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Complex Formation and Ionic Association in Nitromethane Solutions of Poly(ethylene oxide) and Alkali-Metal Salts

Hisashi Honda* and Katsumichi Ono

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Aoba-ku, Sendai 980, Japan

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ABSTRACT: Complexation between poly(ethylene oxide) (PEO) and alkali-metal ions in nitromethane was analyzed by means of conductometry using a one-dimensional lattice model. The binding constants of cation and anion to PEO increased with decreasing size of ions. In the case when the degree of cation binding was high, considerable ionic association on a polymer chain was found to occur. The similarity of this phenomenon to the concept of ion condensation in polyelectrolyte solution is discussed. The distance between charges on PEO–alkali metal ion complex estimated by the lattice model was very close to that calculated from the Manning theory.

Introduction

When complex formation between a neutral polymer and metal ions takes place in solution, two major interactions should be taken into account. One is the interaction between a metal ion and a polymer binding site, and the other is the electrostatic interaction among metal ions bound on a polymer chain. In our previous reports, we have developed a one-dimensional lattice model to separate these interactions.[1,2] This model has been successfully applied to the complex formation between poly(ethylene oxide) (PEO) and alkali-metal ions in organic solvents. It has been found that solvent effect on this complex formation is able to be correlated with the dielectric constant and the donor number of the solvent.[3] Especially the effect of the solvent donicity was large. In high-donicity solvents, metal ions were strongly solvated and the interaction between PEO and the metal ions became weak. On the other hand, in nitromethane the binding constant of alkali-metal ion to PEO was very large. This was ascribed to the low donicity of nitromethane.

When the solvent polarity decreases, considerable ionic association is known to occur. In the presence of polymer, two types of ionic association should be taken into account in the solution. One is the ionic association in bulk solvent, and the other is the ionic association on a polymer chain. The complexation between PEO and alkaline earth metal ions in methanol has already been analyzed by taking into account the ionic association.[4]

Ionic association is associated with the ion solvation as well as the electrostatic interaction between cation and anion. In the case of PEO and alkaline earth metal ions in methanol,[4] the degree of anion binding, i.e., the ionic association on the PEO chain, increased with increasing anion size. This was unexpected from the viewpoint of electrostatic theory of ionic association and was explained by the preferential effect of the solvation of anion.

In this study, the complexation with PEO and the ionic association of several alkali-metal salts were investigated in nitromethane. A preliminary study of this system has been already carried out by us,[5] but the agreement between the experimental and theoretical conductivities of these solutions was rather poor, probably owing to the high charge density on the PEO chain. When the charge density is high, it is difficult to estimate an accurate electrostatic potential around a polymer chain. In order to exclude the possibility of the interchain interaction between highly charged PEO chains, the investigation was limited to solutions having a low concentration of PEO.

There is an important difference between the present system and the previously investigated PEO-alkaline earth salt system in methanol.[4] As has been well-known, methanol has a well-defined solvation site to anion as well as that to cation.[6] Thus the solvation to anion should be stronger with decreasing size of the anion. This is the reason small anions such as Cl^- are stabilized in methanol solution. As the result, the degree of ionic association of Cl^- decreases. On the other hand, acidic nitromethane has only a weak solvation site to anion. Thus the effect of anion size on the solvation should not be important as in methanol solution.

Theory

One-Dimensional Lattice Model. When ionic association occurs on a polymer chain, energies of three states should be assumed on a one-dimensional lattice having N binding sites.[5] The energy of the site was assumed to be 0 if nothing is bound (state 0), E_c if a cation is bound (state 1), and $E_c + E_a$ if a cation and an anion are bound (state 2). State 2 is regarded as the ionic association on a polymer chain. The site specified state 1 has an effective charge and the site specified state 0 or state 2 has no net charge. The interaction between the ith site and the $(i + m)$th site is assumed to be described by a Debye–Hükel potential, J_m, if the electrostatic interaction is the only important interaction exerted along the polymer chain. A statistical weight factor, A_m, is defined by

$$A_m = \exp(-J_m/RT) \tag{1}$$

where R is the gas constant and T is the absolute temperature.

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

$$\xi = \exp[(\mu_c - E_c)/RT] \tag{2}$$

$$\eta = \exp[(\mu_a - E_a)/RT] \tag{3}$$

where μ_c and μ_a are the chemical potentials of the cation and the anion in the bulk solvent.

Using ξ, η, and A_m, 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. The degree of binding is defined for the cation and the anion by the following equations:

$$\theta_c = \left(\frac{1}{N}\frac{\partial \ln \Xi}{\partial \ln \xi}\right)_\eta \tag{4}$$

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$$\theta_a = \left(\frac{1}{N}\frac{\partial \ln \Xi}{\partial \ln \eta}\right)_\xi \tag{5}$$

The binding constants for the cation and anion are defined as

$$K_c = \exp[(\mu_c^\ominus - E_c)/RT] \tag{6}$$

$$K_a = \exp[(\mu_a^\ominus - E_a)/RT] \tag{7}$$

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

The molar conductivities of ions are assumed to obey the Onsager limiting law. The concentrations of free ions and the ionic association constant, K_A, were determined by using the Fuoss–Kraus method[7] so as to reproduce best the experimental plot of the equivalent conductivity, Λ, vs the concentration of the salt, C_s. For a certain PEO concentration, C_p, the equivalent conductivity was calculated by solving a set of simultaneous equations with respect to ξ, η, θ_c, and θ_a.[5] K_c and K_a are determined so as to reproduce best the experimental conductivity curves.[4]

Experimental Section

Reagents. Commercial PEO (Wako Chemicals) with a nominal molecular weight of 2 × 10^4 (viscosity-average molecular weight 2.47 × 10^4) was used throughout this study. Alkali-metal salts were reagent grade and dried under a vacuum. Nitromethane was stirred with a molecular sieve, 4A, and distilled.

Conductivity Measurement. Conductivity was measured by a GenRad GR-1689 digibridge at 3 kHz in a glass cell controlled to 25 ± 0.02 °C by a silicone oil circulating glass jacket. The measurements were repeated three times. Accuracy was normally less than 1%.

In our previous studies, Λ was measured as a function of C_p under a constant C_s. The agreement between theory and experiment was excellent in the Ba^{2+}–PEO–methanol system[4] but it was rather poor in the Na^+–PEO–nitromethane system.[5] One of the reasons for the disagreement in the latter may be ascribed to the high degree of cation binding to PEO. For instance, under the condition of excess salt, θ_c of Ba^{2+} was less than 0.1 in methanol, but θ_c of Na^+ was about 0.4 in nitromethane.[3] Even though the charge of Ba^{2+} is twice of that of Na^+, the total charge density of Na^+–PEO in nitromethane was still very high. This was also depicted by the high intrinsic viscosity of the Na^+–PEO–nitromethane system.[3] That is to say, in the present system, the PEO chain seems to be expanded owing to the electrostatic repulsive force exerted along the polymer chain. Thus the conductivity measurement should be limited to low C_p, because the intermolecular interaction between PEO chains becomes significant at high C_p, where the application of the one-dimensional model becomes inadequate. Taking into account this point, we measured the conductivity under a constant C_s/C_p ratio, instead of constant C_s. The analysis of conductivity was carried out in the range $C_p < 4C_s$. It has been suggested in a previous study[1] that a binding site of PEO is composed of four monomer units. Hence, the above range of C_p corresponds to the condition that the concentration of the binding site is lower than C_s.

Viscosity Measurement. The viscosities of the PEO solutions containing a salt were measured with a Ubbelohde viscometer at 25 °C. In PEO–alkali metal salt solution, the curves of the reduced viscosity vs PEO concentration showed a maximum. This behavior is similar to that of polyelectrolytes with a low concentration of added salt. The value of [η] of PEO was obtained by extrapolating the curve in the range of low PEO concentration to zero concentration.

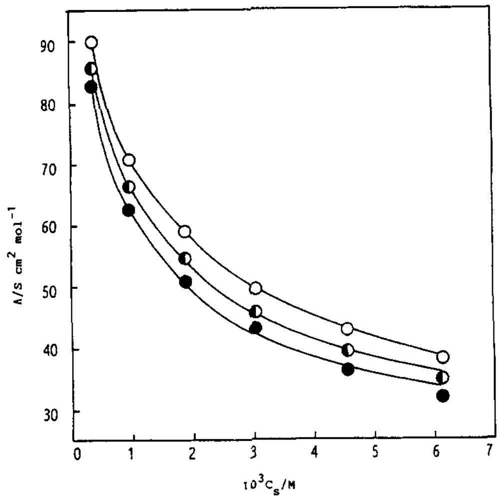

Figure 1. Plots of Λ vs C_s for NaSCN and NaSCN–PEO solutions: (○) $C_p = 0$; (◐) $C_s/(C_p/4) = 2$; (●) $C_s/(C_p/4) = 1$. The solid curves are calculated by the Fuoss–Kraus method and the one-dimensional lattice model.

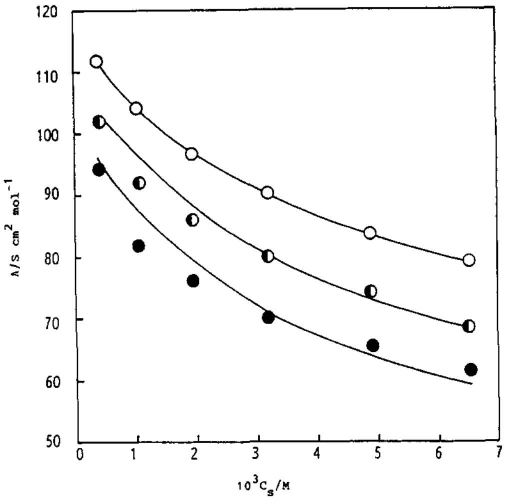

Figure 2. Plots of Λ vs C_s for $NaClO_4$ and $NaClO_4$–PEO solutions. The symbols and the method of calculation for the solid curves are the same as for Figure 1.

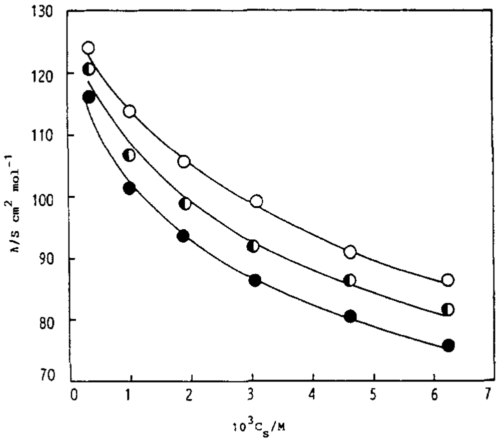

Figure 3. Plots of Λ vs C_s for KSCN and KSCN–PEO solutions. The symbols and the method of calculation for the solid curves are the same as for Figure 1.

Results and Discussion

The conductivity plots of Λ vs C_s at constant C_s/C_p are shown in Figures 1–3 for NaSCN, $NaClO_4$, and KSCN solutions. The uppermost plots of these figures show the conductivity for $C_p = 0$. Solid curves are those calculated by the Fuoss–Kraus method. The observed large decrease of Λ of these plots can be ascribed to the ionic association. The decrement of Λ was largest for NaSCN solution. Calculated K_A values including those of other salts are summarized in Table I. Standard deviations for the repeated measurements were normally less than 1%. K_A decreased with increasing ion size not only for cation but

Table I
Ionic Association Constants for Alkali-Metal Salts in Nitromethane

salt	K_A	salt	K_A
$LiClO_4$	212	$NaClO_4$	117
NaSCN	1330	KSCN	126
NaI	106	KI	46

Table II
Binding Constants of Cation and Anion on the PEO Chain

salt	$C_s/(C_p/4)$	K_c	K_a
$LiClO_4$	1	24000	21
	2	20000	14
NaSCN	1	4700	170
	2	8300	100
NaI	1	13000	6.1
	2	11000	5.6
$NaClO_4$	1	13000	6.5
	2	11000	5.8
KSCN	1	2600	8.8
	2	2000	9.4
KI	1	2900	2.0
	2	2300	2.0

also for anion.

The lower two plots of each figure show the conductivity in the presence of PEO. The addition of PEO has two effects upon the conductivity of the solution. One is the decrease of conductivity due to the cation binding to PEO, and the other is the increase of conductivity due to the dissociation of the ion pair being accompanied by the complexation of cation. Figures 1–3 show that the former effect is dominant; however, some differences in the decrement with PEO addition should be noted.

The decrease of Λ with PEO addition was not so large for NaSCN solution. This is probably due to the strong ion pair formation between Na^+ and SCN^-. The complexation with PEO takes place mainly with free Na^+ ions, but the concentration of free Na^+ ion is low. On the other hand, a relatively large decrease of Λ with PEO addition was observed for the $NaClO_4$ and KSCN systems. In these systems, ionic association in the bulk solvent is not so important. Then free cations are complexed with PEO, which results in the decrease of Λ.

The lower two solid curves in Figures 1–3 are the calculated ones using best-fit K_c and K_a values. The agreement between the calculated curves and the experimental data is fairly good. Determined binding constants K_c and K_a are summarized in Table II. Standard deviations for the repeated measurements were normally less than 10%. The dependence of K_c and K_a on C_s/C_p was not so large. K_c increased with decreasing size of cation.

To check the validity of the present calculation, we compared K_c values with those determined from the analysis of tetraphenylborate salt solution.[3] As has been well-known the ionic association of large tetraphenylborate anion is negligible.[8] K_c values obtained from sodium and potassium tetraphenylborate are in fair agreement with those determined in the present study.

In donor solvents such as acetonitrile, K_c of Na^+ is smaller than that of K^+ because of the stronger solvation to Na^+.[3] On the other hand, in acidic solvents such as nitromethane, the solvation of cation is not important. Therefore K_c for small Na^+ is larger than that for K^+ because of the stronger ion–dipole interaction of Na^+ and PEO.

Figure 4 shows the plot of the logarithm of the anion binding constant, K_a, against the crystallographic radius of the anion. For both sodium and potassium salts, K_a seemed to decrease with increasing anion size. This is the normal behavior expected from the electrostatic theory of ionic association. In a previous study, the situation was reverse for barium salts in methanol.[4] The difference in these two systems would be explained by the relative magnitude of anion solvation. A measure of the solvation to anion is the acceptor number. Since the acceptor numbers of nitromethane and methanol are 20.5 and 41.3, respectively,[9] the desolvation energy of anion is not so important in nitromethane. Then the ionic association of the small anion becomes favorable because of the large electrostatic energy in nitromethane. On the other hand, in methanol the ionic association of the large anion becomes favorable because of the smaller desolvation energy.

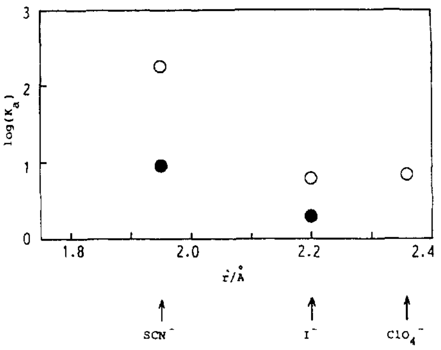

Figure 4. Relationship between the crystallographic ionic radius of anion and log (K_a) in alkali-metal salts–PEO–nitromethane solutions: (○) sodium salts; (●) potassium salts.

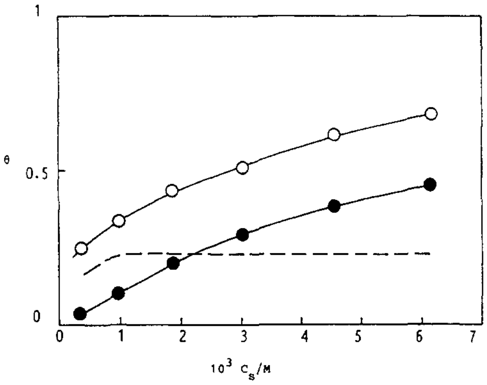

Figure 5. Plots of the degree of ion binding to PEO in the NaSCN–PEO–nitromethane system. $C_s/(C_p/4) = 1$. (○) θ_c; (●) θ_a. The broken line is $\theta_c - \theta_a$.

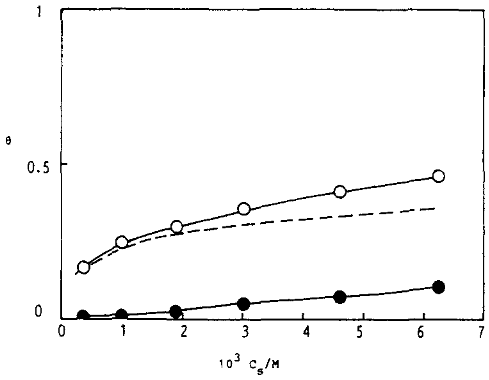

Figure 6. Plots of the degree of ion binding to PEO in the KSCN–PEO–nitromethane system. $C_s/(C_p/4) = 1$. (○) θ_c; (●) θ_a. The broken line is $\theta_c - \theta_a$.

Plots of the degree of ion binding to PEO vs C_s are shown in Figures 5 and 6. The broken line is $\theta_c - \theta_a$, which corresponds to the effective charge density on a polymer chain. In the KSCN–PEO system $\theta_c - \theta_a$ increased slowly

Table III
Distances, b', between the Effective Charges on a PEO Chain Calculated from the Experimental Results

salt	$[\eta]$, dL g^{-1}	$C_s/(C_p/4)$	$\theta_c - \theta_a$	b', Å
$LiClO_4$	0.88	1	0.372	18.4
		2	0.353	18.9
NaSCN	0.79	1	0.237	22.9
		2	0.290	20.5
NaI	0.92	1	0.366	18.7
		2	0.341	19.4
$NaClO_4$	0.93	1	0.375	18.5
		2	0.349	19.2

with increasing C_s but it was almost constant above a certain value of C_s in the NaSCN–PEO system. This phenomenon is similar to the so-called ion condensation in polyelectrolyte solution and was observed in the lithium and sodium salt solutions. In the Manning theory,[10] the charge density parameter, ξ_M, of the polyion is defined by

$$\xi_M = e^2/\epsilon k_B T b \tag{8}$$

where b is the distance between charges, e is the elementary electronic charge, k_B is the Boltzmann constant, and ϵ is the dielectric constant of the solvent. According to his theory, for $\xi_M > 1$ the system becomes unstable and the counterions condense on the polymer chain to achieve a ξ_M value of unity. If $\epsilon = 36$ of nitromethane is substituted in eq 8, b is estimated to be 15 Å, which will be independent of the kind of ions. In our treatment, the average number of sites between nearest-neighbor effective charges may be estimated from $(\theta_c - \theta_a)^{-1}$. Application of the stiff-chain model[1] enables us to calculate the average distance between effective charges, b', where the expansion factor is estimated by the intrinsic viscosity, $[\eta]$. b' values thus estimated are summarized in Table III. The average value of b' is 19.6 Å, which is close to the value obtained from the Manning theory.

The Manning theory has succeeded in describing the equilibrium properties of polyelectrolytes in aqueous solution. The theory insists that the effective charge density would be solely determined by the dielectric constant of the solvent. This is a testable prediction when we use organic solvent. However, the use of organic solvents is limited by the low solubility of the usual polyelectrolyte. Recently, several attempts have been made to clarify the solution behavior of polyelectrolyte in polar organic solvents.[11,12] In highly polar solvents such as dimethyl sulfoxide, typical polyelectrolyte behavior has been observed.[13] No studies have been made, however, about the counterion condensation in organic solvents.

As shown in Figure 5, the present study suggests that the Manning theory is also applicable in organic solvents under certain conditions. Because of the weak solvation to ions in nitromethane, the ionic association in this system would be principally governed by the electrostatic interactions between ions, if ion size is not so large. On the other hand, when ion size increases, the solvation effect becomes important even in the solvent in which the solvation is weak. In this case, the Manning theory is not applicable as shown in Figure 6, and the effective charge density on the chain increases with increasing C_s. As an extreme case, the ionic association is hardly observed when the large tetraphenylborate ion is used.

Another point we should take into account is the effective charge density on the polymer chain. In an organic solvent with a low dielectric constant, the critical charge density for ion condensation predicted from Manning theory would be far lower than that in aqueous solution. Moreover, the electric effect becomes a long-range type in this case. Then the shielding effect of free counterion on the electrostatic interaction between charges on the polymer chain becomes important. The slow increase of the effective charge density of the PEO chain observed in Figure 6 with increasing C_s may be explained by this effect.

In conclusion, the binding behavior of alkali-metal ion to PEO is well explained by a one-dimensional lattice model even when a large amount of ionic association occurs. For small counterions, the result was consistent with the Manning theory of polyelectrolytes. On the other hand, for large ions, the solvation effect becomes important, and the effective charge density on the PEO chain increased with increasing salt concentration even above the critical value predicted from the Manning theory.

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Registry No. PEO, 25322-68-3; $LiClO_4$, 7791-03-9; NaSCN, 540-72-7; NaI, 7681-82-5; $NaClO_4$, 7601-89-0; KSCN, 333-20-0; KI, 7681-11-0.