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The Interaction of a Neutral Polymer with Small Ions in Solution. III. Ionic Association on a Poly(oxyethylene) Chain

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Conductivities of NaSCN and KSCN solutions have been measured in ethanol and nitromethane in the presence of poly(oxyethylene). For poly(oxyethylene)–KSCN solutions in ethanol and nitromethane, a distinct minimum appears in conductivity *vs.* polymer concentration curves. In addition, for a poly(oxyethylene)–NaSCN solution in nitromethane, the conductivity curve rises steeply after passing through the minimum. These anomalies cannot be explained by the cation binding to the polymer alone, and the ionic association on the polymer chain should be taken into account at the same time. In order to analyze the results, a theory based on the duplicate ion binding on a one-dimensional lattice has been developed. The theory not only predicts the appearance of the conductivity minima, but also makes it possible to estimate the ionic association constants.

The authors have investigated by conductometry the the binding of alkali metal ions to poly(oxyethylene) (POE) in various solvents.[1–3] It has been found that the equivalent conductivities of the alkali metal salts, Λ, decrease monotonically with an increase in the concentration of POE (monomer base mole), C_p. For solutions of potassium thiocyanate in methanol, acetonitrile, propylene carbonate, and sulfolane, the amount of potassium ion bound to a POE chain has been evaluated from the decrement of Λ. In these cases, it is not necessary to take into account the contribution of the anion to the decrement of Λ, since the specific interaction between the cation and the anion is virtually negligible. A binding constant, K_0, which does not include the contribution of the interaction between the cation bound to a POE chain, has been obtained on the basis of a one-dimensional lattice model.[2] It has been shown that, over a variety of solvents, a linear correlation exists between the logarithmic binding constant, $\log K_0$, and the standard chemical potential of the cation, $\mu^{\ominus}$.[3]

Thus, it can be expected that the binding of potassium ions to POE occurs extensively in ethanol, nitromethane, or the like, in which $\mu^{\ominus}$ is much larger than in methanol, acetonitrile, *etc.* Similarly to the polyelectrolyte systems, in which counter ions are bound to the polyion, it is expected that anions would be bound to the POE–cation complexes and make no contribution to the conductivity, when the charge density of the cation on the chain is enhanced. In addition, ionic association or ion-pair formation also occurs to a large extent even in the polymer free solutions of some alkali metal thiocyanates in ethanol and nitromethane.

In this paper, we assume that the following three equilibria exist in these systems:

1) binding of the cation to a POE chain; 2) ionic association on a POE chain; 3) ionic association in the bulk solvent.

It is necessary to treat the equilibria 1 and 2 on the basis of the one-dimensional lattice model, because both equilibria might be influenced by the interference between the positive charges bound on the chain. In our treatment, an extended one-dimensional lattice model is proposed to interpret the Λ *vs.* C_p curves in such complicated cases. The outline of the treatment has already been published in our preliminary report.[4]

Theory

An Extension of the One-dimensional Lattice Model. When we extend the one-dimensional lattice model to the case of the duplicate ion binding to POE, the following two basic assumptions are made.

In the first place, we must specify the binding state of a site. Three kinds of binding states were assumed for each site according to their energies. The energy of the site was assumed to be 0 if nothing is bound (state $\underline{0}$), E_c if a cation is bound (state $\underline{1}$), and E_c+E_a if not only a cation but also an anion is bound (state $\underline{2}$).

In the second place, we must specify the interaction energy between the sites. When either or both of the i-th and j-th sites are the state $\underline{0}$ or state $\underline{2}$, then the interaction energy J_{ij} between i-th and j-th sites is represented as:

$$J_{ij} = 0. \tag{1}$$

This means that the site specified as state $\underline{2}$ has no effective charges and does not exert electrostatic potential at the other sites. On the other hand, if both of the i-th and j-th sites are in the state $\underline{1}$, J_{ij} is assumed to be represented as:

$$J_{ij} = \begin{cases} J_m, & m \equiv j-i < k \\ 0, & j-i > k, \end{cases} \tag{2}$$

and k is the range of the number of sites, beyond which the interaction is truncated, and J_m is the Debye-Hückel potential. This has the following form:

$$J_m = \frac{e^2\exp(-\kappa_D r_m)}{4\pi\varepsilon r_m},\quad \kappa_D^2 = \frac{2N_A e^2 I}{\varepsilon k_B T}, \tag{3}$$

where e is the elementary electronic charge, κ_D the Debye's shielding parameter, r_m the intersite distance, ε the dielectric constant of the solvent, N_A the Avogadro constant, I the ionic strength, k_B the Boltzmann constant, and T the absolute temperature. A statistical weight factor A_m is defined by:

$$A_m \equiv \exp(-J_m/RT). \tag{4}$$

If we denote the chemical potentials of the cation and the anion as μ_c and μ_a, respectively, then the normalized activities of these ions are defined as follows:[2]

$$\xi \equiv \exp[(\mu_c - E_c)/RT] \tag{5}$$

$$\eta \equiv \exp[(\mu_a - E_a)/RT]. \tag{6}$$

The grand partition function of this system may be conveniently described in terms of the following matrix product:

$$\Xi = \boldsymbol{e}\,\boldsymbol{U}_k^N \boldsymbol{e}' \tag{7}$$

where $\boldsymbol{e}$ and $\boldsymbol{e}'$ are row and column vectors such as:

$$\boldsymbol{e} = (1,1,1,\cdots\cdots,1) \qquad \boldsymbol{e}' = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ \vdots \\ 0 \end{pmatrix}. \tag{8}$$

In Eq. 7, N is the number of a lattice point on a chain, and $\boldsymbol{U}_k$ is a statistical weight matrix whose order is 3^k. A few examples of the matrix are shown below:

for $k = 1$,

$$\mathrm{U} = \begin{array}{c|ccc} i+1 & \underline{0} & \underline{1} & \underline{2} \\ i & & & \\ \hline \underline{0} & 1 & 1 & 1 \\ \underline{1} & \xi & \xi A_1 & \xi \\ \underline{2} & \xi\eta & \xi\eta & \xi\eta \end{array} \tag{9}$$

for $k = 2$,

$$\boldsymbol{U} = \begin{array}{cc|ccccccccc} & i+2 & \underline{0} & \underline{1} & \underline{2} & \underline{0} & \underline{1} & \underline{2} & \underline{0} & \underline{1} & \underline{2} \\ i & i+1 & \underline{0} & \underline{0} & \underline{0} & \underline{1} & \underline{1} & \underline{1} & \underline{2} & \underline{2} & \underline{2} \\ \hline \underline{0} & \underline{0} & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \underline{0} & \underline{1} & 0 & 0 & 0 & 1 & 1 & 1 & 0 & 0 & 0 \\ \underline{0} & \underline{2} & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 \\ \underline{1} & \underline{0} & \xi & \xi A_2 & \xi & 0 & 0 & 0 & 0 & 0 & 0 \\ \underline{1} & \underline{1} & 0 & 0 & 0 & \xi A_1 & \xi A_1 \xi A_2 & \xi A_1 & 0 & 0 & 0 \\ \underline{1} & \underline{2} & 0 & 0 & 0 & 0 & 0 & 0 & \xi & \xi A_2 & \xi \\ \underline{2} & \underline{0} & \xi\eta & \xi\eta & \xi\eta & 0 & 0 & 0 & 0 & 0 & 0 \\ \underline{2} & \underline{1} & 0 & 0 & 0 & \xi\eta & \xi\eta & \xi\eta & 0 & 0 & 0 \\ \underline{2} & \underline{2} & 0 & 0 & 0 & 0 & 0 & 0 & \xi\eta & \xi\eta & \xi\eta \end{array} \tag{10}$$

Extrapolation to $k \to \infty$ can be carried out in a similar manner as was shown in our previous paper of this series.[2)]

It is convenient to define the degree of binding in terms of the probability that a site is occupied by the cation or the anion, respectively. This probability is *formally* represented for the cation and the anion by;[5)]

$$\theta_c = \left(\frac{1}{N}\frac{\partial \ln \Xi}{\partial \ln \xi}\right)_\eta, \tag{11}$$

$$\theta_a = \left(\frac{1}{N}\frac{\partial \ln \Xi}{\partial \ln \eta}\right)_\xi. \tag{12}$$

The binding constants for the cation and the anion are defined as:

$$K_0^c \equiv \exp[(\mu_c^{\ominus} - E_c)/RT] \tag{13}$$

$$K_0^a \equiv \exp[(\mu_a^{\ominus} - E_a)/RT], \tag{14}$$

where $\mu_c^{\ominus}$ and $\mu_a^{\ominus}$ are the standard chemical potentials of cation and the anion, respectively.

Reproduction of Conductivity Curves. From Eqs. 5, 6, 13, 14, the concentration of the free cation, C_c, and that of the free anion, C_a, are given by:

$$C_c = (\xi/K_0^c y_\pm)C^{\ominus}, \tag{15}$$

$$C_a = (\eta/K_0^a y_\pm)C^{\circ}, \tag{16}$$

where $y_\pm$ is the mean activity coefficient on the molar concentration basis. This is approximately estimated by the Debye-Hückel limiting law, and $C^{\ominus}$ is the standard value of molar concentration, being equal to 1 mol dm^{-3}. According to the principle of electron-neutrality, C_c and C_a are related to one another, and the following relationship holds:

$$C_c + (\theta_c - \theta_a)C_p/4 = C_a. \tag{17}$$

The second term of the lefthand side of Eq. 17 corresponds to the concentration at the site where only a cation is bound (state $\underline{1}$), and the denominator of this term is introduced on the assumption that a site is compcsed of four oxyethylene units.[1)] Substituting Eqs. 15 and 16 into Eq. 17, we obtain:

$$C_p = \frac{4(\eta/K_0^a - \xi/K_0^c)C^{\ominus}}{y_\pm(\theta_c - \theta_a)}. \tag{18}$$

Next we introduce an ionic association constant K_A.

$$K_A \equiv \frac{C_{assoc}/C^{\ominus}}{(C_c y_\pm/C^{\ominus})(C_a y_\pm/C^{\ominus})}. \tag{19}$$

Where C_{assoc} is the concentration of the ion-pair, the activity coefficient being assumed to be 1. C_{assoc} is obtained by subtracting the concentration of the free anion and that of the bound anion from the total anion concentration, C_s, as follows:

$$C_{assoc} = C_s - C_a - \theta_a C_p/4. \tag{20}$$

Substituting Eq. 20 into Eq. 19, and combining with Eqs. 15 and 16 we finally obtain:

$$\eta = K_0^a y_\pm \frac{(C_s - \theta_a C_p/4)/C^{\ominus}}{1 + K_A y_\pm \xi/K_0^c}. \tag{21}$$

For a fixed value of ξ, the set of Eqs. 11, 12, 18, and 21 are simultaneous equations with respect to η, θ_c, θ_a, and C_p. Athough the equations cannot be solved analytically, we can obtain a solution by an iterative method. Then C_c and C_a are calculated from Eqs. 15 and 16.

Molar conductivity is estimated by the following equation,

$$\Lambda = (C_c\lambda_c + C_a\lambda_a)/C_s, \tag{22}$$

where λ_c and λ_a are the molar conductivities of the cation and anion, respectively, in the absence of ionic association. These values are calculated in terms of the Onsager's limiting law.[6)]

$$\lambda = \lambda^\infty - (\alpha\lambda^\infty + \beta)\sqrt{I}, \tag{23}$$

where λ^∞, the limiting molar conductivity of the ion, can be found in the literature, α and β are the Onsager parameters, and for a uni-univalent electrolyte;

$$\alpha = \frac{e^2}{3k_B\varepsilon T}\frac{q}{1+\sqrt{q}}\frac{\kappa_D}{\sqrt{I}}, \quad q = \frac{1}{2}$$

$$\beta = \frac{Fe}{6\pi\eta_v}\frac{\kappa_D}{\sqrt{I}}, \tag{24}$$

where η_v is the viscosity of the solvent and F is the Faraday constant. In this way, we can calculate the relationship between Λ *vs.* C_p for a POE–alkali metal salt–solvent system.

Experimental

Poly(oxyethylene) samples, with a nominal molecular weight range from 200 to 5×10^6 (Wako pure chemicals and Union Carbide Co.) were used. Except where indicated, measurements were performed for a sample with molecular weight 2×10^4 (viscosity average MW, 2.47×10^4). Reagent grade potassium and sodium thiocyanates were dried under vacuum before use. Ethanol was stirred with molecular sieve 4A, and distilled. $\kappa=3\times10^{-7}$ S cm^{-1}. Reagent grade nitromethane was used without further purification. $\kappa=2\times10^{-6}$ S cm^{-1}. The measurement of the conductivity was carried out in the manner previously reported.

Results and Discussion

The conductivity curves for the KSCN–EtOH systems are shown in Fig. 1. It may be seen that with increasing C_p conductivity first decreases, passes through a minimum, and then increases gradually at higher C_p. Such a minimum was not observed in the solvent systems studied previously.[3)] The minimum becomes more pronounced as C_p becomes greater.

In Fig. 2, the conductivity curve for 5 mmol dm^{-3} NaSCN–EtOH is compared with that of KSCN solution. The minimum is not observed in this case, and the conductivity decreases continually.

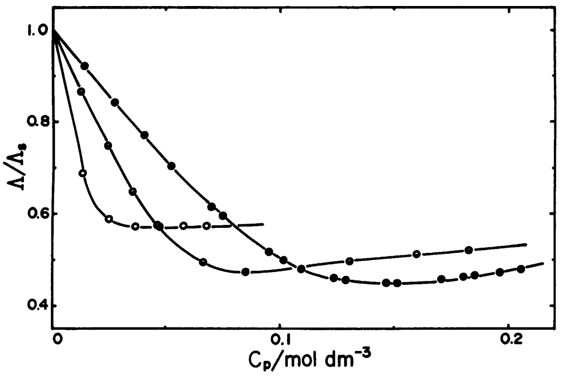

Fig. 1. Plots of relative conductance *vs.* concentration of POE for KSCN–EtOH solutions at 298.15 K. ●, $C_s=10$ mmol dm^{-3}; ◒, $C_s=5$ mmol dm^{-3}; ○, $C_s=1$ mmol dm^{-3}.

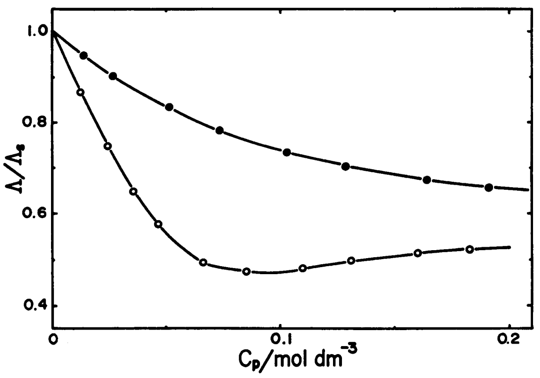

Fig. 2. Plots of relative conductance *vs.* concentration of POE for 5 mmol dm^{-3} KSCN- and NaSCN–EtOH solutions at 298.15 K. ○, KSCN; ●, NaSCN.

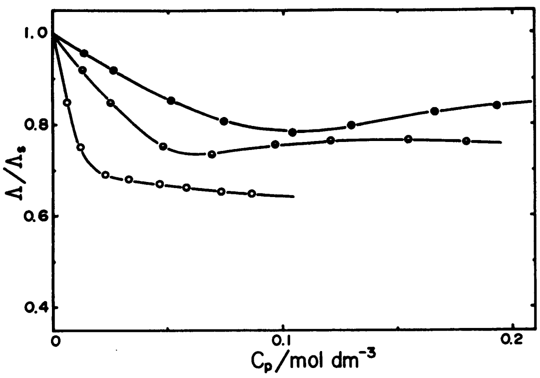

Fig. 3. Plots of relative conductance *vs.* concentration of POE for KSCN–nitromethane solutions at 298.15 K. ●, $C_s=10$ mmol dm^{-3}; ◒, $C_s=5$ mmol dm^{-3}; ○, $C_s=1$ mmol dm^{-3}.

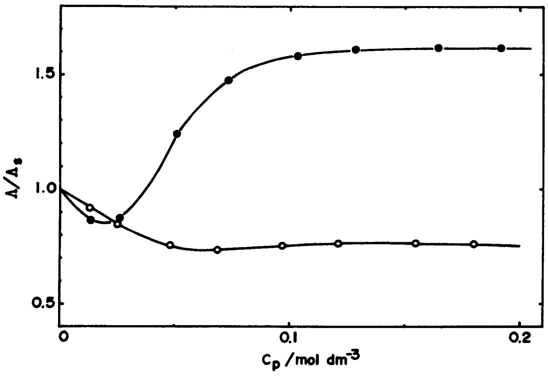

Fig. 4. Plots of relative conductance *vs.* concentration of POE for 5 mmol dm^{-3} KSCN- and NaSCN–nitromethane solutions at 298.15 K. ○, KSCN; ●, NaSCN.

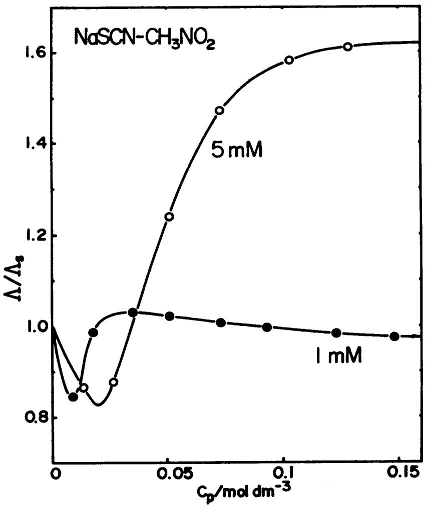

Fig. 5. Plots of relative conductance *vs.* concentration of POE for 5 mmol dm^{-3} and 1 mmol dm^{-3} NaSCN–nitromethane solutions at 298.15 K.

The conductivity curves for KSCN–nitromethane systems are shown in Fig. 3. The minimum in the conductivity is also observed. As is different from that observed in the KSCN–EtOH systems, the intrinsic

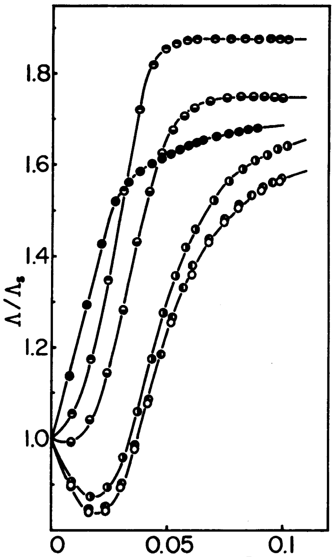

Fig. 6. Molecular weight dependence of the relative conductance *vs.* C_p plots for 5 mmol dm^{-3} NaSCN–nitromethane solutions at 298.15 K. Average molecular weigth; ●, 200; ◓, 400; ◒, 1500; ◑, 7500; ◐, 2×10^4; ○, more than 5×10^6.

value of the conductivity value of the conductivity in the large C_p increases with increasing C_s.

In contrast to the above systems, the behavior in the NaSCN–nitromethane solutions is anomalous. After the conductivity passes through a small minimum, Λ increases tremendously as can be seen in Fig. 4. The degree of the increase in the conductivity is dependent on C_s (Fig. 5). The effect of the molecular weight is shown in Fig. 6. The curves are almost independent of the molecular weight above 2×10^4. This means that the effect of the bulk viscosity of the solution is virtually negligible. In addition, it can be deduced that the electric mobility of the bound ions may be neglected as compared with that of the free ions, if the molecular weight of POE is above 2×10^4. As the molecular weight of POE decreases, the minimum of the curve becomes less prominent and finally diminishes. This is probably due to the increasing contribution of the bound ion to the conductivity.

Similar minima in the conductance plots were also observed by Smid and his coworkers, for the mixture of poly(vinylbenzo crown ether)s and potassium tetraphenylborate in methyl ethyl ketone.[7] The main reason for the appearance of the minima was ascribed to the reduction of viscosity in the higher C_p, where the charge density of the bound cation is relatively low. In view of our results, this is not likely because the conductivity does not depend on molecular weight above 2×10^4, so that the viscosity effect is negligible. We propose alternatively that the ion association on a polymer chain is the main cause of the occurence of the minima.

Before considering the systems quantitatively we should evaluate the ionic association constants in the absence of POE. These constants are calculated by the Fuoss-Kraus method[8] using molar conductivity data cited in the literatures[9,10] (Table 1). It should be noted that the ionic association constant of NaSCN in nitromethane is extremely large.

Table 1. Ionic association constants in polymer free solutions calculated by the Fuoss-Kraus method[8]

Solvent	KSCN	NaSCN
EtOH[a]	47.53	32.32
Nitromethane[b]	109.3	1591

a) Ref. 9, b) Ref. 10.

To calculate the Λ *vs.* C_p relationships in terms of the extended one-dimensional model, we must know the values for K_A, K_0^c, K_0^a, λ_c^∞, and λ_a^∞. The data in Table 1 can be used for the values for the K_A, and λ_c^∞ and λ_a^∞ values are cited in literatures.

In our previous paper, we have shown that a linear relationship exists between the binding constant and the standard chemical potential of the cation.[3] Using the relative values of the standard chemical potential of potassium ion to that of a reference solvent, reported by Owensby and his coworkers,[11] K_0^c for potassium ion is estimated as 4270 in ethanol and 23400 in nitromethane, respectively. For sodium ion in nitromethane, no reliable estimations of K_0^c are possible, but we tentatively use the same K_0^c value for the potassium ion.

The calculated curves are shown in Figs. 7 through 9, together with the observed values. It is necessary to take into account the ion association on a POE chain in reproducing the conductance minimum. As shown in the figures, the conductance minimum becomes sharper with increasing K_0^a. An optimum fitting is obtained by assuming that $K_0^a\simeq50$ for KSCN–ethanol, $\simeq20$ for KSCN–nitromethane, and $\simeq10$ for NaSCN–nitromethane. Thus, it appears that the ion association occurs to a considerable extent along POE chains.

In Fig. 10, the dependence of the calculated conductivity curves on C_s is shown for KSCN–EtOH solutions. From this figure and Fig. 1, it is noted that the calculated curves well reproduce the qualitative aspect of the C_s dependence of the observed curve as well as that of the conductivity minimum, thereby giving further support on the present model.

The quantitative agreement, however, is rather poor,

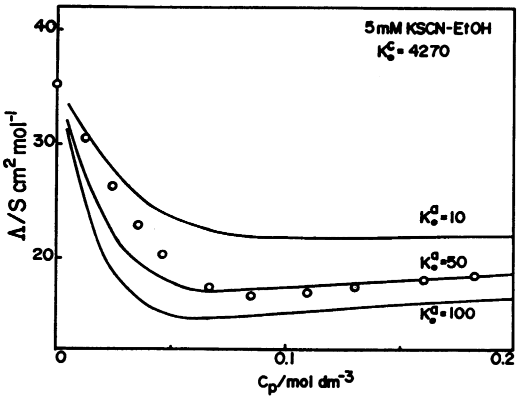

Fig. 7. Calculated Λ *vs.* C_p curves for 5 mmol dm^{-3} KSCN–EtOH solution, together with the observed plots.

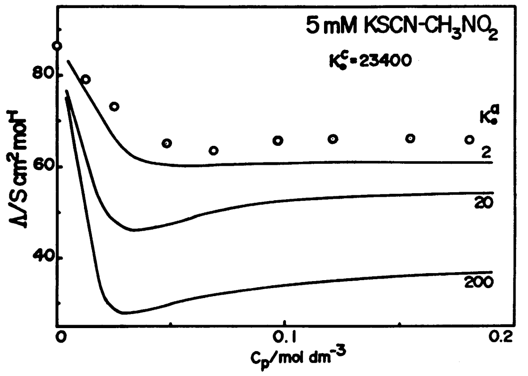

Fig. 8. Calculated Λ *vs.* C_p curves for 5 mmol dm^{-3} KSCN–nitromethane solution, together with the observed plots.

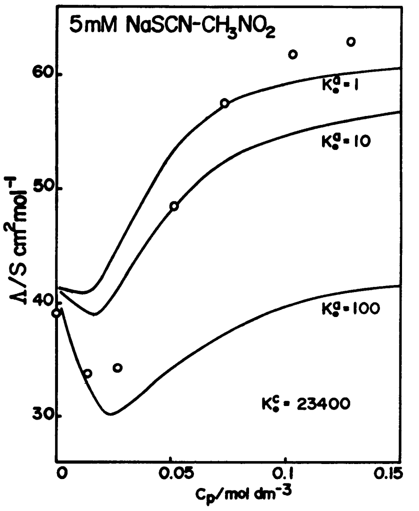

Fig. 9. Calculated Λ *vs.* C_p curves for 5 mmol dm^{-3} NaSCN–nitromethane solution, together with the observed plots.

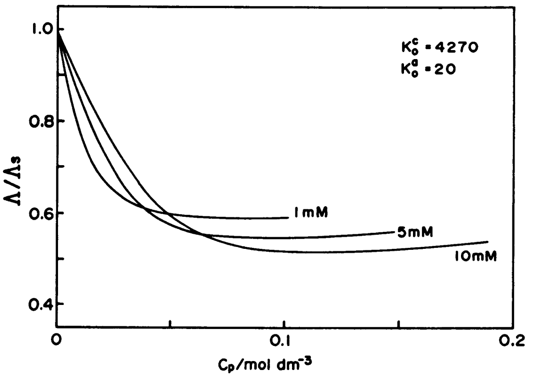

Fig. 10. Dependence of calculated Λ *vs.* C_p curves on total KSCN concentration for KSCN–EtOH solutions.

especially for NaSCN–nitromethane. The theoretical curve can not reproduce the steep rise in conductivity with C_p. One of the causes for the disagreement is the uncertainty in the determination of λ^∞. The precise determination of λ^∞ is difficult in a solvent where the ionic association constant is very large. Another possible cause is the inadequacy of the model where the charge density of the bound cation is high. In the present model, the statistical weight factor of the i-th site being in state $\underset{\sim}{2}$ is assumed to be $\xi\eta$ irrespective of the binding state of the neighboring sites. In practice, however, this factor may be related to whether $(i+1)$-th site is occupied or not.

It is worth noting that K_0^a values for NaSCN solutions are comparable in ethanol and in nitromethane, despite of the great difference in the ionic association constant, K_A, in the polymer free solution. This result is qualitatively explained by the solvation effects on the sodium ion.[12] In the acidic solvents, such as nitromethane, the solvating power for a cation is very low. On the other hand, basic POE strongly coordinates to sodium ion, which results in the reduction of ionic association if the charge density of the cation on the POE chain is low. This is the reason why the conductance increases in the high C_p for the nitromethane solution.

On the contrary, the hydrogen-bonding solvents, such as ethanol, have well-defined basic sites for the solvation to cation.[12] Consequently, the degree of association is small both in POE free solution and in solutions at high POE concentration. The association is only appreciable in the intermediate regions, where the charge density of the bound cation is high.

We observed a great difference in the behavior of NaSCN and KSCN solutions in nitromethane. As has been stated above, the ionic association constant for sodium ion is much larger than that for potassium ion in the absence of polymer. In the presence of excess POE, almost all the cations are bound to the POE chain. As the effective ion sizes of complexed sodium and potassium ions seem to be identical, the degree of the ionic association of these ions would be similar in magnitude. Consequently, the degree of ionic association for the sodium ion is greatly reduced by the addition of POE, while the reduction is less for the potassium ion.

Finally, we should briefly discuss the correlation with the Manning theory of polyelectrolyte solutions.[13] In his elegant theory, Manning stated that the so-called ion condensation of counter ions is uniquely determined by the charge density parameter ξ_M of the polyion, which is defined by;

$$\xi_M = \frac{e^2}{\varepsilon k_B T b}, \tag{25}$$

where b is the average distance between charges on the polyelectrolyte. According to the theory, for $\xi_M > 1$ the system becomes unstable and the counter ions condense on the polymer chain to achieve the ξ_M value of unity. While the Manning model explains the equilibrium properties of polyelectrolytes in aqueous solutions, the applications to the organic solvent systems are few in the literature.

According to the original theory, the Manning model assumes that the unbound free ions may be treated in the Debye-Hückel approximation. Therefore, the application of the model to the POE–NaSCN–nitromethane system is inadequate, since extensive ionic association occurs even in the POE free solution. We have examined the applicability of the Manning model to 5 mM KSCN–ethanol and –nitromethane systems, because the ionic association of KSCN is less in these solvents.

It follows from the above that the increase of the conductivity at higher C_p is due to the decrease of ionic association on a POE chain. Thus the POE concentration at the onset of ionic association may be estimated from the point that the increase of the conductivity is no longer detectable in Λ *vs.* C_p curves. From Figs. 1 and 3, for POE–5 mM KSCN–ethanol and –nitromethane systems, this point corresponds to $C_p \simeq 0.2$ and 0.13 M, respectively. Using the intersite distances calculated by a stiff-chain model,(2) ξ_M is estimated to be about 0.4 in both cases. This value is far lower than the limit of the ion condensation predicted from the Manning theory.

It should be noted that the Manning theory is based on the Bjerrum theory(14) of the ionic association between low-molecular weight ions. In the Bjerrum theory, the ionic association is a function only of the dielectric constant of the solvent and the inter-ionic distance. Recent investigations of the solvent effect of ionic association, however, have revealed that this is not true for the ionic association in organic solvents and that it also depends on a specific interaction between the ion and the solvent molecules.(12) This is also the case for the present systems, since the anion binding to the POE chain is related not only to the interaction between the POE–cation complex and the anion but also to that between the cation and the anion in the bulk solvent. As the result, the application of the Manning model to the present systems is inappropriate.

In conclusion, the anomalous conductivity curves for POE-alkali metal ions in ethanol and nitromethane are well explained by a duplicate ion binding model based on the one-dimensional lattice. An improvement of the model would be necessary to achieve a more sufficient agreement between the theoretical and the experimental conductivity curves.

References

1) K. Ono, H. Konami, and K. Murakami, *J. Phys. Chem.*, **83**, 2665 (1 79).

2) Part I of this series: H. Awano, K. Ono, and K. Murakami, *Bull. Chem. Soc. Jpn.*, **55**, 2525 (1982).

3) Part II of this series: H. Awano, K. Ono, and K. Murakami, *Bull. Chem. Soc. Jpn.*, **55**, 2530 (1982).

4) H. Awano, K. Ono, and K. Murakami, *Chem. Lett.*, **1982**, 149.

5) Since from the electro-neutrality principle, ξ and η are dependent with each other, partial differentiations represented in Eqs. 11 and 12 are mathematically impossible. Nevertheless, formal calculations are possible, because Ξ is the functions of ξ and η.

6) L. Onsager, *Phys. Z.*, **28**, 277 (1927).

7) S. C. Shah, S. Kopolow, and J. Smid, *J. Polymer Sci., Polymer Chem. Ed.*, **14**, 2023 (1976).

8) R. M. Fuoss, *Chem. Rev.*, **17**, 27, (1935); D. J. Mead, R. M. Fuoss, and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

9) M. Barak and H. Hartley, *Z. Phys. Chem.*, **A165**, 272 (1933).

10) C. P. Wright, D. M. Murray-Rust, and H. Hartley, *J. Chem. Soc.*, **1931**, 199.

11) D. A. Owensby, A. J. Parker, and J. W. Diggle, *J. Am. Chem. Soc.*, **96**, 2682 (1974).

12) R. M. Kay, D. F. Evans, and M. A. Matesich, "Solute-Solvent Interactions," ed by J. F. Coetzee and C. D. Richie, Marcel Dekker, New York (1976), Vol. 2, Chap. 10.

13) G. S. Manning, *J. Chem. Phys.*, **51**, 924 (1969).

14) N. Bjerrum, *Dan. Vidensk. Selesk. Mat. Fiz. Medd.*, **7**, 9 (1926).