The Interaction of a Neutral Polymer with Small Ions in Solution. I. A Method for the Analysis of Ion Binding to a Neutral Polymer

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(Received October 28, 1981)

A method for the analysis of ion binding to a neutral polymer, such as poly(oxyethylene) (POE), based on the one-dimensional lattice model has been proposed. The grand partition function for the one-dimensional lattice has been given by the product of the statistical weight matrix. Interaction between the ions bound to the lattice points has been well approximated by the Debye-Hückel pair-by-pair potential, and the distance between the bound ions has been assumed to be the root mean square end-to-end distance of the partial chain. Based on the model, an equilibrium constant has been defined which is referred to the *binding constant.*

It has been well known that a neutral polymer, such as poly(oxyethylene) (POE), forms complexes with a variety of metal salts in organic solvents.[1-6] In our previous paper,[6] we have given a method for elucidating the quantitative aspects of the ion binding to POE by means of conductometry. This method, which is based on a discrete site-binding model, enables us to calculate the minimum separation between two adjacent bound charges as a function of the ionic strength. The stoichiometry of the potassium ion complex in a methanol solution was determined to be four monomer units per ion from the intrinsic value of the charge separation at a high concentration limit.

The next important step in the investigation is the interpretation of the binding behavior in terms of the electrostatic potential set up by bound cations. The investigation along this line has been developed extensively for the potentiometric titration of polyacid,[7] but, because of the high charge density on the polymer chain, the straightforward application of the screened Debye-Hückel potential fails to reproduce the experimental titration curves in most cases. For the POE–salt systems, however, the charge density on a polymer chain is far lower than in the cases of typical polyelectrolyte systems. Thus the electrostatic interaction can be expected to be represented by the sum of the Debye-Hückel pair-by-pair interactions between bound cations.

In this paper, we propose a method for analyzing ion binding to POE based on the one-dimensional lattice model. It is therein assumed that a lattice point is composed of four monomer units; that is to say, a bound cation is surrounded by four ether-oxygen atoms.[6] The grand partition function for the one-dimensional lattice is expressed by means of a matrix method. In calculating the Debye-Hückel pair-by-pair potential, the distance between bound cations is approximated by the root mean square end-to-end distance of the partial chain, which is given by the Porod-Kratky model. The concrete application of the method will be discussed in the following paper.[8]

Treatment of Binding Equilibria. It can be considered that there are three approaches to treat the binding equilibria of linear polymer and small ions in solutions.

The first approach is to treat the equilibrium as a usual chemical equilibrium, regarding each polymer and its complexes as a different chemical species. In general, however, a ligand containing n sites can be completely characterized by $2^{n-1}n$ equilibrium constants.[9] For a very large n, an infinite number of species must be considered, and the problems becomes quite complicated and no effective results are obtained. Therefore, we must abandon this approach.

The second approach is to assume that binding sites supposed to be arranged on a polymer chain are uniformly distributed in the solution and behaved like low-molecular ligand; this is the so called *low-molecular analogy*. Many workers in this field have used this approach, but it has several defects. The assumption of a uniform distribution of binding sites becomes less tenable as the solution is more dilute, since the binding sites are connected with one another on a polymer chain. Next, since all the thermodynamic quantities are usually defined as adopting an infinite dilution as the reference state, these quantities, including the equilibrium constant, have an ambiguous physical meaning in the case of these polymer systems. In dilute solutions, the interaction between bound ions are, in general, greater than those between unbound ones. As a result, a marked anti-cooperativity appears on ion binding. In this approach, therefore, the equilibrium constant does not only depend intensely on the concentrations of the polymer and of the ion, but also has itself an ambiguous physical meaning, whereas the treatment is very easy. An example will be discussed in the following paper.[8]

The third approach is to regard the polymer chain as a one-dimensional lattice and to consider the binding equilibrium as the equilibrium between the *bulk* solution and the lattice (*one-dimensional lattice model*). The equilibrium constant can be defined as a measure of the tendency of the occupation of the lattice points, as will be discussed below, and the equilibrium constant has no ambiguity in its physical meaning, unlike the equilibrium in low-molecular analogy. If the interaction between the ions occupying the lattice points can be estimated by any method, analysis can be performed without difficulty. This approach, which keeps of the connectivity of the polymer, seems to be the most appropriate. Liem *et al.*[7] analyzed the potentiometric titration curves of polyacid using this approach, but they confused the one-dimensional lattice model with the low-molecular analogy throughout their discussion. In this paper, we overcome this type of confusion and develop a systematic discussion based on the one-dimensional lattice model.

The One-dimensional Lattice Model. We consider a one-dimensional lattice having N lattice points, where the total energy of the system may be expressed by the following equation:

$$\Phi(N,M) = \sum_{i=1}^{N} E\sigma_i + \sum_{i=1}^{N}\sum_{j=i+1}^{N} J_{ij}\sigma_i\sigma_j, \quad (1)$$

$$M = \sum_{i=1}^{N} \sigma_i, \quad (2)$$

where E is the binding energy; J_{ij}, the interaction energy between the particles occupying the ith and jth lattice points, and σ_i, the index whose value is 1 or 0 when the ith lattice point is occupied or unoccupied respectively. Thus, the partition function of the system is given by:

$$Z(N,M) = \sum_{\text{all}} \exp[-\Phi(N,M)/RT], \quad (3)$$

where $\sum_{\text{all}}$ means the summation over all the states in which M out of N lattice points are occupied. Introducing the chemical potential, μ, of the particle, we have the grand partition function given by:

$$\Xi = \sum_{M=0}^{N} Z(N,M)\exp(M\mu/RT). \quad (4)$$

Now we alter the form of Eq. 3 to:

$$Z(N,M) = \exp(-ME/RT) \times \sum_{\text{all}} \exp\left(-\sum_{i=1}^{N}\sum_{j=i+1}^{N} J_{ij}\sigma_i\sigma_j/RT\right). \quad (5)$$

If we define the normalized activity of the particle as:

$$\xi = \exp[(\mu-E)/RT], \quad (6)$$

then Eq. 4 becomes:

$$\Xi = \sum_{M=0}^{N} \xi^M \sum_{\text{all}} \exp\left(-\sum_{i=1}^{N}\sum_{j=i+1}^{N} J_{ij}\sigma_i\sigma_j/RT\right). \quad (7)$$

If we calculate Ξ, then the degree of binding, that is, probability that a lattice point is occupied, will be given by:

$$\theta = \frac{RT}{N}\frac{\partial \ln \Xi}{\partial \mu} = \frac{1}{N}\frac{\partial \ln \Xi}{\partial \ln \xi}. \quad (8)$$

Calculation of the Grand Partition Function by the Matrix Method. It is actually impossible to calculate the grand partition function straightforwardly using Eq. 7, particularly in the case of a very large N, so we shall use the matrix method as follows.

Let us first truncate the range of the interaction, supposing that, for a positive integer, k:

$$J_{ij} = \begin{cases} -RT\ln A_m, & \text{for } m \equiv j-i \leqslant k. \\ 0, & \text{for } j-i > k. \end{cases} \quad (9)$$

Thus, Ξ is given by the product of a statistical weight matrix:[7]

$$\Xi = \boldsymbol{e}\boldsymbol{U}_k^N \boldsymbol{e}', \quad (10)$$

where $\boldsymbol{e}$ and $\boldsymbol{e}'$ are the end vectors, as follows:

$$\boldsymbol{e} = (1,1,\cdots,1), \quad \boldsymbol{e}' = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}.$$

$\boldsymbol{U}_k$ is a statistical weight matrix with dimensions of $2^k \times 2^k$, as follows:

For $k=1$,

$$\boldsymbol{U}_1 = \begin{pmatrix} 1 & 1 \\ \xi & \xi A_1 \end{pmatrix}.$$

For $k=2$,

$$\boldsymbol{U}_2 = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ \xi & \xi A_2 & 0 & 0 \\ 0 & 0 & \xi A_1 & \xi A_1 A_2 \end{pmatrix}.$$

For $k=3$,

$$\boldsymbol{U}_3 = \begin{pmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ \xi & \xi A_3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \xi A_2 & \xi A_2 A_3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \xi A_1 & \xi A_1 A_3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \xi A_1 A_2 & \xi A_1 A_2 A_3 \end{pmatrix}.$$

Similarly, $\boldsymbol{U}_k$ can be expressed for $k>3$.

Equation 8 can be rewritten in the following form in obtaining θ:

$$\theta = \frac{\xi}{\Xi}\frac{\partial \Xi}{\partial \xi} = \frac{\xi \sum_{m=0}^{N-1} \boldsymbol{e}\,\boldsymbol{U}_k^m\,\boldsymbol{U}_k'\,\boldsymbol{U}_k^{N-m-1}\boldsymbol{e}'}{\boldsymbol{e}\,\boldsymbol{U}_k^N\,\boldsymbol{e}'}, \quad (11)$$

where

$$\boldsymbol{U}_k' = \frac{\partial \boldsymbol{U}_k}{\partial \xi}.$$

The values of θ can be calculated with a computer using the method of Jernigan.[10] The above method, which is based on the one-dimensional lattice model, follows the method discussed by Liem *et al.*[7] Since, However, a few mistakes regarding thermodynamics appear in their discussion, we have developed the discussion above.

Calculation of the Interaction Energy and Estimation of the Distance between Bound Ions. We shall confine ourselves to the POE-metal salt system as a model one. As has been stated before, it can be expected that, for the present system, the electrostatic interaction is represented by the sum of Debye-Hückel pair-by-pair interactions between bound cations. We therefore suppose that the statistical weight factor, A_m, in Eq. 9 can be expressed by:

$$RT\ln A_m = -\frac{e^2\exp(-\kappa r_m)}{4\pi\varepsilon r_m}, \quad (12)$$

where e is the elementary charge; ε, the permittivity of the solvent; r_m, the distance between the ions bound to the ith and the $(i+m)$th sites (lattice points), and κ, the Debye's parameter, which is given by:

$$\kappa^2 = \frac{2N_A e^2 I}{\varepsilon k_B T}, \quad (13)$$

in which N_A is the Avogadro constant; I, the ionic strength, and k_B, the Boltzmann constant.

In order to obtain the Debye-Hückel pair-by-pair interaction from Eq. 12, it is necessary to estimate the distance between the bound ions, r_m. Let us now assume that r_m is given by the root mean square end-to-end distance, $\langle R^2{}_m\rangle^{1/2}$, for a partial chain of POE corresponding to m binding sites.

In the first place, let us estimate the mean square end-to-end distance in the unperturbed state, $\langle R_m^2\rangle_0$. According to Maeda *et al.*,[11] the real chain can be well approximated by a stiff chain, even in the case of a fairly short chain. Therefore, we will use the following equation for the stiff chain:

$$\langle R^2\rangle_0 = 2a_0L\left[1 - \frac{a_0}{L}(1-e^{-L/a_0})\right], \tag{14}$$

in which we take a contour length, L, in the following form:

$$L = nl\sin(\theta/2), \tag{15}$$

where a_0 is the persistence length; n, the number of bonds; l, the bond length, and θ, the bond angle. We thus obtain this relation:

$$\frac{2a_0}{l}\sin(\theta/2) = C_\infty, \tag{16}$$

in which C_∞ is the characteristic ratio. C_∞ is given by the following Flory-Fox relation:

$$C_\infty = \left(\frac{K}{\Phi}\right)^{2/3}\frac{M_b}{l^2}, \tag{17}$$

where $\Phi = 2.6\times10^{21}$ (universal constant), M_b is the molecular weight per bond, and K is the viscosity constant, which is given by $K = [\eta]_\theta/M^{1/2}$ if $[\eta]_\theta$ is the intrinsic viscosity in a theta solvent and M is the molecular weight of the polymer. Thus, Eq. 14 becomes:

$$\langle R_2^m\rangle_0 = C_\infty nl^2 \times\left[1 - \frac{C_\infty}{2n\sin^2(\theta/2)}\left\{1 - \exp\left(-\frac{2n\sin^2(\theta/2)}{C_\infty}\right)\right\}\right]. \tag{18}$$

If we suppose that a binding site is composed of four monomer units,[6] then we obtain:

$$\langle R_m^2\rangle_0 = 132.7\,m \times\left[1 - \frac{0.3150}{m}\{1 - \exp(-3.174\,m)\}\right]\text{Å}^2,** \tag{19}$$

by substituting the following values in Eq. 18:

$$n = 12\,m,$$
$$l = 1.46\text{ Å},**$$
$$\theta = 111.5°,$$
$$K = 1.7\times10^{-3}\text{ dl g}^{-1}.^{12)}**$$

Next, let us estimate the expansion factor, α. Since α depends on m in general, we will express the expansion factor as $\alpha(m)$. If $\alpha(m)$ follows the fifth power law, then:

$$\alpha(m)^5 - \alpha(m)^3 = Cm^{1/2}, \tag{20}$$

where the constant, C, is determined from the value of m corresponding to the total number of binding sites on a polymer chain, m_0 (for example, $m_0 = 140.2$ for a chain of $M = 2.47\times10^4$), and from:

$$\alpha(m_0) = ([\eta]/[\eta]_\theta)^{1/3}, \tag{21}$$

that is,

$$C = \frac{\alpha(m_0)^5 - \alpha(m_0)^3}{m_0{}^{1/2}}. \tag{22}$$

By substituting Eq. 22 in Eq. 20, the value of $\alpha(m)$ corresponding to an arbitrary m is obtained. Finally, we obtain the distance between bound ions in the perturbed state from this relation:

$$\langle R_m^2\rangle = \alpha(m)^2\langle R_m^2\rangle_0. \tag{23}$$

Introduction of the Binding Constant. The chemical potential of the ion is written in the following form:

$$\mu = \mu^\ominus + ET\ln a, \tag{24}$$

where $\mu^\ominus$ is the standard chemical potential and a, the relative activity of the ion. Hence, experimentally the degree of binding θ, is obtained as a function of a. On the other hand, the degree of binding is calculated as a function of ξ. Let us now introduce the *binding constant* defined as follows:

$$K_0 = \exp[(\mu^\ominus - E)/RT]. \tag{25}$$

Thus, the normalized activity is expressed as:

$$\xi = K_0a. \tag{26}$$

Therefore, we can obtain a shift factor, $\log K_0$, which best fits the observed plots of θ *vs.* $\log a$ to the calculated curve of θ *vs.* $\log\xi$.

Discussion

Expansion Factors. We have calculated the mean square end-to-end distances for a partial chain of POE both in the unperturbed state and in the 2 mmol dm^{-3} KSCN-methanol system ($\alpha(m_0) = 1.386$). The dependence of these quantities on the number of bonds is shown in Fig. 1. In a perturbed state such as this system, the polymer chain is expanded to a great extent. However, for $m = 6$, that is, $\log n = 1.86$ below the point at which

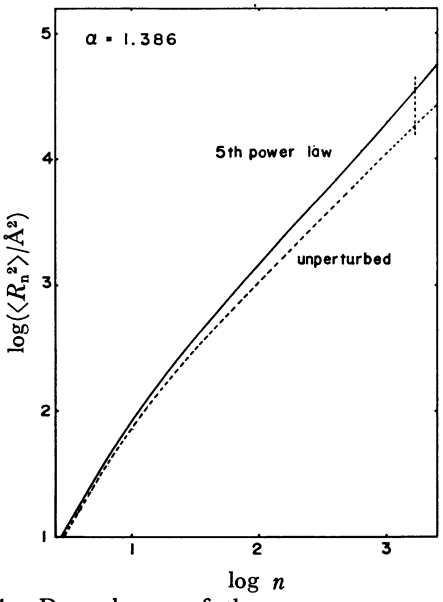

Fig. 1. Dependences of the mean square end-to-end distances for poly(oxyethylene) on the number of bonds, n, in the unperturbed state and in 2 mmol dm^{-3} KSCN–methanol system.

** 1 Å = 1×10^{-10} m; 1 dl = 1×10^{-4} m^3.

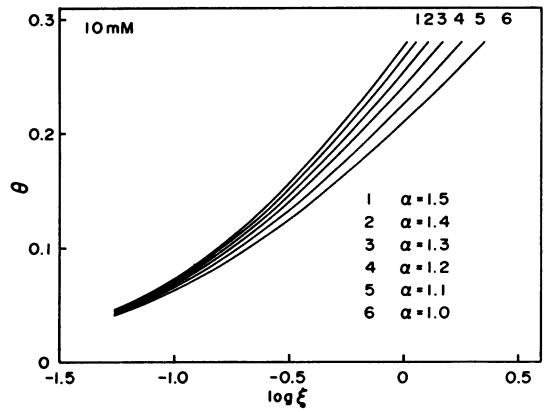

Fig. 2. Dependence of θ *vs.* log ξ curves on the expansion factor, α, for 10 mmol dm^{-3} KSCN–methanol system.

we are concerned, α is less than 1.15, and it is expected that the binding curve (θ *vs.* log ξ) is not very sensitive to the variation in α.

In Fig. 2, the dependence of the binding curve on $\alpha(m_0)$ is shown for the 10 mmol dm^{-3} KSCN–methanol system. As is suggested in Eq. 21, α is proportional to $[\eta]^{1/3}$, so the binding curve is quite insensitive to the variation in $[\eta]$.

Electrostatic Repulsion as a Long-range Interaction. In the foregoing discussion, the electrostatic interaction between bound ions has been assumed to range over only k sites. However, since the electrostatic interaction is a long-range one it is necessary to take a sufficiently large k. Figure 3 shows the binding curves for $k=0$—6, together with the extrapolated curve for $k\rightarrow\infty$ (see below). The degree of binding θ, decreases with an increase in k because of the long range electrostatic repulsion. Apparently, the convergence of the binding curve seems to be bad even for $k=6$. As k increases, however, the order of the statistical weight matrices exponentially increases. Hence it is actually impossible to obtain the degree of binding for a very large k in a

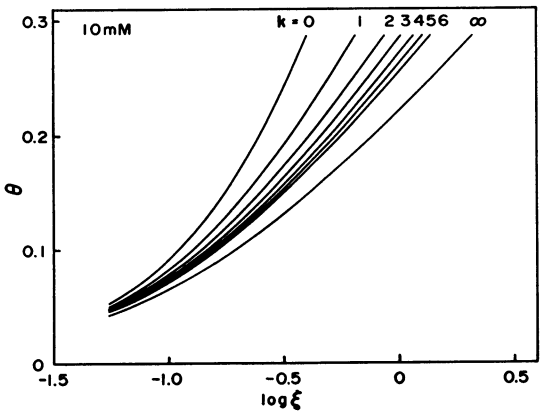

Fig. 3. Dependence of θ *vs.* log ξ curves on the number of sites over which the interaction ranges, k, for 10 mmol dm^{-3} KSCN–methanol system. The curve corresponding to $k\rightarrow\infty$ has been estimated from the extrapolation procedure shown in Fig. 4.

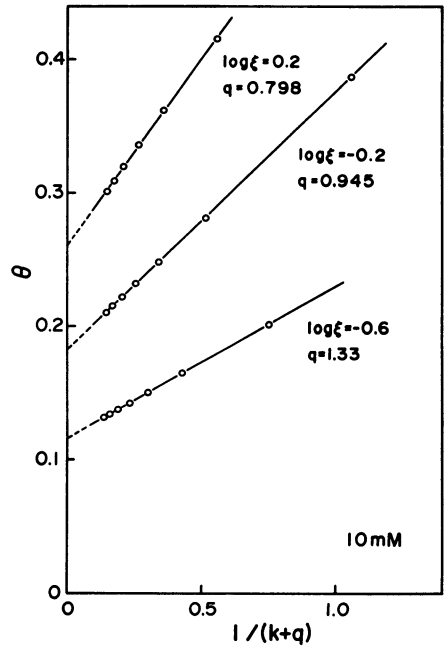

Fig. 4. Extrapolation procedure with the use of parameter, q, for 10 mmol dm^{-3} KSCN–methanol system.

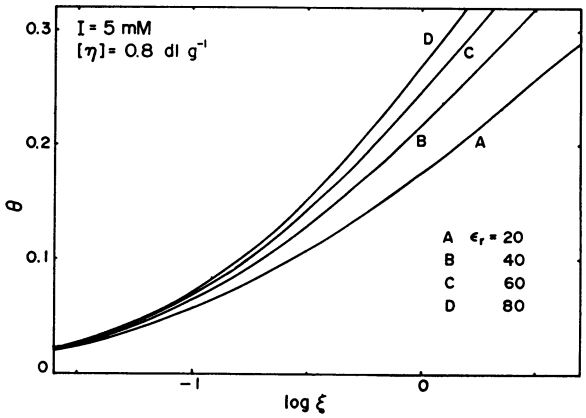

Fig. 5. Dependence of θ *vs.* log ξ curves of the relative permittivity of the solvent for an imaginary system.

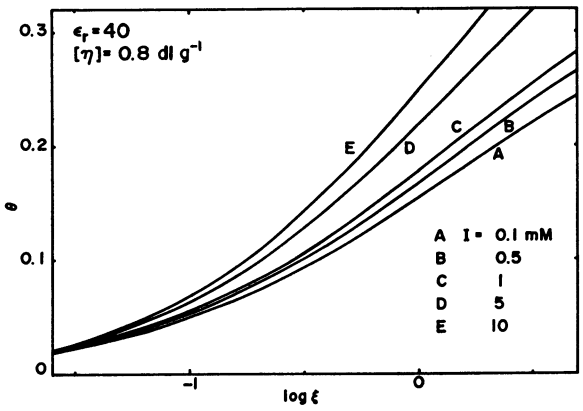

Fig. 6. Dependence of θ *vs.* log ξ curves on the ionic strength for an imaginary system.

straightforward manner.

For the extrapolation, we plotted θ against $1/(k+q)$, where q is a parameter which has been determined so that the correlation coefficient of the plot takes a maximum value. Figure 4 shows the plot thus obtained for several sets of log ξ and q for a fixed ion concentration. The degree of binding corresponding to $k\rightarrow\infty$ is determined as the intercept on the θ axis. This procedure seems to give a more precise extrapolated value than that of Liem *et al.*,[7] who have plotted the degree of the dissociation of polyacids against the reciprocal of the number of sites over which the interaction ranges.

The dependences of the binding curve on the relative permittivity, ε_r, of the solvent and on the ionic strength, I, are shown in Figs. 5 and 6 respectively for an imaginary model system. Both figures show that the degree of binding is less and the binding curve has a smaller slope when the interaction range is longer, that is, when the permittivity or the ionic strength is smaller, as has been expected.

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