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COMPLEX FORMATION AND IONIC ASSOCIATION IN METHANOL SOLUTIONS OF POLY(ETHYLENE OXIDE) AND ALKALINE EARTH SALTS

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ABSTRACT

Complex formation of poly(ethylene oxide) (PEO) with divalent barium and strontium salts was investigated in methanol. In these systems the complexation was accompanied by a considerable degree of ionic association. An analytical model for the polymer-ion complexation based on a one-dimensional lattice model was proposed. According to this model, the electrostatic effects between the bound ions were separated from the total free energy change of the binding. Three binding constants, i.e., the ionic association constant K_A, the cation binding constant, K_c, and the anion binding constant, K_a, could be estimated. K_A for barium and strontium salts was comparable, and the effect of counteranions on K_A was not large. K_c for barium salts was almost independent of the kind of counteranion and larger than that for corresponding strontium salts, indicating stronger polymer-ion interaction for barium salts. The anion binding constant, K_a, was strongly dependent upon the kind of anion, and the order was $Cl^- < Br^- < SCN^- < ClO_4^-$. The pronounced ion binding for larger anions may be explained by the more favorable free energy change of desolvation. Finally, the concentration of free and bound ionic species was determined as a function of PEO concentration.

INTRODUCTION

The complexation equilibria between polymers and metal ions are frequently much different from the corresponding equilibria between low molecular weight compounds and metal ions. The difference is mainly due to the existence of an attractive and/or a repulsive interaction operating along the polymer chain. It was realized that these interactions are responsible for cooperative or anticooperative effects in polymer-metal ion complexes, and the term "polymer effect" is often used to denote the peculiar interaction of polymers. The conventional treatment of polymer-metal ion equilibria, such as the modified Bjerrum theory [1], does not take into account the polymer effect,but the interaction term is introduced only by considering a macroscopic overall potential.

Since the polymer effect plays an essential role in the functionality of polymer-metal ion complexes, the quantitative description of the polymer effect is one of the central problems in the chemistry of polymer-metal ion complexation. However, this is rather difficult because the interaction that is responsible for the polymer effects is frequently of a long-range type and is accompanied by large conformational changes of the polymer chain.

Three factors should be separately evaluated to describe the quantitative aspects of the polymer-metal ion complexation. The first is the hydrophobic interaction which changes the chemical potentials of the polymer and the metal ion by changing the water structure. This interaction is regarded as short-range. The second is the electrostatic interaction. An important characteristic of this is that it is a long-range interaction except in solutions of high concentration of electrolytes. The third is the conformational change of the polymer chain due to the complexation. This is closely associated with the first and second factors since the hydrophobic and the electrostatic interactions are strongly dependent upon the intramolecular distance between the complexation sites on the polymer chain.

In water solutions the hydrophobic effect is very important, but the quantitative evaluation of this effect at the molecular level is difficult. In organic solvents, on the other hand, the hydrophobic interaction is not operative, and the analysis of the complexation equilibria should be simpler. The first purpose of this work is to develop a general method for evaluating the interactions exerted along the polymer chain in an organic solvent, using a model polymer-ion system.

In our previous studies [2-5] we developed a one-dimensional lattice model to describe the complex equilibria between poly(ethylene oxide) (PEO) and alkali metal ions in various organic solvents. The model was highly successful for the analysis of the complexation between PEO and potassium ion in medium "donicity" solvents [2, 3], while the agreement between the experiment and the calculation was rather poor for complexation in solvents of low "donicity" and low dielectric constant [4, 5]. This may be partly attributed to the difficulty in estimating the ionic association on the polymer chain as well as in the bulk solvents.

In order to generalize our treatment, it seems important to extend the model to divalent-ion systems, in which extensive ionic association is known to occur even in aqueous solution. Thus, the second purpose of this work is to check the applicability of our model to polymer-divalent ion complexation. As a model system, we investigated the complexation between PEO and barium ions in methanol.

THEORY

We considered a polymer-divalent ion systems with a medium degree of interaction between counterions. The interaction between the polymer and the divalent metal ion is also assumed not to be very large. Then the only important associated species is MX^+, which is formed by the following equilibrium in the bulk solution,

$$M^{2+} + X^- \rightleftharpoons MX^+, \tag{1}$$

where M^{2+} and X^- denote a divalent metal cation and a counteranion, respectively. According to the one-dimensional lattice model, the polymer phase should be regarded as a separate phase isolated from the bulk solution [2]. In this case the overall equilibrium is conveniently represented by the following scheme:

$$\begin{tikzcd}
M^{2+} & +\ X^- \arrow[r, shift left, "K_A"] & MX^+ \arrow[l, shift left] \\
+ & & + \\
\boxed{P} \arrow[d, shift left] & & \boxed{P} \arrow[d, shift left] \\
\boxed{P\text{-}M^{2+}} \arrow[u, shift left, "K_c"'] & +\ X^- \arrow[r, shift left, "K_a"] & \boxed{P\text{-}MX^+} \arrow[u, shift left] \arrow[l, shift left]
\end{tikzcd} \tag{2}$$

where P denotes a lattice site of a polymer one-dimensionally distributed along the main chain, and P-M^{2+} and P-MX^+ are the polymer-metal ion and polymer-associated metal ion complexes, respectively. Rectangular blocks mean that the species forms a separate phase. K_A is the ionic association constant in the bulk solvent. K_c and K_a are the binding constants of M^{2+} and X^- to the one-dimensional lattice and will be defined later.

As has been described before, the only important interaction exerted along the polymer chain of a polymer-metal ion complex in an organic solvent is the electrostatic one. Since the binding of the neutral species, MX_2, is neglected, it is not necessary to take into account ion-dipole and dipole-dipole interactions. Hence, the only interaction we must consider is the ion-ion interaction between the bound cation species M^{2+} and MX^+.

Let us represent the binding energy of a cation and an anion as E_c and E_a. Then the energy of a lattice site is zero, when nothing is bound, E_c, when an M^{2+} ion is bound, $E_c + E_a$, when an MX^+ ion is bound. E_c or E_a could be regarded as the chemical part of the binding free energy. According to our model, the electrostatic part of the binding free energy is represented by the electrostatic interactions between bound ion species along the polymer chain. Because of the long-range nature of these interactions, we should take into account the interactions between the bound ions separated by a number of vacant lattice sites. If we could truncate the interactions beyond k sites apart, and if we assume a Debye-Hückel type potential [2], then the interaction energy, J_{ij}, between ith and jth sites ($i < j$) is represented by

$$J_{ij} \equiv J_m = \frac{z_i z_j e^2 \exp(-\kappa_D r_m)}{4\pi \epsilon r_m}, \qquad \kappa_D{}^2 = \frac{2N_A e^2 I}{\epsilon k_B T}, \qquad \text{for } m \equiv j - i \leqq k, \tag{3}$$

and

$$J_{ij} \equiv J_m = 0, \qquad \text{for } m \equiv j - i > k \tag{4}$$

where z_i and z_j are the valence charges of the ith and the jth sites, e is the elementary electronic charge, κ_D is the Debye shielding parameter, r_m is the intersite distance, ϵ is the dielectric constant of the solvent, N_A is Avogadro's number, I is the ionic strength, k_B is the Boltzmann constant, and T is the absolute temperature. Then the statistical weight factor for the intersite interaction, A_{ij}, becomes

$$A_{ij} = \exp(-J_{ij}/RT), \tag{5}$$

where R is the gas constant. Equation (5) has the meaning that the statistical weight for ion binding of the ith site is multiplied by a factor of A_{ij} on account of the intersite interaction with the jth site.

Intrinsic statistical weight factors for the binding of a cation and an anion, ξ and η, are defined by

$$\xi \equiv \exp\,[(\mu_c - E_c)/RT] \tag{6}$$

$$\eta \equiv \exp\,[(\mu_a - E_a)/RT] \tag{7}$$

where μ_c and μ_a are the chemical potentials of the cation and the anion in the bulk solution, respectively. The meanings of ξ and η are that the statistical weight of the site occupied by the M^{2+} or MX^+ ion is ξ or η times that of a vacant site if intersite interactions are absent.

Using ξ, η, and A_{ij}, we can represent all the statistical weights of the lattice sites, and thus can formulate a grand partition function, Ξ, of a one-dimensional lattice [5]. Ξ is conveniently written in a matrix form

$$\Xi = e\, U_k^N\, e', \tag{8}$$

where e and e' are row and column vectors, such as

$$e = (1,1,\text{- - - -},1), \qquad e' = \begin{pmatrix} 1 \\ 2 \\ \\ \\ 0 \end{pmatrix} \tag{9}$$

where N is the number of lattice site on a polymer chain and U_k is a statistical weight matrix whose order is 3^k. For $k = 1$, the matrix has a form

$$\mathbf{U}_1 = \begin{array}{c|ccc} i+1 & 0 & 1 & 2 \\ i & & & \\ \hline 0 & 1 & 1 & 1 \\ 1 & \xi & \xi A_{1_2}^{\;4} & \xi A_1^{\;2} \\ 2 & \xi\eta & \xi\eta A_1 & \xi\eta A_1 \end{array} . \tag{10}$$

This is the statistical weight matrix of the one-dimensional lattice in which only nearest-neighbor interactions are operative. The higher-order matrix is represented in a similar way.

The final purpose of this work is to determine the binding constants of the cation, K_c, and the anion, K_a. In the one-dimensional lattice, the definition of these quantities is somewhat different from those in homogeneous solution, and is represented by [5],

$$K_c \equiv \exp\ [(\mu_c^{\ominus} - E_c)/RT] \tag{11}$$

$$K_a \equiv \exp\ [(\mu_a^{\ominus} - E_a)/RT] \tag{12}$$

where $\mu_c^{\ominus}$ and $\mu_a^{\ominus}$ are the standard chemical potentials of the cation and the anion, respectively. The degree of binding, also an important quantity, is defined for the cation and the anion by the following equations:

$$\theta_c = \left(\frac{1}{N}\frac{\partial \ln \Xi}{\partial \ln \xi}\right)_{\eta}, \tag{13}$$

$$\theta_a = \left(\frac{1}{N}\frac{\partial \ln \Xi}{\partial \ln \eta}\right)_{\xi}, \tag{14}$$

where θ_c or θ_a is the probability that the site is occupied by M^{2+} or MX^+, respectively.

As will be shown in the following section, the estimation of the ion binding was carried out by reproducing the conductivity curves as a function of polymer concentration, C_p. As shown in our previous paper [5], this was done by solving a set of simultaneous equations with respect to ξ, η, θ_c, θ_a, and C_p by an iterative computer method. K_c and K_a are determined so as to give the best fit to the experimental conductivity curves. Minor modifications were made to improve the calculation procedure and to reduce the sum-of-square errors. An important point of modification is that the statistical weight factors are determined for a fixed value of C_p, while C_p was calculated for a fixed value of ξ in our previous work. The modification made the calculation faster and the reproduction better. The extrapolation of k to infinity was carried out as shown in our previous paper [2].

EXPERIMENTAL

Reagents and Measurements

PEO with a nominal molecular weight of 20 000 was used throughout this study. Reagent grade barium chloride, barium bromide, barium thiocyanate, and barium perchlorate were used. For comparison, strontium chloride and strontium thiocyanate were also used. These salts were dried well under vacuum before dissolving in methanol.

The degree of ion binding and ionic association were estimated by conductometry in methanolic solution. The total concentration of the ion was between 1 to 5 m*M* (mmol/L). Conductivity was measured by a GenRad GR-1689 Digibridge at 3 kHz in a glass cell controlled to 25 ± 0.1°C by a water-circulating glass jacket. As shown previously, the contribution to the conductivity of the ions bound on the PEO chain may be neglected in comparison with the contribution from the free ionic species if the molecular weight of PEO is above 20 000. This results in the independence of the conductivity of the system on the molecular weight of PEO [6].

RESULTS AND DISCUSSION

Estimation of Ionic Association in the Bulk Solvent

The strong electrostatic potential of the divalent barium ion facilitates ionic association. Thus we should first determine the ionic association constant, K_A, in the absence of PEO. This was done by modifying Monk's method [7]. According to this method, the equivalent conductance, Λ, of the solution of a divalent salt is given by

$$\Lambda = \frac{1}{2c} \left\{ 2[\mathrm{Ba}^{2+}]\Lambda_{21} + [\mathrm{BaX}^{+}]\Lambda_{11} \right\}, \tag{15}$$

where c is the concentration of the barium salt and Λ_{21} is the hypothetical conductance when the salt BaX_2 is completely dissociated. Λ_{11} is the conductance of a hypothetical salt between the ion pair, BaX^+ and X^-, and is given by

$$\Lambda_{21} = \Lambda_{21}{}^0 + S_{21}\sqrt{I} + BI, \tag{16}$$

$$\Lambda_{11} = \Lambda_{11}{}^0 + S_{11}\sqrt{I}, \tag{17}$$

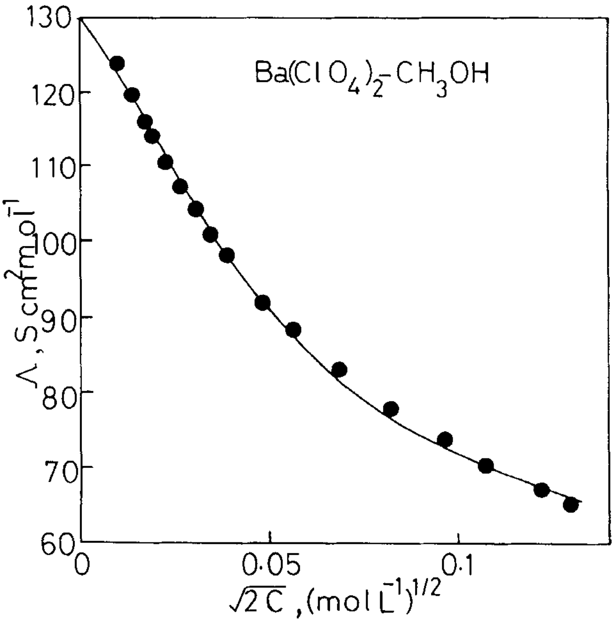

FIG. 1. Conductivity curve for a methanolic solution of barium perchlorate. The solid curve was calculated by the modified Monk method.

where $\Lambda_{21}{}^0$ and $\Lambda_{11}{}^0$ are the limiting equivalent conductances corresponding to Λ_{21} and Λ_{11}, S_{21} and S_{11} are Onsager's theoretical parameters, and B is an experimental parameter. Following Monk, we assumed that the limiting ionic equivalent conductance of the BaX^+ ion is equal to half that of the Ba^{2+} ion and then determined $\Lambda_{11}{}^0$. The concentrations of Ba^{2+} and BaX^+ ions were calculated by an iterative method to give the best fit to the experimental Λ vs $\sqrt{2c}$ curves. Then the ionic association constant, K_A, could be calculated by

$$K_A = \frac{y_\pm [BaX^+]}{y_\pm [Ba^{2+}] y_\pm [X^-]}, \tag{18}$$

where $y_\pm$ represents the mean activity coefficient of the ions. Figure 1 shows an example of the calculated Λ vs $\sqrt{2c}$ curve. Agreement with the experimental points was excellent. Table 1 shows K_A values for barium and strontium salts. It should be noted that K_A for barium and strontium salts was similar in magnitude and was not much influenced by the kind of counteranion.

TABLE 1. Ionic Association Constants and Binding Constants of Divalent Cations and of Anions with the PEO Chain

Salts	K_A[a]	c, mmol/L	K_c[a]	K_a[a]	$[\eta]$, dL/g[b]
$Ba(ClO_4)_2$	360	1	220	1300	0.735
		2	130	2100	0.509
		3[c]	580	1100	0.437
$Ba(SCN)_2$	350	1	170	860	0.779
		2	260	560	0.707
		3	260	660	0.647
$BaBr_2$	280	1	130	410	0.780
		2	170	190	0.739
		3	260	660	0.647
$BaCl_2$	310	1	180	70	0.794
		2	190	20	0.822
		3	200	3.5	0.828
$Sr(SCN)_2$	470	1	30	410	0.454
		2	40	450	0.399
		3	40	390	0.442
$SrCl_2$	320	1	30	80	0.431
		2	20	220	0.455
		3	20	210	0.467

[a] In L/mol.

[b] 25°C in methanol.

[c] Precipitation was observed above this concentration.

Calculation of Binding Constants

Figure 2 shows a plot of the relative conductivity of the solution against the PEO concentration C_p. The concentration of divalent salts was 2 m*M*. In all cases, especially for barium salts, large decreases in the conductivity

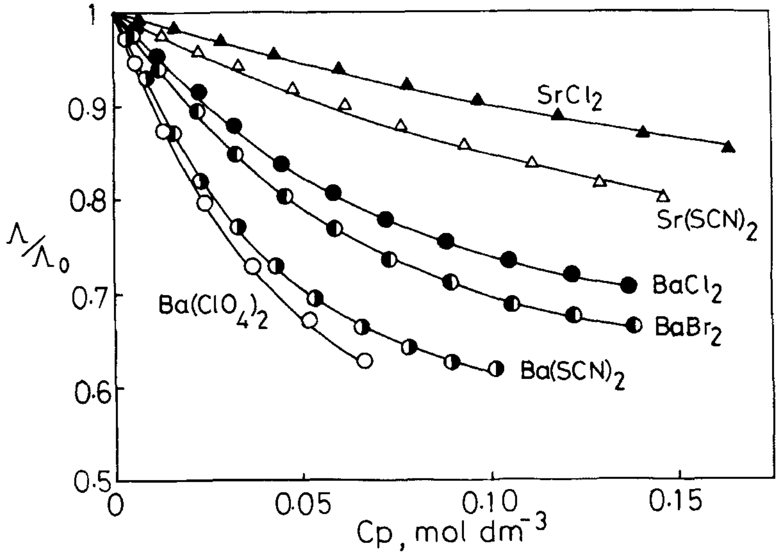

FIG. 2. Observed (points) and calculated (curves) conductivities as functions of PEO concentration for 2 m*M* divalent salts.

were observed with increasing PEO concentration. This is due to the binding of divalent cations to the PEO chain, resulting in the loss of ionic mobility. The decrease of the conductivity of strontium salts was not as large, indicating the relatively low binding ability of this ion. The solid curves in the figure are curves calculated on the basis of the one-dimensional lattice model by assuming that the binding sites for divalent cations consist of four oxyethylene units of PEO [6]. The agreement between the calculated curves and the experimental data is excellent, suggesting the validity of our basic assumptions.

The curves for barium salts are all similar in shape, but it should be emphasized that there is much difference in the degree of conductivity decrease for the different counteranions. This is due to the difference in the degree of association of the anion on the PEO chain, which will be elucidated in the following section. The order of anion association on the PEO chain is $Cl^- < Br^- < SCN^- < ClO_4^-$ (see Fig. 2). Figure 3 shows the effect of the concentration of salts on the conductivity curves. At a fixed PEO concentration the relative conductivity decrease is larger for lower salt concentrations.

The determined binding constants K_c and K_a are summarized in Table 1 together with the intrinsic viscosities of the solutions. The binding constants

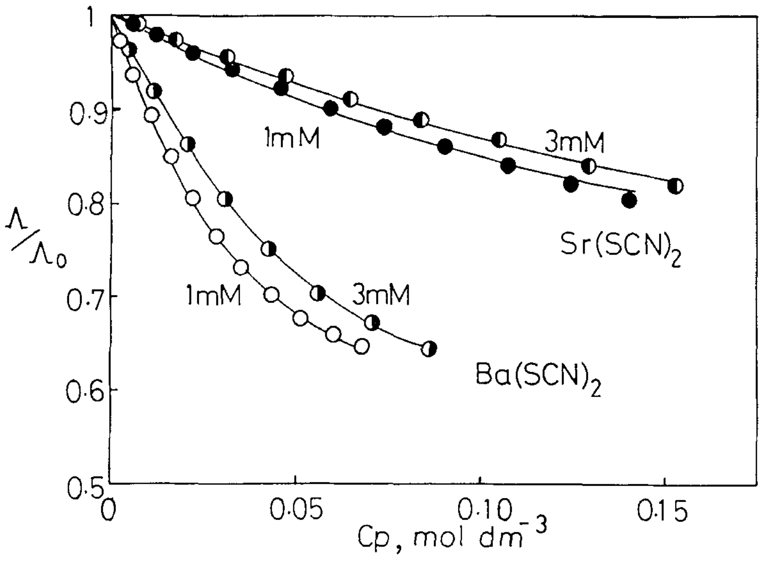

FIG. 3. Observed (points) and calculated (curves) conductivities as functions of PEO concentration. Effect of salt concentration.

of Ba^{2+} are not much influenced by the type of counteranion. The dependence on the salt concentration is also not large, indicating the validity of our procedure for separating the chemical and electrostatic parts of the binding free energy. On the other hand, K_a is strongly dependent upon the anion species. It rises with increasing anion size, which is contrary to the prediction from Bjerrum's ionic association theory. Ionic association would reduce the net charge on the polymer chain, resulting in contraction of the polymer coil. This is indeed observed since the intrinsic viscosities decrease with an increase in K_a as shown in Table 1.

Figure 4 shows that K_A is almost independent of anion size, while K_a increases sharply with increasing anion size.

Concentration of Ionic Species

Why does the binding constant of the anion, K_a, increase with increasing anion size? This is unexpected in view of the strong electrostatic effect on the ionic association. An explanation would only be possible by taking into account the solvation of the anion by methanol.

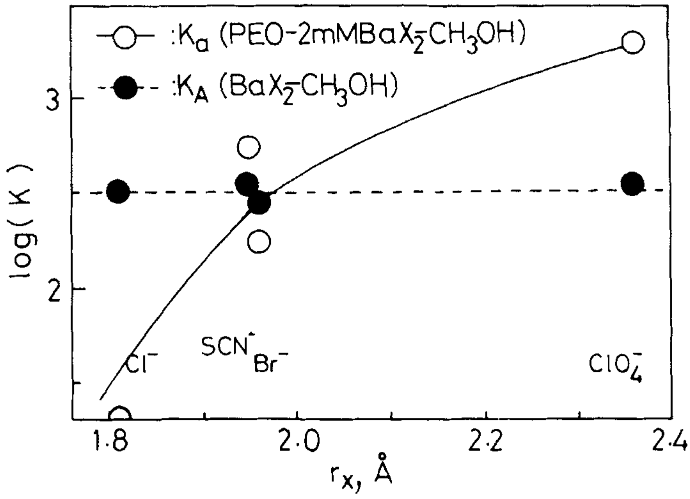

FIG. 4. Relationship between the crystallographic ionic radius of anion and the ionic association constant in the absence (K_A) or presence (K_a) of PEO.

It is well known that a methanol molecule has an acidic solvating site as well as a basic site [8]. This gives the methanol molecule a Lewis acid character, and solvation of anions as well as of cations becomes possible. Generally, the free energy change accompanying the ionic association, ΔF_{assoc}, can be divided into two independent terms, i.e., the free energy change due to the desolvation of the solvent, ΔF_{desol}, and the free energy change due to the electrostatic effect of ion pairing, ΔF_{el}:

$$\Delta F_{\text{assoc}} = \Delta F_{\text{desol}} + \Delta F_{\text{el}}. \tag{19}$$

For a small anion, ΔF_{el} is more negative because of the short interionic distance of the ion pair. In the case of a solvent with acidic solvation sites, however, this effect is canceled out by a more positive ΔF_{desol} owing to the strong solvation of the anion. As a consequence, the net free energy change becomes insensitive to the anion size. This seems to be the reason for the independence of K_A on anion size.

In the presence of PEO, on the other hand, ΔF_{el} becomes more positive because of a partial neutralization of the charge of the Ba^{2+} ion by the coordinated oxyethylene units. This effect decreases the contribution of the elec-

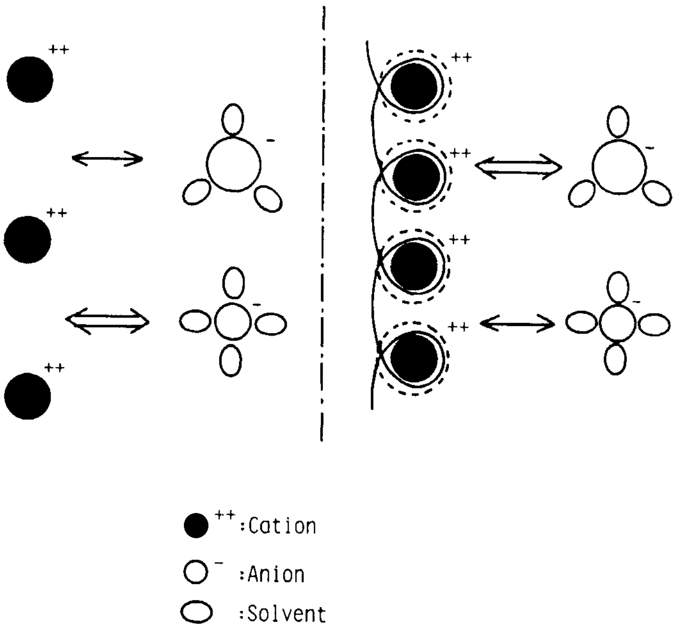

FIG. 5. Schematic illustration of the relative strength of the ionic association in the presence and absence of PEO. The breadth of the arrows indicates the relative strength of ionic association.

trostatic part of the free energy change, ΔF_{el}, and $\Delta F_{\mathrm{assoc}}$ will be primarily determined by $\Delta F_{\mathrm{desol}}$. Then the ionic association of the large anion becomes favorable because of a more negative $\Delta F_{\mathrm{desol}}$. In other words, the less solvated and unstable anions associate more strongly with the PEO chain than the more solvated anions. These considerations explain satisfactorily why K_a increases with increasing anion size (illustrated schematically in Fig. 5).

The entire situation of ion binding is summarized in Fig. 6 where the calculated concentrations of ionic species are plotted against the concentration of PEO, C_p, for three barium salts. The upper half of each figure represents the concentration of the anion; the lower half represents that of the cation. The binding profiles are classified into three cases, i.e., $K_a < K_A$, $K_a \approx K_A$, and $K_a > K_A$. In the first case the ionic association occurs mainly in bulk solution, and the only important binding species is Ba^{2+}. Increasing the concentration of PEO decreases the concentration of Ba^{2+} by ion binding, resulting in an increase of the free anion concentration according to the Le Chatelier-

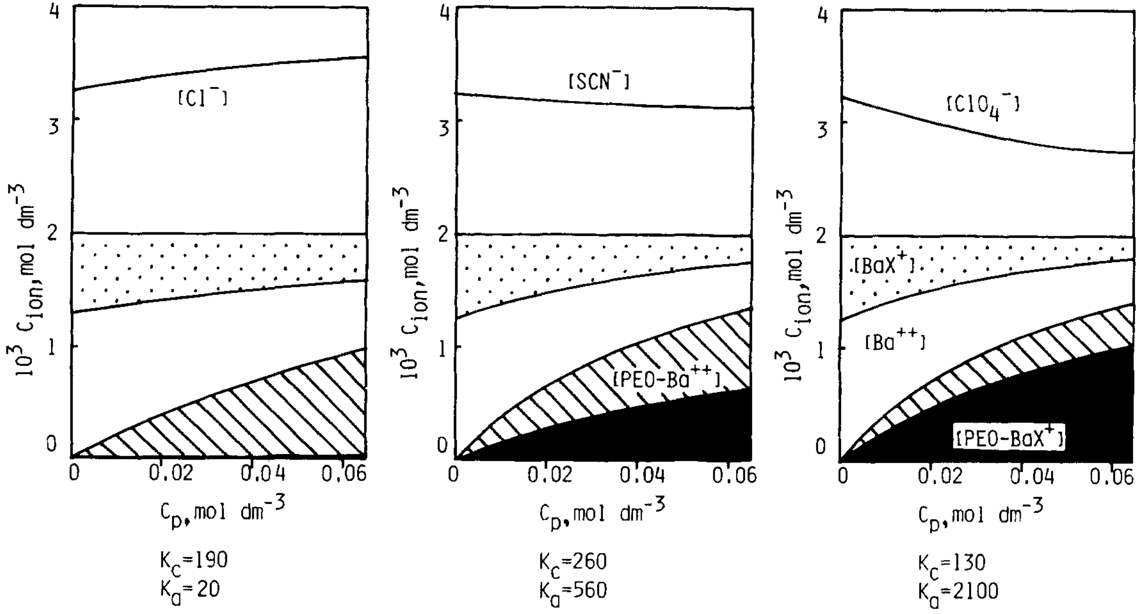

FIG. 6. General illustration of the concentrations of ionic species as functions of PEO concentration for different barium salts (2 m*M*).

Braun law. This case is observed for the barium chloride system. In the second case of $K_a \approx K_A$, ionic associations in bulk solution and on the PEO chain are both important. Thus the concentrations of bound Ba^{2+} and BaX^- ions are comparable. As is observed for the barium thiocyanate system, increasing the concentration of PEO has no effect on the concentration of free anion. This is the expected result since the ionic association occurs equally in the solution and on the polymer chain. In the last case, $K_a > K_A$, the ionic association occurs mainly on the PEO chain. The concentration of free anion decreases with increasing PEO concentration because of strong association on the PEO chain. This case is observed for barium perchlorate. As summarized in Fig. 6, the ion binding behavior in divalent ion systems can be understood by the relative strength of ionic association in solution and on the polymer chain.

CONCLUSIONS

Several conclusions can be drawn from the analysis of the complexation between divalent metal ion and polymer by means of a one-dimensional lattice model. These are:

1. The complexation equilibria between PEO and divalent cations can be successfully analyzed by means of a one-dimensional lattice model by taking into account not only the ionic association in solution but also on the polymer chain.
2. The electrostatic part of the "polymer effect" was elucidated by separating the chemical and electrostatic parts of the binding energy.
3. Although the ionic association constant of barium ions in methanol is not sensitive to the anion species, the binding constants of these ions on PEO are considerably dependent on the kind of counteranion.
4. Ionic association on the PEO chain is more favorable for large and weakly solvated anions.

In order to elucidate a more general behavior of the binding of divalent metal ions, it will be necessary to investigate the binding equilibrium in a variety of solvents with wide ranges of "donicity" and dielectric constant.

REFERENCES

[1] H. P. Gregor, L. B. Luttinger, and E. M. Label, *J. Phys. Chem.*, *59*, 34 (1955).

[2] H. Awano, K. Ono, and K. Murakami, *Bull. Chem. Soc. Jpn.*, *55*, 2525 (1982).

[3] H. Awano, K. Ono, and K. Murakami, *Ibid.*, *55*, 2530 (1982).

[4] H. Awano, K. Ono, and K. Murakami, *Chem. Lett.*, p. 149 (1982).

[5] H. Awano, K. Ono, and K. Murakami, *Bull. Chem. Soc. Jpn.*, *56*, 1715 (1983).

[6] K. Ono, H. Konami, and K. Murakami, *J. Phys. Chem.*, *83*, 2665 (1979).

[7] I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, p. 68 (1951).

[8] R. M. Kay, D. F. Evans, and M. A. Matesich, *Solute-Solvent Interactions*, Vol. 2 (J. F. Coetzee and C. D. Ritchie, eds.), Dekker, New York, 1976, Chap. 10.