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The Interaction of a Neutral Polymer with Small Ions in Solution. II. The Binding of Alkali Metal Ions to Poly(oxyethylene) in Several Organic Solvents

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The conductivities for several solutions of alkali metal salts, such as potassium thiocyanate, containing poly(oxyethylene) (POE) have been measured as functions of the POE concentration, C_p. A decrease in the conductivity with an increase in C_p has been observed, particularly in methanol, acetonitrile, propylene carbonate, and sulfolane. For these systems, the binding of the cation has been evaluated from the decrease in conductivity and analyzed by a method based on the one-dimensional lattice model. As well as the solvent effects, the effects of the salt concentration and the effect of the alteration of salt on the binding constant have been discussed.

In the preceding paper in this series,[1] we have established a method for the theoretical prediction of the ion binding to a neutral polymer, such as poly(oxyethylene) (POE), in solution.

In this paper, the binding of alkali metal ions to POE is observed by means of conductometry, and the results are analyzed by applying this method, which is based on the one-dimensional lattice model. Also discussed are the solvent effects on the binding of potassium ion, the effects of the salt concentration on the binding of the potassium ion in propylene carbonate (PC), and the effects of the alteration of salt on the binding of the cation in PC.

Experimental

Reagents. The poly(oxyethylene) sample, with an average molecular weight of 2.47×10^4, was obtained from Wako Pure Chemicals and was used without further purification. Methanol (Wako, >99.6%) was dried over calcium hydride, followed by distillation. The conductivity of the purified substance, κ, was 7×10^{-7} S cm^{-1}. Acetonitrile (Wako) was stirred with calcium hydride to dryness and then distilled in the presence of calcium hydride; $\kappa=3\times10^{-8}$ S cm^{-1}. Propylene carbonate (Wako) was stirred with a molecular sieve, 4A, to dryness, and then distilled under reduced pressure (87 °C at 2 mmHg†); $\kappa<10^{-8}$ S cm^{-1}. Sulfolane (Wako) was stirred with sodium hydroxide and distilled in the presence of sodium hydroxide under reduced pressure (105 °C at 4 mmHg) until a small amount of the sample did not show any development of visible color within 5 min after the addition of an equal volume of 100% sulfuric acid.[2] $\kappa<10^{-8}$ S cm^{-1}. *N,N*-Dimethylformamide (Kanto) was stirred with a molecular sieve, 4A, and distilled under reduced pressure; $\kappa=2\times10^{-8}$ S cm^{-1}. Dimethyl sulfoxide (Wako) was stirred with calcuim hydride and distilled under reduced pressure; $\kappa=2\times10^{-8}$ S cm^{-1}. Deionized water was used; $\kappa=3\times10^{-6}$ S cm^{-1}. All the salts used were reagent-grade and were dried under a vacuum.

Viscosity Measurements. The viscosity of a POE solution containing a salt was measured with a Ubbelohde viscometer. The effect of the shear rate was disregarded.

Conductivity Measurements. The conductiovity of the solution was measured in a fashion similar to the method of Ono *et al.*[3]

Results and Discussion

Evaluation of the Cation Binding. *Procedure*: In order to evaluate the degree of binding of the cation from the relationships between the equivalent conductivity of the salt, Λ, and the POE concentration (monomer base mole), C_p, we make the following assumptions: the decrease in the conductivity of the solution with the increase in C_p is solely due to the binding of the cation to POE, and the bound cations make no contribution to the conductivity. The reasonability of this assumption will be later checked in detail. According to Ono *et al.*,[4] the fraction of the unbound, free cation is given by:

$$\alpha = \frac{\Lambda - \Lambda_{ps}}{\Lambda_s - \Lambda_{ps}}, \tag{1}$$

where Λ_s is the equivalent conductivity at $C_p=0$ and Λ_{ps} is that supposing all the cations are bound. Λ_{ps} may be the ionic equivalent conductivity of the anion, based on the above assumption, and we assume, as a zeroth-order approximation, that:

$$\Lambda_{ps} = \Lambda_s[\lambda_-^\infty/(\lambda_+^\infty + \lambda_-^\infty)], \tag{2}$$

where λ_+^∞ and λ_-^∞ are the limiting ionic equivalent conductivities of the cation and the anion respectively. The values of λ_+^∞ and λ_-^∞ used here, together with those of $\lambda_-^\infty/(\lambda_+^\infty+\lambda_-^\infty)$ for the salts, are shown in Table 1. If we assume that a binding site is composed of four successive monomer units on a POE chain,[3] then the degree of binding θ, is:

$$\theta = \frac{(1-\alpha)C_s}{C_p/4}, \tag{3}$$

where C_s is the salt concentration. On the other hand, the relative activity of the cation in the bulk solution phase is given by:

$$a = \alpha y C_s, \tag{4}$$

where y is the activity coefficient on the molar concentration basis, which is regarded as equal to the activity coefficient on the molarity basis, γ, for a dilute solution. Hence, it is estimated using the Debye-Hückel extended equation for an activity coefficient. We thus obtain experimentally the relation of θ *vs.* log a.

Reasonability of Some Assumptions in the Evaluation of the Cation Binding. Although the assumptions presented above seem to be very daring, we shall verify

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† 1 mmHg ≈ 133.322 Pa.

Table 1. Limiting ionic equivalent conductivity, λ_+^∞ and λ_-^∞, and $\lambda_-^\infty/(\lambda_+^\infty+\lambda_-^\infty)$ at 298.15 K

Solvent	Ion	$\dfrac{\lambda_+^\infty \text{ or } \lambda_-^\infty}{\text{S cm}^2\text{ mol}^{-1}}$	Electrolyte	$\dfrac{\lambda_-^\infty}{\lambda_+^\infty+\lambda_-^\infty}$
Methanol[a)]	Na^+	42.5	KSCN	0.565
	K^+	50.2	NaI	0.608
	Rb^+	53.0	KI	0.568
	Cs^+	59.2	RbI	0.555
	SCN^-	65.2	CsI	0.527
	I^-	66.0		
Acetonitrile[a)]	K^+	85.9	KSCN	0.620
	SCN^-	140	KI	0.540
	I^-	101.0		
Propylene carbonate[b)]	Na^+	9.45	$KClO_4$	0.623
	K^+	11.17	KSCN	0.665
	Rb^+	11.90	KBr	0.629
	Cs^+	12.66	KI	0.622
	ClO_4^-	18.44	NaI	0.660
	SCN^-	22.12	RbI	0.607
	Br^-	18.91	CsI	0.592
	I^-	18.35		
Sulfolane[c)] (303.15 K)	K^+	4.04	KSCN	0.705
	SCN^-	9.63		

The values of λ_+^∞ and λ_-^∞ are cited in: a) Ref. 4; b) Ref. 5; Ref. 6.

in detail that these assumptions bring about no fatal results and that the derived conclusions are virtually correct.

In the first place, we have assumed that all the cations and anions behave freely and are independent of each other in the solution. If ionic association should occur, then, in addition to the equilibrium of binding of the cation to the POE lattice, another chemical equilibrium would have to be considered. According to the analysis of the equivalent conductivity data in the literature,[7)] however, the ionic association constant is sufficiently small for the salt–solvent systems studied in this paper. Therefore, the influence of the ionic association is practically negligible. Moreover, since the degree of ion binding is not very large and the charge density on the polymer chain is small, the binding of the anion to the POE–cation complex can not be expected to occur.

Secondary, we have measured the equivalent conductivity by diluting a salt–POE solution with a salt solution which does not contain POE. If the volume changed on the dilution of POE, accurate values of the equivalent conductivity could not be obtained in this manner. Searching the literature for examples of the measurements of volume change on the dilution of ion–polymer solution systems, we find a few data for aqueous solutions of maleic acid–olefin copolymer[8,9)] and of poly(acrylic acid).[9)] The volume change accompanied by the protonation of the polyanion is, for both systems, in the order of $\Delta V \approx 10$ cm^{-3} mol^{-1} (monomer base mole). If, in our systems, the volume change is in this order, then $\Delta V\ C_p \approx 10^{-3}$ in the concentration of $C_p \approx 10^{-1}$ mol dm^{-3} and the error of the equivalent conductivity accompanied by the volume change is in the order of 0.1%. Although it will be necessary, in the future, to investigate this problem in detail, neglecting the influence of the volume change would not bring about any serious errors.

Thirdly, let us discuss the influence of the increase in the viscosity of the solution. It has been well known that, in a solution containing a polymer, the relationship between the equivalent conductivity and the viscosity of the solvent (a solution composed of a pure solvent and a polymer, in this case) deviates enormously from the Walden rule.[3,10)] We have measured the equivalent conductivity as a function of C_p for the tetrapropylammonium iodide(TPrAI)–POE–PC system, in which the cation is expected not to be bound to POE. As may be seen in Fig. 1, the decrease in Λ with an increase in C_p is found to be very small. It is impossible, however, to conclude whether the decrease is caused by the binding of the cation or by the increase in the viscosity of the solvent. Even if the decrease in Λ were caused by an increase in the viscosity of the solvent in this case, neglecting the descent of Λ would bring about no serious errors in the systems in which the binding of the cation occurs to a large extent, because the contribution of the increase in the viscosity of the solvent to the decrease of Λ is expected to be very small. As long as no quantitative law has been established for the relationship between equivalent conductivity and viscosity in a system containing a polymer, we unavoidably neglect the influence of the increase in viscosity.

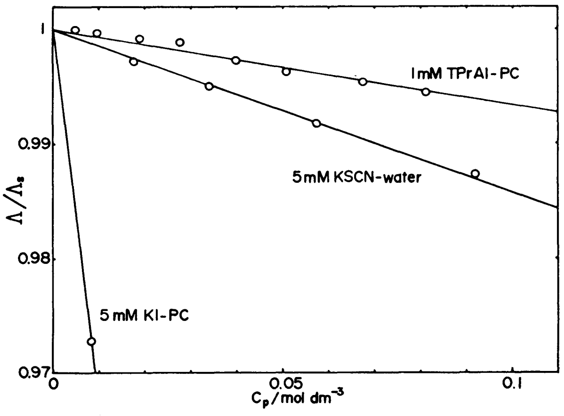

Fig. 1. The relation between Λ/Λ_s and C_p for 1 mmol dm^{-3} tetrapropylammonium iodide (TPrAI)–PC system, together with 5 mmol dm^{-3} KI–PC and 5 mmol dm^{-3} KSCN–water systems.

Fourthly, we shall examine the reasonability of Eq. 2. For ionic equivalent conductivity on the right-hand side of Eq. 2, it must be better to use the values of ionic equivalent conductivity in the salt concentration studied than to use those in the limit of $C_s \rightarrow 0$. For the KI–PC system, the limiting ionic equivalent conductivities of K^+ and I^- are, respectively, 11.17 and 18.35 S cm^2 mol^{-1},[5)] so that $\lambda_-^\infty/(\lambda_+^\infty+\lambda_-^\infty)=0.6216$. On the other hand, if the Onsager limiting law holds, then the ionic equivalent conductivities of K^+ and I^- are, respectively, 10.09 and 17.12 S cm^2 mol^{-1} at 5 mmol dm^{-3}, so that $\lambda_-^\infty/(\lambda_+^\infty+\lambda_-^\infty)=0.6290$. Using these values, we analyzed the binding curve by a method to be described below; we found that the logarithmic binding constant is 1.99 in the former case and 2.02 in the latter case. As this difference is very small, it is concluded that the approximation in Eq. 2 causes no essential errors.

Finally, we shall refer to the assumption that the bound cations make no contribution to the conductivity. As was observed by Ono *et al.*,[3] the conductivity of the solution at a given C_p decreases with an increase in the molecular weight of POE, M, but for $M > 10^4$ the conductivity becomes independent of M. This finding implies that the assumption is reasonable.

In conclusion, the assumption in question does not reverse the quantitativity of the results which will be presented below.

The Solvent Effects on the Binding of the Potassium Ion. Binding Behavior in Various Solvents. Figure 2 shows η_{sp}/c *vs.* c relationships for POE in 5 mmol dm^{-3} KSCN solutions. The curves have a maximum in the methanol (MeOH), acetonictrile (AN), PC, and sulfolane (tetramethylene sulfone, TMS) systems, similar to the behavior of polyelectrolytes in added salt systems. These results imply that the polymer chain has some charges for these systems. The value of the intrinsic viscosity of the polymer, $[\eta]$, obtained by extrapolation to $c \to 0$, are shown in Table 2. As has been stated in the preceding paper,[1] these values can be used for the estimation of the intrinsic distance in a POE chain forming a one-dimensional lattice.

Table 2. Intrinsic viscosity of POE in the 5 mmol dm^{-3} KSCN system at 298.15 K

Solvent	$[\eta]$/dl g^{-1}
Methanol	0.57
Acetonitrile	0.72
Propylene carbonate	0.87
Sulfolane[a]	0.54
DMF	0.44
DMSO	0.44
Water	0.47

a) 303.15 K.

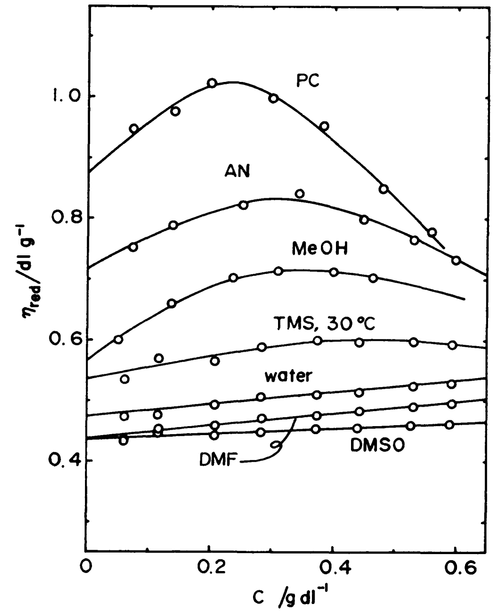

Fig. 2. Dependence of the reduced viscosity of POE, η_{red}, on POE concentration, c, in 5 mmol dm^{-3} KSCN solutions at 25 °C.

Figure 3 shows the relation between Λ/Λ_s and C_p for 5 mmol dm^{-3} of KSCN in seven solvent systems. In MeOH, AN, PC, and TMS systems, the degrees of the decrease in Λ/Λ_s with the increase in C_p are very large compared with other solvent systems. Thus, it can be qualitatively said that, in the MeOH, AN, PC, and TMS systems, ions are bound to the polymer. The preceding paper[1] states that log K_0 is a shift factor obtained by fitting the observed plots of θ *vs.* log a to the calculated curve of θ *vs.* log ξ, where ξ is the normalized activity.[1] Figure 4 shows the binding data obtained from the conductance values as well as the calculated binding curves. These binding data are in excellent agreement with the calculated curves over a wide range of activity of the potassium ion, using a single choice of the parameter, K_0. The binding constants obtained through this procedure are shown in Table 3. σ^2 is a measure of fitting (see Footnotes to Table 3). By the way, for the DMF, DMSO, and aqueous systems, the decrease in the conductivity with an increase in C_p is small, so the data are difficult to analyze with precision.

Comparison with the Method Based on the Low-molecular Analogy. As has been seen above, the analysis based on the one-dimensional lattice model seems to be most appropriate. We shall now compare this method with the method based on the low-molecular

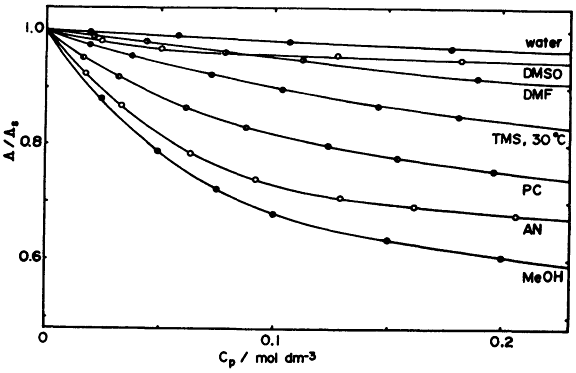

Fig. 3. The relation between the equivalent conductivity of KSCN, Λ, and POE concentration, C_p, at 25 °C.

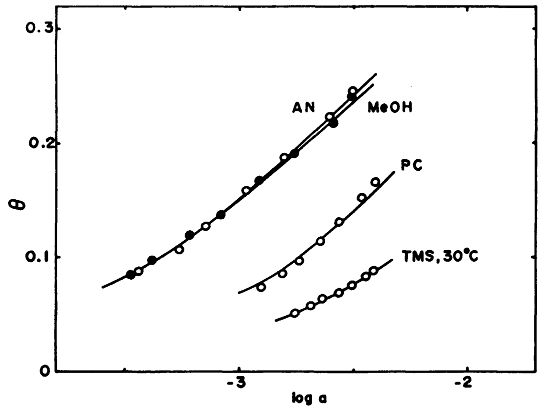

Fig. 4. Plots of the degree of binding, θ, against the logarithm of relative activity of potassium ion at 25 °C, together with the calculated curves.

TABLE 3. BINDING CONSTANT OF THE POTASSIUM ION TO POE DETERMINED FOR THE 5 mmol dm^{-3} KSCN SYSTEMS AT 298.15 K

Solvent	$\log K_0$	σ^2 a)
Methanol	2.74	0.000173
Acetonitrile	2.68	0.000400
Propylene carbonate	1.97	0.00150
Sulfolane b)	1.63	0.000133

a) $\sigma^2=\frac{1}{n}\sum_{i=1}^{n}[(\theta_i^{\text{calcd}}-\theta_i^{\text{obsd}})/\theta_i^{\text{calcd}}]^2$. b) 303.15 K.

analogy. Based on the low-molecular analogy, we consider the following equilibrium:

$$\begin{array}{lcl} \text{Site} \;+ & \text{Ion} \rightleftarrows & \text{Site-ion complex.} \\ (1-\theta)C_p/4 & C_s a & \theta(C_p/4) \end{array} \qquad (5)$$

We define the equilibrium constant, K, as in the following equation:

$$K=\frac{\theta}{(1-\theta)C_s a}. \qquad (6)$$

Each simbol has the same meaning as that used in the preceding sections. In the system containing a polymer, however, the equilibrium constant defined in Eq. 6 intensively depends on θ, and K becomes greater as θ is smaller, in general. That is the problem that we brought forward in the introducion in the preceding paper.[1] The procedure often used in analyzing the proton dissociation of polyacids is to regard the intrinsic equilibrium constant as the value of K extrapolated to $\theta \rightarrow 0$, in which there is no interaction between the sites. Let us apply this procedure to our present systems. The relation of $\log K$ *vs.* θ is shown in Fig. 5. The degree of binding, θ, ranges widely, and the extrapolation to $\theta \rightarrow 0$ is then considerably easy in the MeOH and AN systems, whereas there is uncertainty in the extrapolation in PC and TMS systems. Even if the extrapolated value of log K can be accurately obtained, its physical meaning is ambiguous. As a result, it can be concluded that it is not effective to apply the method based on the low-molecular analogy to these systems.

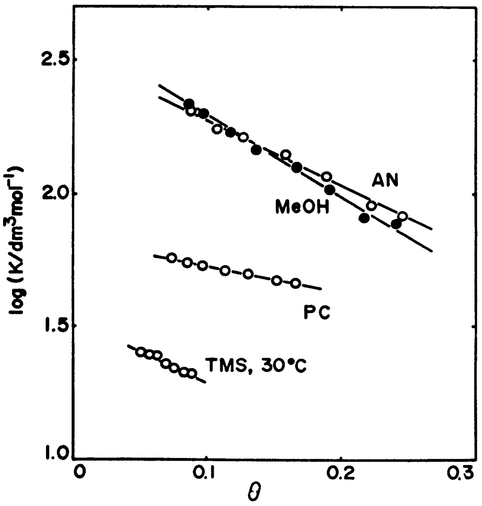

Fig. 5. Dependence of the equilibrium constant, K, which is defined in Eq. 6 based on the low-molecular analogy, on the degree of binding, θ, for 5 mmol dm^{-3} KSCN systems at 25 °C.

Interpretation of the Solvent Effects on the Binding Constant. We have obtained the binding constant, K_0, a quantity closely related to the intrinsic interaction between the site and the cation. Our next task is to discuss the solvent effects on K_0. In our treatment based on the one-dimensional lattice model, it is postulated that the solvent is to be regarded as a continuum. From the molecular-theoretical point of view, however, the cation binding to POE involves a process in which the solvent molecules coordinating to the cation are released. Thus, it can be said qualitatively that the cation binding to POE is less favorable as the solvent becomes a stronger solvator, *i.e.*, a stronger electron donor, to the cation. One of the parameters which represents the electron donicity of a solvent is the donor number (DN), proposed by Gutmann.[11] The DN values for several solvents are shown in Table 4. Roughly speaking, the binding of the potassium ion to POE occurs significantly in the solvents which have comparatively small DN values. By the way, the DN of diethyl ether, which is the low-molecular analog of POE, is 19.2. It might be noted that, in a solvent whose DN is larger than that of diethyl ether, the cation binding to POE is no longer observed. These quantitative considerations tell us that, in the interpretation of the solvent effects on K_0, we must pay attention to the problem of the solvation of the cation. However, the correlation between K_0 and DN is found to be bad.

TABLE 4. CORRELATION AMONG THE BINDING CONSTANT, K_0; THE DONOR NUMBER OF THE SOLVENT, DN, AND THE STANDARD CHEMICAL POTENTIAL OF THE POTASSIUM ION, $\mu^\ominus$

Solvent	DN a)	$\Delta\mu^{\ominus}$ b,c) / kJ mol^{-1}	$\Delta\log K_0$ b,c)
Nitromethane	2.7	9.64	
Ethanol		5.45	
Methanol	19.0	2.51	0.06
Acetonitrile	14.1	0	0
Propylene carbonate	15.1	−4.19	−0.71
Sulfolane e)	14.8	−6.70	−1.05
Diethyl ether	19.2		
Water	18.0 f)	−13.8	
DMF	26.6	−20.1	
DMSO	29.8	−25.1	

a) Ref. 11. b) Δ means that AN is chosen as the reference solvent. c) Ref. 13. d) This work (from Table 3). e) 303.15 K. For other solvent systems, 298.15 K. f) It is said that, although there is no theoretical ground for it, the value of 30 often explains experimental findings better for water as a solvent.[12]

Next let us try to correlate K_0 and the standard chemical potential of the potassium ion in each solvent, $\mu^\ominus$, which is a thermodynamic quantity reflecting the strength of the solvation of this ion as a whole. K_0 is composed of two factors, $\exp(\mu^\ominus/RT)$ and $\exp(-E/RT)$, where E is the binding energy to the site (for details, see the preceding paper[1]). We introduce a rough assumption that E is constant, independent of the solvent. The binding energy, E can be expected to contain the complexation energy of the binding site and the desolvation energy of the polymer, the latter being dependent on the solvent. This assumption, however, seems to be sufficient as a zeroth-order approximation. According to this assumption, if we consider the ratio of the binding constant in an arbitrary solvent, S, $K_0(\mathrm{S})$, to that in a reference solvent, R, $K_0(\mathrm{R})$, then:

$$\begin{aligned}\Delta\log K_0 &\equiv \log[K_0(\mathrm{S})/K_0(\mathrm{R})]\\ &= [\mu^{\ominus}(\mathrm{S}) - \mu^{\ominus}(\mathrm{R})]/2.303\,RT\\ &\equiv \Delta\mu^{\ominus}/2.303\,RT, \qquad (7)\end{aligned}$$

where $\mu^{\ominus}(\mathrm{R})$ and $\mu^{\ominus}(\mathrm{S})$ are the standard chemical potential of the cation in the R and S solvents respectively. The $\Delta\mu^{\ominus}$'s of the potassium ion when AN is chosen as the reference solvent have been measured by Owensby *et al.***[13] They have measured the $\Delta\mu^{\ominus}$'s by several kinds of methods. We adopt the values obtained by assuming a negligible liquid-junction potential, which is believed to be the most reliable method. If we plot $\Delta\log K_0$ against $\Delta\mu^{\ominus}/2.303RT$, we find that Eq. 7 holds roughly, as is shown in Fig. 6. In the DMF, DMSO, and aqueous systems, we can say that, since $\Delta\mu^{\ominus}$ is very small, the cation is not bound in fact. As has been seen above, the solvent effects on the binding constant are mainly governed by the standard chemical potential of the cation in the solvent.

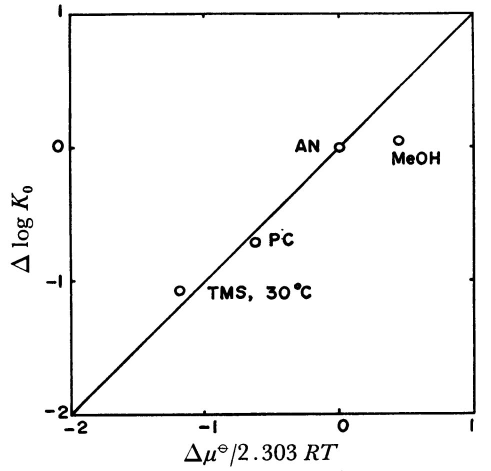

Fig. 6. The relationship between $\Delta\log K_0$ obtained in this study and $\Delta\mu^{\ominus}$ cited in Ref. 13. Acetonitrile (AN) is chosen as a reference solvent.

The Effects of the Salt Concentration on the Binding Constant. Figures 7 and 8 show the η_{sp}/c *vs.* c relationships for POE in various concentrations, C_s, of the KI-AN and -PC solutions. The curve is more raised in the region of small c values as C_s becomes smaller. This behavior closely resembles that of polyelectrolytes in salt-added systems.

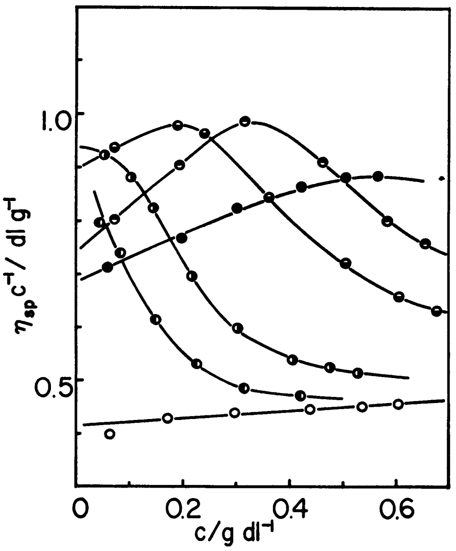

Fig. 7. η_{sp}/c *vs.* c relationships for POE in various concentration, C_s, of KI–AN solution at 25 °C.
●: $C_\mathrm{s}=10$ mM, ◓: 5 mM, ◒: 3 mM, ◑: 1 mM, ◐: 0.5 mM, ○: salt-free.

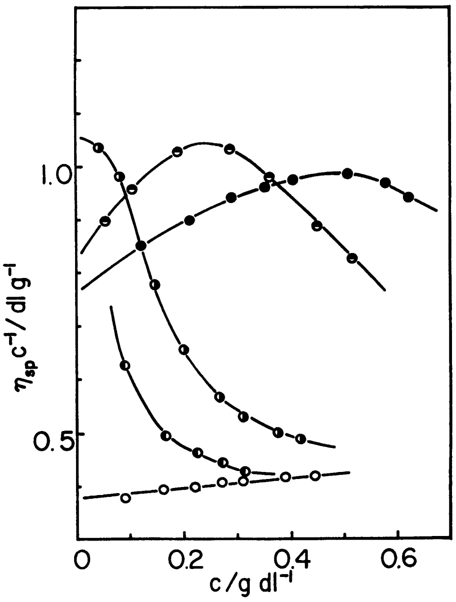

Fig. 8. η_{sp}/c *vs.* c relationships for POE in various concentration, C_s, of KI–PC solution at 25 °C.
●: $C_\mathrm{s}=10$ mM, ◓: 5 mM, ◑: 1 mM, ◐: 0.4 mM, ○: salt-free.

We shall now investigate the dependence of the binding constant on the salt concentration. Plots of the degree of binding, θ, against log a and the calculated curves for the KI-POE-AN and KI-POE-PC systems are shown in Figs. 9 and 10 respectively. The binding constants for these systems are tabulated in Table 5. These results show that the binding constant, K_0, depends markedly on C_s in PC, whereas K_0 depends on it only a little in AN. As is illustrated in Fig. 11, K_0 increases with a decrease in C_s in both systems. The increase in K_0 can be explained by one of the following two ideas: (a) The cation is bound to a delocalized site

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** Owensby *et al.* have quantitatively discussed the relationship between $\Delta\mu^{\ominus}$ and the molecular structure of a solvent.

by nature, while our model has assumed a localized site, so that the entropy increment caused by the delocalized binding might result in an increase in K_0. (b) The factor of which K_0 is composed, $\exp(-E/RT)$, increases. The (a) idea will be discussed in the future. We will now verify phenomenologically that the (b) idea is valid.

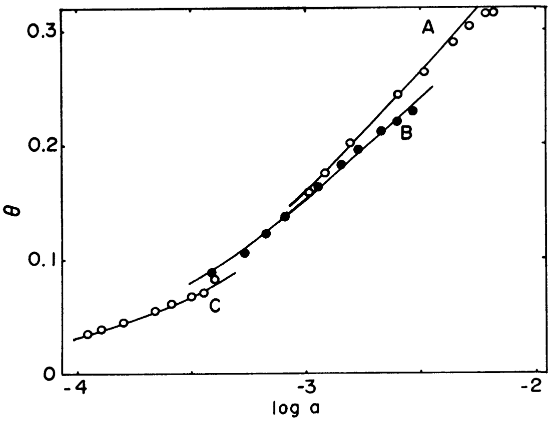

Fig. 9. Plots of θ *vs.* log a, together with the calculated curves, for KI–POE–acetonitrile systems at 25 °C. A: C_s=10 mM, B: C_s=5 mM, C: C_s=1 mM.

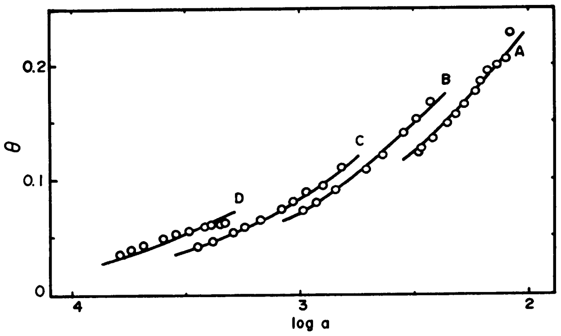

Fig. 10. Plots of θ *vs.* log a, together with the calculated curves, for KI–POE–propylene carbonate systems at 25 °C. A: C_s=10 mM, B: C_s=5 mM, C: C_s=2 mM, D: C_s=0.5 mM.

Table 5. Dependence of the binding constant, K_0, on the salt concentration, C_s, at 298.15 K

KI–Acetonitrile		KI–Propylene carbonate	
C_s / mmol dm^{-3}	log K_0	C_s / mmol dm^{-3}	log K_0
0.1	2.86	0.5	2.38
0.5	2.70	1	2.28
1	2.63	2	2.15
5	2.56	5	1.99
10	2.42	10	1.83

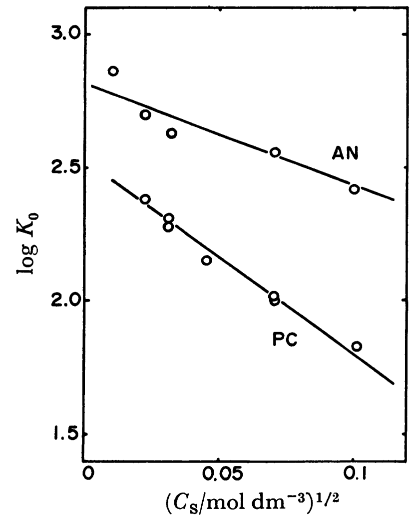

Fig. 11. Dependence of the binding constant, K_0, on the salt concentration, C_s, for KI–POE–AN and -PC systems at 25 °C.

In the preceding paper,[1] the binding constant, K_0, has been defined as follows:

$$K_0 = \exp[(\mu^\ominus - E)/RT]. \tag{8}$$

Let us differentiate the logarithm of Eq. 8 with respect to $1/T$. If we assume that:

$$\frac{\partial E}{\partial T} = 0, \tag{9}$$

then:

$$\frac{\partial \log K_0}{\partial(1/T)} = \frac{h^\ominus - E}{2.303RT}, \tag{10}$$

where $h^\ominus$ is the standard partial molar enthalpy of the cation. Figure 12 shows the plots of log K_0 against $1/T$ for 5 mmol dm^{-3} and 1 mmol dm^{-3} KI-POE-AN and -PC systems. The values of $h^\ominus - E$ obtained from the slope are tabulated in Table 6. Since $h^\ominus$ is common in both solvents, the differences between E in the 5 mmol dm^{-3} KI system and in the 1 mmol dm^{-3} KI system are 0.3 kJ mol^{-1} and 3.3 kJ mol^{-1} in AN and PC respectively. This finding phenomenologically supports

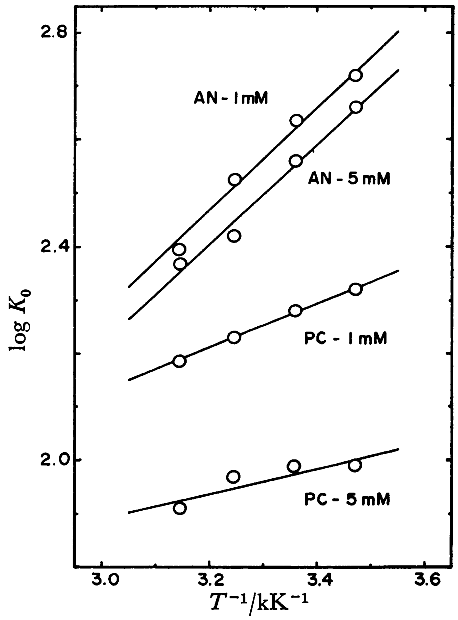

Fig. 12. Temperature dependence of the binding constant, K_0, for 1 mM and 5 mM KI-POE-AN and -PC systems.

the ideas that, as C_s grows smaller, E becomes smaller, that is, K_0 becomes greater, and that this tendency is notable in PC. The differences in the log K_0 calculated from the difference in E which has been just obtained are found to be 0.05 for the AN system and 0.58 for the PC system. These values do not agree with the observed values (AN, 0.07; PC, 0.26) very well. Taking account of the quality of the data, however, this result can be regarded as in rather better agreement and seems to support the idea (b).

TABLE 6. VALUES OF $h^\ominus - E$ OBTAINED FROM THE SLOPE OF THE PLOT OF log K_0 AGAINST $1/T$.

Solvent	C_s/mmol dm^{-3}	$(h^\ominus - E)$/kJ mol^{-1}
Acetonitrile	1	18.2
	5	17.9
Propylene carbonate	1	7.9
	5	4.6

The Effects of the Variety of Salt. Table 7 shows the binding constants for various potassium salt–POE–PC systems. It is found that K_0 is little dependent on the variety of anion, as has been expected.

TABLE 7. BINDING CONSTANTS FOR POTASSIUM SALT–POE–PROPYLENE CARBONATE SYSTEMS AT 298.15 K

Salt	log K_0
$KClO_4$	1.98
KSCN	1.97
KBr	1.91
KI	1.99

Table 8 shows the binding constants for various alkali metal iodide–POE–MeOH and –PC systems. It is clear that a large difference is found between the NaI and KI systems in MeOH, but not in PC. The differences between log K_0 values in the PC and MeOH systems are also shown in Table 8. $\Delta \log K_0$ is positive for NaI, but negative for other alkali metal iodides. The standard transfer Gibbs energies, $\Delta\mu^\ominus$, of the alkali metal ions from MeOH to PC[14] are added to Table 8 in the form of $\Delta\mu^\ominus/2.303\,RT$. The reason for the different behavior of NaI and KI is that $\Delta\mu^\ominus$ is negative for the potassium ion, but positive for the sodium ion.

TABLE 8. BINDING CONSTANTS FOR ALKALI METAL IODIDE–POE–METHANOL AND –PROPYLENE CARBONATE SYSTEMS AT 298.15 K

Salt	log K_0		$\Delta\log K_0$ [a)]	$\dfrac{\Delta\mu^{\ominus\,\text{b)}}}{2.303RT}$
	Methanol	Propylene carbonate		
NaI	1.43	1.85	0.42	1.17
KI	2.72	1.99	−0.73	−0.74
RbI	2.77	1.93	−0.84	−2.28
CsI	2.58	1.80	−0.78	−3.82

a) $\Delta\log K_0 = \log K_0(\text{PC}) - \log K_0$ (MeOH). b) $\Delta\mu^\ominus$ is the standard transfer Gibbs energy from methanol to propylene carbonate (Ref. 11).

Conclusion

As has been seen above, the present method, which is based on the one-dimensional lattice model, is of great help in obtaining a unified understanding of the binding behavior on the solvent, the salt concentration, and the variety of salt.

This method, however, can be applied only to a system in which a strong interaction exists between POE and the ion and in which no specific interaction exists between the cation and the anion. If ionic association and/or binding of the anion to the polymer cation complex occurs, a modified method is required. The treatments for such systems will be discussed in the following paper.[15]

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