effect of counterions, the contribution of the long range interaction becomes almost constant with the first approximation, and decreases with the second and third approximations. Evidently, the term $e_0\psi/kT$ decreases in value with increasing degree of approximation. The term, however, cannot be neglected even in the case of the third approximation, as shown in fig. 2.

3.2. Comparison of the theory with the experiments

In the calculation of the potentiometric titration curve, local conformation of the polymer chain is assumed to be stretched so that the overall electrostatic energy may be minimum.

Bond lengths and bond angles of PAA used in the calculation are summarized in table 1 [21]. The local conformation of a syndiotactic PAA (PAA_s) is assumed to be characterized as (—t—t—t—t—) and that of an isotactic PAA (PAA_i) as ($—g^-—t—g^+—t—$). Here t, g^+ and g^- assign the internal rotation angles to 0°, 120° and −120°, respectively. These conformations indicate that two adjacent ionizable groups are separated as far as possible, and that the overall shape of the macromolecule is an extended rod.

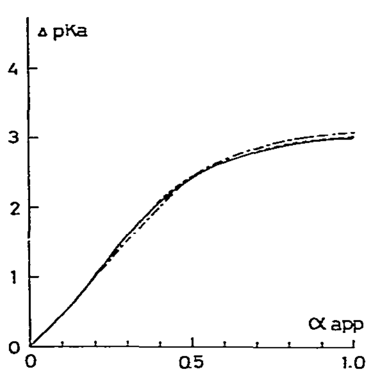

Fig. 3. Calculated apparent dissociation constant, ΔpK_a, for the case that cation binding exists to some extent. —·—·—, first approximation; ------, second approximation; ———, third approximation. The parameters used in the calculation are the same as those in fig. 2 except $pM_0 = -1.5$.

A section of a syndiotactic PAA in all-trans conformation is shown in fig. 5. The internal rotation angle around the bond between atoms *i* and *j* is designated by $R_{i,j}$, whose positive sense corresponds to that the atomic group bonded to atom *j* moves counterclockwise relative to the atomic group bonded to atom *i* when viewing from atom *i*. The backbone internal rotation angle is defined as 0 for the trans position. Since two oxygen atoms of a carboxyl group are considered to be equivalently ionized in the ionized state, two bond lengths, $C_{11}—O_{22}$ and $C_{11}—O_{23}$ shown in fig. 5-B, are assumed to be the same and the ionized site is assumed to be placed at the midpoint of the two oxygen atoms of the carboxyl group.

The distance between *n*-th and $(n+j)$-th ionizable groups, $r_{n,n+j}$ ($n = 1, 2$ and $j = 1 \ldots, 10$), and the average intervals of the ionizable groups projected to the polymer backbone, *b*, are computed for the conformations mentioned above. Table 2 shows the calculated

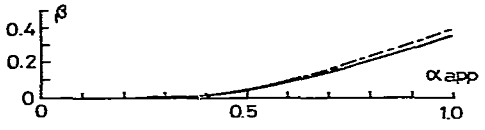

Fig. 4. Curves of the degree of counterion binding, β versus α_{app}. —·—·—, first approximation; ------, second approximation; ———, third approximation. In this figure, the curves for the second and third approximations coincide with each other.

Table 1
Bond lengths and bond angles of PAA_s

Bond	Bond length (Å)	Bond angle	Angle (deg.)
C_2-C_{21}	1.485	$C_1-C_2-C_3$	115
$C_{21}-O_{22}$	1.287	$C_2-C_3-C_4$	115
C_1-C_2	1.54	$C_1-C_2-C_{21}$	110

results of these values. Since the distance $r_{n,n+j}$ is independent of n, the matrices $M_i^{(l)}$ in eq. (28) are the same for any i, similar to the case of equidistant distribution of the ionizable groups.

The computation of the potentiometric titration curve for PAA_i and PAA_s is carried out according to the procedure presented in sections 2 and 3.1. A fairly good agreement of the calculated curves with the experimental results by Kawaguchi and Nagasawa [14], is obtained as shown in fig. 6. There are some discrepancies between the calculated curves and the experimental values at the low degree of ionization ($\alpha_{app} < 0.3$), due to the coiling of the polymer chain in this region. Namely, at low α, the entropy force which drives the polymer chain into a random coil, exceeds the repulsive force between the ionized groups.

The values of a, d and pM_0 used in the present calculation are 10 Å, 5 Å and −0.2, respectively, they provide the best agreement with experiment. These values correspond to a situation where the sum of the thickness of the hydration layers of the free counterion and the ionized group is 7 ~ 8 Å (= difference of the radius a and the distance of the ionized group from the axis of the rod), and indicates that the bound counterion destroys the outer part of the hydration layer but not the inner part whose thickness is 5 Å.

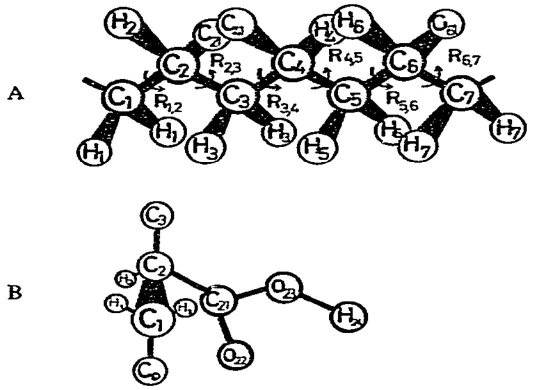

Fig. 5. A section of PAA_s in all-trans conformation. (A and B).

4. Discussion

Theoretically, the present equation describes the electrostatic nature of the polyelectrolyte solution very precisely. Lifson's theory [12] is amplified by clarifying the role of neighbor and long range interactions as well as the effect of ion binding. The effect of neighbor interactions is tested by comparing computations based on one neighbor, two neighbor and three neighbor interactions as described in section 3.1. Cation binding also provides some contribution to the titration profile.

Usually cation binding is understood as a result of ion condensation based on the theory of Oosawa [1, 15] as well as that of Manning [16]. In the present theory, however, the cation binding is treated in the same way as the association equilibrium between hydrogen ions and polyion in order to construct the grand partition function. Effect of the electrostatic potential is introduced by modifying the form of the chemical

Table 2
The distance between the ionizable groups for PAA

	h										
	1	2	3	4	5	6	7	8	9	10	b
$r_{i,i+h}$ (Å) for PAA_i	4.34	5.76	6.57	9.53	11.58	13.15	15.79	17.92	19.72	22.23	2.21
$r_{i,i+h}$ (Å) for PAA_s	4.34	5.20	8.53	10.39	13.45	15.59	18.51	20.78	23.64	25.98	2.60

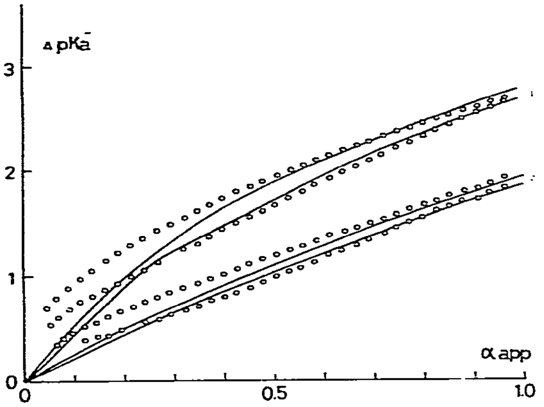

Fig. 6. Potentiometric titration curves of PAA_i and PAA_s. Open circles show experimental data obtained by Kawaguchi and Nagasawa [14], and solid lines are the calculated results for the second approximation. Salt concentrations: 1, 10 mN; 2, 100 mN. Upper and lower curves or circles correspond to PAA_i and PAA_s, respectively.

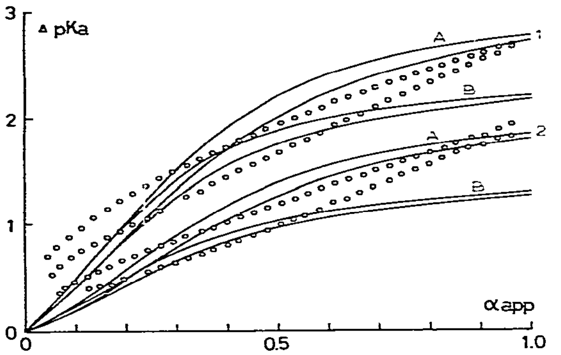

Fig. 7. Calculated potentiometric titration curves when neglecting the dipole–dipole interaction. Open circles show experimental data [14], and solid lines are the calculated results. Parameters used in the calculations are: a = 7 Å; pM_0 = −1.3 (A), −0.6 (B); and C_s = 10 mN (1), 100 mN (2). Upper and lower curves or circles correspond to PAA_i and PAA_s, respectively.

potential of the cation-bound site. Numerical values of the cation binding are approximately the same as those obtained by the ion condensation theories.

As a secondary effect of the cation binding, the dipole–dipole interaction cannot be neglected. Fig. 7 shows a typical result when dipole–dipole interaction is neglected in the computation. The theoretical curves have larger curvatures than the experimental ones. This discrepancy suggests that the dipole moment formed by an ion-pair of the bound counterion and the ionized group is large enough to affect the binding of another counterion.

The fact that the most suitable value for d is 5 Å for PAA means that counterion is bound loosely to the carboxyl group. As a result, the bound counterion is mobile in the vicinity of the ionizable group, which induces a large dipole moment along the polymer skeleton when applying an external field [16–19].

Recently, the ^{23}Na chemical shift observed in Na-PAA solution was found to vary with the degree of neutralization [20]. These NMR data indicate the existence of bound counterions. Variation of the ^{23}Na chemical shift with the degree of neutralization is consistent with estimates of counterion binding calculated by use of the present theory. This is shown in fig. 8. However, the concept of counterion binding is somewhat ambiguous in the present theory. It means that

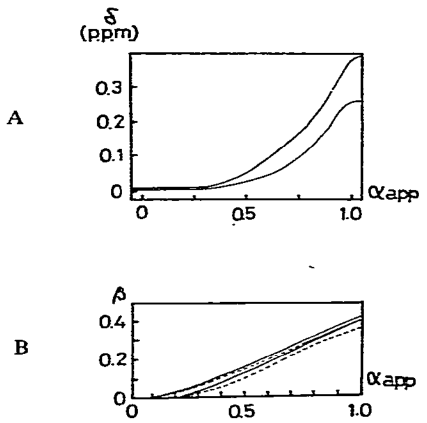

Fig. 8. A. Variation of the ^{23}Na chemical shift as a function of α_{app} obtained by Gustavsson et al. [20]. Polymer concentration (C_p) and sodium ion concentration (C_{Na^+}) are: C_p = 0.88 N, C_{Na^+} = 0.11 N (1); C_p = 0.25 N, C_{Na^+} = 0.30 N (2). Details of the experimental conditions are described in ref. [20]. B. Calculated degree of counterion binding, β, as a function of α_{app} for PAA_i (——) and PAA_s (- - - -) by use of the present theory. Upper and lower curves are those for C_s = 100 mN and C_s = 10 mN, respectively. Other parameters used in the calculation are the same as those in the calculation of the potentiometric titration curves in fig. 6.

the energy state of the counterion in the vicinity of the ionized group is different from that in the bulk of the solution, due mainly to the coulombic interaction between them. Also other factors such as changes in hydration around the ion and the ionized group should be considered carefully in evaluating the equilibrium constant and other related quantities.

In the present theory, precise description of the titration behavior is a result of the introduction of several parameters such as a, d and pM_0. The effective radius of the polymer chain, a, and the distance between the bound counterion and the ionized group, d, cannot be determined precisely by any experiment at present. These parameters need to be adjusted by use of the experimental data obtained from both pH and pM measurements. In this paper, the values of these parameters are chosen as described in section 3, since no experimental data are available for the values of pM in $\mathrm{PAA_i}$ and $\mathrm{PAA_s}$.

It should be noted that eq. (3)′ for the 0-th approximation coincides with the equation proposed by Kotin and Nagasawa [2], when no counterion is bound to the ionized group and the following relation is satisfied,

$$\sum_{|j-i|=1}^{N} \frac{e_0^2}{r_{i,j}} = \frac{e_0^2}{Db} \ln\left(\frac{Nb+\sqrt{N^2b^2+a^2}}{a}\right) \quad \text{for } N \gg 1.$$

This fact indicates that the equation derived from the smeared charge model is in accordance with an approximation of the present theory. The present theory may be more appropriate to study the nature of the short range interaction of the ionizable groups of the polyion

Acknowledgment

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Appendix I

The explicit expressions of $a^{(l)}$ and $M^{(l)}$ from $l = 1$ to $l = 3$ are shown in this appendix. For brevity, the following quantities are defined,

$$a_\epsilon = a_{\epsilon_i}, \qquad u_{\epsilon,\epsilon} = u_{\epsilon_i,\, \epsilon_{i+1}},$$
$$u_{\epsilon,\epsilon,\epsilon} = \prod_{h=1}^{2} u_{\epsilon_i,\epsilon_{i+h}}, \qquad u_{\epsilon,\epsilon,\epsilon,\epsilon} = \prod_{h=1}^{3} u_{\epsilon_i,\epsilon_{i+h}} \tag{I-1}$$

Then $a_l^{(l)}$ can be written as

$$\boldsymbol{a}_1^{(1)} = \begin{bmatrix} a_- \\ a_0 \\ a_\mathrm{m} \end{bmatrix}, \qquad \boldsymbol{a}_2^{(2)} = \begin{bmatrix} u_{--}a_-^2 \\ u_{-0}a_-a_0 \\ u_{-\mathrm{m}}a_-a_\mathrm{m} \\ u_{0-}a_0a_- \\ u_{00}a_0^2 \\ u_{0\mathrm{m}}a_0a_\mathrm{m} \\ u_{\mathrm{m}-}a_\mathrm{m}a_- \\ u_{\mathrm{m}0}a_\mathrm{m}a_0 \\ u_{\mathrm{mm}}a_\mathrm{m}^2 \end{bmatrix} \qquad \boldsymbol{a}_3^{(3)} = \left[\begin{matrix} u_{---}a_-^3 \\ u_{--0}a_-^2a_0 \\ u_{--\mathrm{m}}a_-^2a_\mathrm{m} \\ u_{-0-}a_-^2a_0 \\ u_{-00}a_-a_0^2 \\ u_{-0\mathrm{m}}a_-a_0a_\mathrm{m} \\ u_{-\mathrm{m}-}a_-^2a_\mathrm{m} \\ u_{-\mathrm{m}0}a_-a_\mathrm{m}a_0 \\ u_{-\mathrm{mm}}a_-a_\mathrm{m}^2 \\ u_{0--}a_0a_-^2 \\ u_{0-0}a_-a_0^2 \\ u_{0-\mathrm{m}}a_0a_-a_\mathrm{m} \\ u_{00-}a_0^2a_- \\ u_{000}a_0^3 \end{matrix}\right. \left.\begin{matrix} u_{00\mathrm{m}}a_0^2a_\mathrm{m} \\ u_{0\mathrm{m}-}a_0a_\mathrm{m}a_- \\ u_{0\mathrm{m}0}a_0^2a_\mathrm{m} \\ u_{0\mathrm{mm}}a_0a_\mathrm{m}^2 \\ u_{\mathrm{m}--}a_\mathrm{m}a_-^2 \\ u_{\mathrm{M}-0}a_\mathrm{m}a_-a_0 \\ u_{\mathrm{m}-\mathrm{m}}a_\mathrm{m}^2a_- \\ u_{\mathrm{m}0-}a_\mathrm{m}a_0a_- \\ u_{\mathrm{m}00}a_\mathrm{m}a_0^2 \\ u_{\mathrm{m}0\mathrm{m}}a_\mathrm{m}^2a_0 \\ u_{\mathrm{mm}-}a_\mathrm{m}^2a_- \\ u_{\mathrm{mm}0}a_\mathrm{m}^2a_0 \\ u_{\mathrm{mmm}}a_\mathrm{m}^3 \end{matrix}\right] \tag{I-2}$$

If the dipole–dipole and dipole–ion interactions are neglected ($u_{\mathrm{m}_i,\mathrm{m}_{i+h}} = u_{\mathrm{m}_i,0_{i+h}} = u_{0_i,\mathrm{m}_{i+h}} = 1$), the dimensions of column vectors can be reduced and eq. (I-2) can be rewritten in a simplified form as

$$\boldsymbol{a}_1^{(1)} = \begin{bmatrix} a_- \\ a_0 + a_\mathrm{m} \end{bmatrix} \qquad \boldsymbol{a}_2^{(2)} = \begin{bmatrix} u_{--}a_0^2 \\ u_{-0}a_-(a_0 + a_\mathrm{m}) \\ u_0(a_0 + a_\mathrm{m})a_- \\ u_{00}(a_0 + a_\mathrm{m})^2 \end{bmatrix} \qquad \boldsymbol{a}_3^{(3)} = \begin{bmatrix} u_{---}a_-^3 \\ u_{--0}a_-^2(a_0 + a_\mathrm{m}) \\ u_{-0-}a_-(a_0 + a_\mathrm{m}) \\ u_{-00}a_-(a_0 + a_\mathrm{m})^2 \\ u_{0--}a_-^2(a_0 + a_\mathrm{m}) \\ u_{0-0}a_-(a_0 + a_\mathrm{m})^2 \\ u_{00-}(a_0 + a_\mathrm{m})^2a_- \\ u_{000}(a_0 + a_\mathrm{m})^3 \end{bmatrix} \tag{I-3}$$

where the relation, $u_{\epsilon,\mathrm{m}} = u_{\epsilon,0}$ and so on, are used. According to these expressions of $\boldsymbol{a}^{(l)}$, $\boldsymbol{M}^{(l)}$ can also be defined as

$$M^{(1)} = \begin{bmatrix} a_-u_{--} & a_-u_{-0} & a_-u_{-m} \\ a_0u_{0-} & a_0u_{00} & a_0u_{0m} \\ a_mu_{m-} & a_mu_{m0} & a_mu_{mm} \end{bmatrix}$$

$$M^{(2)} = \begin{bmatrix} a_-u_{---} & a_-u_{--0} & a_-u_{--m} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & a_-u_{-0-} & a_-u_{-00} & a_-u_{-0m} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & a_-u_{-m-} & a_-u_{-m0} & a_-u_{-mm} \\ a_0u_{0--} & a_0u_{0-0} & a_0u_{0-m} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & a_0u_{00-} & a_0u_{000} & a_0u_{00m} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & a_0u_{0m-} & a_0u_{0m0} & a_0u_{0mm} \\ a_mu_{m--} & a_mu_{m-0} & a_mu_{m-m} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & a_mu_{m0-} & a_mu_{m00} & a_mu_{m0m} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & a_mu_{mm-} & a_mu_{mm0} & a_mu_{mmm} \end{bmatrix} \qquad \text{(II-A-4)}$$

Here the expression of $M^{(3)}$ is omitted, since the dimension of $M^{(3)}$ is too large (27-th) to write down explicitly. The matrices, when neglecting the dipole–dipole and dipole–ion interactions, are expressed as

$$M^{(1)} = \begin{bmatrix} a_-u_{--} & a_-u_{-0} \\ (a_0+a_m)u_{0-} & (a_0+a_m)u_{00} \end{bmatrix}$$

$$M^{(2)} = \begin{bmatrix} a_-u_{---} & a_-u_{--0} & 0 & 0 \\ 0 & 0 & a_-u_{-0-} & a_-u_{-00} \\ (a_0+a_m)u_{0--} & (a_0+a_m)u_{0-0} & 0 & 0 \\ 0 & 0 & (a_0+a_m)u_{00-} & (a_0+a_m)u_{000} \end{bmatrix}$$

$$M^{(3)} = \begin{bmatrix} a_-u_{----} & a_-u_{---0} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & a_-u_{--0-} & a_-u_{--00} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & a_-u_{-0--} & a_-u_{-0-0} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & a_-u_{-00-} & a_-u_{-000} \\ (a_0+a_m)u_{0---} & (a_0+a_m)u_{0--0} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & (a_0+a_m)u_{0-0-} & (a_0+a_m)u_{0-00} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & (a_0+a_m)u_{00--} & (a_0+a_m)u_{00-0} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & (a_0+a_m)u_{000-} & (a_0+a_m)u_{0000} \end{bmatrix} \qquad \text{(I-5)}$$

Appendix II

Eqs. (33), (37), (38) and (39) can be easily transformed into the following expressions of the 0-th, 1-st, 2-nd and 3-rd approximations, respectively. For simplicity, hereafter we omit the superscripts showing the order of approximation.

II-A. The 0-th approximation

In the 0-th approximation all the neighbor interactions are neglected in the calculation of the grand partition function. Then

$$\Xi_p = \sum_{\nu}^{p} \sum_{\omega}^{(p-\nu)} \frac{P!}{\nu!\omega!(P-\nu-\omega)!} a_-^{\nu} a_0^{\omega} a_{\mathrm{m}}^{(P-\nu-\omega)} = (a_- + a_0 + a_{\mathrm{m}})^P \tag{II-A-1}$$

Therefore α and β can be easily obtained as

$$\alpha \equiv P_{\mathrm{r}}(-_j) = \frac{a_-}{P} \frac{\partial \ln \Xi_p}{\partial a_-} = \frac{a_-}{a_- + a_0 + a_{\mathrm{m}}}, \qquad \beta \equiv P_{\mathrm{r}}(\mathrm{m}_j) = \frac{a_{\mathrm{m}}}{P} \frac{\partial \ln \Xi_p}{\partial a_{\mathrm{m}}} = \frac{a_{\mathrm{m}}}{a_- + a_0 + a_{\mathrm{m}}}. \tag{II-A-2}$$

On the other hand, eq. (38) can be given by

$$\begin{aligned} P_{\mathrm{r}}(-_j, -_{j+k}) = (\Xi_p)^{-1} & \sum_{\nu_1}^{P_1} \sum_{\omega_1}^{(P_1-\nu_1)} \frac{P_1!}{\nu_1!\omega_1!(P_1-\nu_1-\omega_1)!} a_-^{\nu_1} a_0^{\omega_1} a_{\mathrm{m}}^{(P_1-\nu_1-\omega_1)} \\ \times & \sum_{\nu_2}^{(k-1)} \sum_{\omega_2}^{(k-1-\nu_2)} \frac{(k-1)!}{\nu_2!\omega_2!(k-1-\nu_2-\omega_2)!} a_-^{\nu_2} a_0^{\omega_2} a_{\mathrm{m}}^{(k-1-\nu_2-\omega_2)} \\ \times & \sum_{\nu_3}^{P_2} \sum_{\omega_3}^{(P_2-\nu_3)} \frac{P_2!}{\nu_3!\omega_3!(P_2-\nu_3-\omega_3)!} a_-^{\nu_3} a_0^{\omega_3} a_{\mathrm{m}}^{(P_2-\nu_3-\omega_3)}, \end{aligned} \tag{II-A-3}$$

that is

$$P_{\mathrm{r}}(-_j, -_{j+k}) = \left(\frac{a_-}{a_- + a_0 + a_{\mathrm{m}}}\right)^2 = \alpha^2,$$

where $P_1 = P - j - k$ and $P_2 = j - 1$. From eqs. (II-A-2) and (II-A-3), the activity ratios a_-/a_0 and a_-/a_{m} can be derived as

$$a_-/a_0 = \alpha/(1 - \alpha - \beta), \tag{II-A-4}$$

$$a_-/a_{\mathrm{m}} = \alpha/\beta. \tag{II-A-5}$$

By use of eqs. (II-A-4) and (II-A-5), eqs. (3)′ and (4)′ can be rewritten as

$$\mathrm{pH} = \mathrm{pK}_0 + \log \frac{\alpha}{1 - \alpha - \beta} + 0.4343\, e_0\psi/kT, \tag{II-A-6}$$

and

$$\mathrm{pM} = \mathrm{pM}_0 + \log \alpha/\beta + 0.4343\, (e_0\psi/kT - \Phi_{\mathrm{m}}/kT), \tag{II-A-7}$$

where

$$e_0\psi = 2\alpha\left\{\sum_{j-i=1}^{j-i=N} \frac{e_0^2}{Dr_{i,j}} - \frac{e_0^2}{Db}\ln\left(\frac{Nb+\sqrt{N^2b^2+a^2}}{a}\right)\right\} + e_0\psi(a),$$

$$\Phi_{\mathrm{m}} = 2\beta \sum_{j-i=1} (e_0 d)^2/Dr_{i,j}^3 .$$

If no metal binding occurs, eq. (II-A-7) can be expressed in the form of the familiar equation of potentiometric titration as

$$\mathrm{pH} = \mathrm{pK}_0 + \log\frac{\alpha}{1-\alpha} + 0.4343\ \Delta\mathrm{Gel}/kT \qquad \text{(II-A-8)}$$

where

$$\Delta\mathrm{Gel} = e_0\psi .$$

II-B. The 1-st approximation

The higher order approximations are a little more complicated, since the neighbor interactions are contained in the grand partition function. Let λ_1 be the maximum eigenvalue of $\boldsymbol{M}$; then we can rewrite eq. (33) by considering that P is large enough to maintain the relation $\lambda_1^p \gg \lambda_2^p$ and $\lambda_1^p \gg \lambda_3^p$, to obtain the following expression

$$\Xi_p = \lambda_1^{p-1} \sum_{i=1}^{3} t_{i,1} \sum_{j=1}^{3} t_{1,1}^{-1} a_j , \qquad \text{(II-B-1)}$$

where $t_{i,j}$, $t_{k,l}^{-1}$ and a_i are the i,j-th component of the matrix $\boldsymbol{T}$, the k,l-th component of the matrix $\boldsymbol{T}^{-1}$ and the i-th component of the column vector $\boldsymbol{a}_1$. In a similar manner, eq. (35) can be rewritten as

$$\alpha \equiv P_{\mathrm{r}}(-_j) = t_{1,1}^{-1} t_{1,1}, \qquad \beta \equiv P_{\mathrm{r}}(\mathrm{m}_j) = t_{1,3}^{-1} t_{3,1} \qquad \text{(II-B-2)}$$

and

$$\begin{aligned} P_{\mathrm{r}}(-_j, -_{j+k}) &= \sum_{s=1}^{3} t_{1,1}^{-1} t_{1,s} \left(\frac{\lambda_s}{\lambda_1}\right)^k t_{s,1}^{-1} t_{1,1}, \\ P_{\mathrm{r}}(\mathrm{m}_j, \mathrm{m}_{j+k}) &= \sum_{s=1}^{3} t_{1,3}^{-1} t_{3,s} \left(\frac{\lambda_s}{\lambda_1}\right)^k t_{s,3}^{-1} t_{3,1} . \end{aligned} \qquad \text{(II-B-3)}$$

II-C. The 2-nd and the 3-rd approximation

By a similar procedure to the 1-st approximation we can easily obtain expressions of eqs. (33), (37) and (38), which are more adapted to numerical calculation. Final results are expressed by the following equations.

$$\Xi_p^{(2)} = \lambda_1^{p-2} \sum_{i=1}^{9} t_{i,1} \sum_{j=1}^{9} t_{1,j}^{-1} a_j , \qquad \text{(II-C-1)}$$

$$\alpha \equiv P_{\mathrm{r}}(-_j) = \sum_{i=1}^{3} t_{1,i}^{-1} t_{i,j}, \qquad \beta \equiv P_{\mathrm{r}}(\mathrm{m}_j) = \sum_{i=7}^{9} t_{1,i}^{-1} t_{i,1}, \qquad \text{(II-C-2)}$$

$$
\begin{aligned}
P_{\mathrm{r}}(-_j, -_{j+k}) &= \sum_{s=1}^{9} \left(\frac{\lambda_s}{\lambda_1}\right)^k \sum_{q=1}^{3} t_{1,q}^{-1} t_{q,s} \sum_{r=1}^{3} t_{s,r}^{-1} t_{r,1}, \\
P_{\mathrm{r}}(\mathrm{m}_j, \mathrm{m}_{j+k}) &= \sum_{s=1}^{9} \left(\frac{\lambda_s}{\lambda_1}\right)^k \sum_{q=7}^{9} t_{1,q}^{-1} t_{q,s} \sum_{r=7}^{9} t_{s,r}^{-1} t_{r,1},
\end{aligned}
\qquad \text{(II-C-3)}
$$

where the notations are the same as those in eqs. (II-B-1)—(II-B-3) except that the superscript represents the degree of the approximation. Also

$$
\Xi_p^{(3)} = \lambda_1^{p-3} \sum_{i=1}^{27} t_{i,1} \sum_{j=1}^{27} t_{1,j}^{-1} a_j, \qquad \text{(II-C-4)}
$$

$$
\alpha \equiv P_{\mathrm{r}}(-_j) = \sum_{i=1}^{9} t_{1,i}^{-1} t_{i,1}, \qquad \beta \equiv P_{\mathrm{r}}(\mathrm{m}_j) = \sum_{i=19}^{27} t_{1,t}^{-1} t_{i,1}, \qquad \text{(II-C-5)}
$$

$$
\begin{aligned}
P_{\mathrm{r}}(-_j, -_{j+k}) &= \sum_{s=1}^{27} \left(\frac{\lambda_s}{\lambda_1}\right)^k \sum_{q=1}^{9} t_{1,q}^{-1} t_{q,s} \sum_{r=1}^{9} t_{s,r}^{-1} t_{r,1}, \\
P_{\mathrm{r}}(\mathrm{m}_j, \mathrm{m}_{j+k}) &= \sum_{s=1}^{27} \left(\frac{\lambda_s}{\lambda_1}\right)^k \sum_{q=19}^{27} t_{1,q}^{-1} t_{q,s} \sum_{r=19}^{27} t_{s,r}^{-1} t_{r,s}.
\end{aligned}
\qquad \text{(II-C-6)}
$$

II-D. The case of neglecting the dipole—dipole and dipole—ion interaction.

If the dipole—dipole and dipole—ion interactions are neglected, the expressions of eqs. (II-B-1)—(II-C-6) are slightly simplified as follows. Eqs. (II-B-1)—(II-B-3) for expressing the first approximation are rewritten as

$$
\Xi_p = \lambda_1^{p-1} \sum_{i=1}^{2} t_{i,1} \sum_{j=1}^{2} t_{i,j}^{-1} a_j, \qquad \text{(II-D-1)}
$$

$$
\alpha \equiv P_{\mathrm{r}}(-_j) = t_{1,1}^{-1} t_{1,1}, \qquad \text{(II-D-2)}
$$

$$
P_{\mathrm{r}}(-_j, -_{j+k}) = \sum_{s=1}^{2} t_{1,1}^{-1} t_{1,s} \left(\frac{\lambda_s}{\lambda_1}\right)^k t_{s,1}^{-1} t_{1,1}. \qquad \text{(II-D-3)}
$$

And eqs. (II-C-1)—(II-C-6) are also reduced to

$$
\Xi_p^{(2)} = \lambda_1^{p-2} \sum_{i=1}^{4} t_{i,1} \sum_{j=1}^{4} t_{1,j}^{-1} a_j, \qquad \text{(II-D-4)}
$$

$$
\alpha \equiv P_{\mathrm{r}}(-_j) = \sum_{i=1}^{2} t_{1,i}^{-1} t_{i,1}, \qquad \text{(II-D-5)}
$$

$$
P_{\mathrm{r}}(-_j, -_{j+k}) = \sum_{s=1}^{4} \left(\frac{\lambda_s}{\lambda_1}\right)^k \sum_{q=1}^{2} t_{1,q}^{-1} t_{q,s} \sum_{r=1}^{2} t_{s,r}^{-1} t_{r,1}, \qquad \text{(II-D-6)}
$$

$$
\Xi_p^{(3)} = \lambda_1^{p-3} \sum_{i=1}^{8} t_{i,1} \sum_{j=1}^{8} t_{1,j}^{-1} a_j, \qquad \text{(II-D-7)}
$$

$$\alpha \equiv P_{\mathrm{I}}(-_{j}) = \sum_{i=1}^{4} t_{1,i}^{-1}\, t_{i,1}, \tag{II-D-8}$$

$$P_{\mathrm{I}}(-_{j}, -_{j+k}) = \sum_{s=1}^{8} \left(\frac{\lambda_s}{\lambda_1}\right)^{k} \sum_{q=1}^{4} t_{1,q}^{-1}\, t_{q,s} \sum_{r=1}^{4} t_{s,r}^{-1}\, t_{r,1}. \tag{II-D-9}$$

The equivalence of eq. (II-D-2) to Lifson's equation (eq. (49) of ref. [12]) can be shown as follows. From the relation between the components of *M*, eigenvalues and eigenvectors, the following equation can be derived

$$t_{1,1} t_{1,1}^{-1} = (a_{-} u_{--} - \lambda_2)/(\lambda_1 - \lambda_2). \tag{II-D-10}$$

Also the relations between the eigenvalues and the matrix elements are given as

$$\lambda_1 + \lambda_2 = u_{--} a_{-} + u_{00}(a_0 + a_{\mathrm{m}}), \qquad \lambda_1 \cdot \lambda_2 = a_{-}(u_{--} u_{00} - u_{-0} u_{0-})(a_0 + a_{\mathrm{m}}). \tag{II-D-11}$$

Then by using eqs. (II-D-2) and (II-D-10)–(II-D-11) the following relations are obtained,

$$\frac{(1-2\alpha)^2}{\alpha(1-\alpha)} = \frac{\{u_{--} a_{-} - u_{00}(a_0 + a_{\mathrm{m}})\}^2}{u_{-0} u_{0-} a_{-}(a_0 + a_{\mathrm{m}})}. \tag{II-D-12}$$

Eq. (II-D-12) can be easily reduced to Lifson's equation (49) [12].

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