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Solvent Effect on the Complexation between Poly(ethylene oxide) and Alkali-Metal Ions

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ABSTRACT: Solvent effect on the complexation between poly(ethylene oxide) and alkali-metal ions in organic solvent was correlated with the dielectric constant, ϵ, and the donor number, DN, of the solvent. The binding constant of the cation to the polymer, K_0, was determined by the method based on the one-dimensional lattice model. For the purpose to separate these two solvent effects, solvent mixtures with isodielectric constant and isodonicity were investigated. A linear relationship between log K_0 and ϵ^{-1} was found. This was explained by the contribution of ϵ to the electrostatic interaction energy. A linear relationship was also shown to hold between log K_0 and DN, which could be accounted for the model base on the preferential solvation to the ion. It was concluded that the strength of the complexation was mainly governed by DN.

Introduction

The solvent effect on the complexation between metal ions and macromolecular ligand has not so far been investigated quantitatively, while a great number of experimental data have been accumulated for low molecular weight ligands. This is due to the difficulty in determining the intrinsic formation constant for the polymer, since the binding metal ions on a polymer chain strongly interact with each other. In our previous report, we have devel-

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oped a one-dimensional lattice model to separate the intrinsic interaction between a metal ion and a polymeric binding site from the electrostatic interaction between bound ions.[1] The model has been successfully applied to the complex formation between poly(ethylene oxide) (PEO) and alkali-metal ion. This system is very convenient in the investigation of the solvent effect, since PEO is soluble in many common organic solvents. It has been revealed that the logarithmic formation constant has a linear relationship with the standard chemical potential of a metal ion.[2] However, the relationship between the formation constant and the more practical solvent parameters was not clear yet.

Two explanations of the solvent effect on the complexation between a neutral polymer and metal ions in organic solvent should be taken into account. One is the dipolar effect. If the solvent is simply regarded as a homogeneous medium, the ion–dipole interaction between the polymer and metal ions must be inversely proportional to dielectric constant, ϵ, of the solvent.[3] The other is the solvation effect to metal ions. The most widely used index representing the strength of the solvation to cation is the donor number, DN.[4]

For the purpose of separating the dipolar and solvation effects, it is desirable to change one parameter, keeping another parameter constant. This cannot be realized in the investigation of a set of single-solvent systems, because both parameters vary from solvent to solvent. However, this difficulty can be overcome by selecting a binary solvent mixture, where one of the parameters is nearly constant, while the other is much different from the first. In this study, we tried to elucidate the relationship between the binding constant of potassium and sodium ions to PEO and the parameters using the isodielectric constant solvent mixture and the isodonicity solvent mixture. In order to avoid the difficulty arising from ionic association, tetraphenylborates were used.

Theory

One-Dimensional Lattice Model Taking into Account Long-Range Interaction. In our previous investigation,[1] the interaction between bound cations ranging more than a critical number of site was truncated. In order to take into account long-range interactions, a slight modification of the calculation was made.

Consider a one-dimensional lattice having N lattice points. If the electrostatic interaction between the bound ions is represented by Debye–Hückel type potential, the interaction energy between ith and jth sites is expressed by

$$J_{ij} = J_m = \frac{N_A e^2 \exp(-\kappa_D r_m)}{4\pi\epsilon_0\epsilon r_m} \qquad (1)$$

$$m = j - i$$

where N_A is Avogadro's number, e the elementary charge, ϵ_0 the dielectric constant in a vacuum, κ_D the Debye's shielding parameter, and r_m the distance between the ith and jth sites. Then the statistical weight factor for the intersite interaction, A_m, is represented by

$$A_m = \exp(-J_m/RT) \qquad (2)$$

where R is the gas constant. We represented all short-range interactions between the ith and the $(i + k)$th site as A_m where m is up to k and the average long-range interaction between the ith and all the $(i + m)$th sites as A_l where m is beyond k. A_l was estimated by the following method. If we assume only the nearest-neighbor interaction on the one-dimensional lattice, the conditional probability, P_{ij}, of the occupation of the jth site when the ith site is occupied is given by

$$P_{ij} = \theta + (\lambda_2/\lambda_1)^{j-i}(1 - \theta) \qquad (3)$$

$$\lambda_1 = 0.5(X + Y) + 1 \qquad \lambda_2 = 0.5(X - Y) + 1$$

$$X = A_1 - 1 \qquad Y = (X^2 + 4\xi)^{1/2}$$

$$\xi = \exp[(\mu - E)/RT] \qquad (4)$$

where θ is the degree of binding, ξ the intrinsic statistical weight factor for the binding of a cation defined by eq 4, μ the chemical potential of cation in the bulk solution, and E the binding energy of a cation. From eq 1 and 3 A_l is approximately expressed by

$$A_l = \exp[-\sum_{j=i+k+1}^{N} J_{ij}P_{ij}/RT] \qquad (5)$$

Then the grand partition function of this system is described in terms of the following matrix product

$$\Xi = \mathbf{e}\mathbf{U}_k{}^N\mathbf{e}' \qquad (6)$$

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

$$\mathbf{e} = (1,1,1, ..., 1) \qquad \mathbf{e}' = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{pmatrix} \qquad (7)$$

For $k = 1$, the matrix has a form

$$\mathbf{U}_1 = \begin{pmatrix} 1 & 1 \\ \xi A_l & \xi A_l A_1 \end{pmatrix} \qquad (8)$$

Then θ is calculated by

$$\theta = \frac{1}{N}\frac{\partial \ln \Xi}{\partial \ln \xi} \qquad (9)$$

The binding constant, K_0, is defined as

$$K_0 = \exp[(\mu^\ominus - E)/RT] \qquad (10)$$

where $\mu^\ominus$ is the standard chemical potential of cation. From eq 4 and 10, log K_0 is expressed as

$$\log K_0 = \log \xi - \log a \qquad (11)$$

where a is the activity of cation. K_0 was determined by the method of Ono et al.[1]

Solvent Effect. Perfect analysis of the solvent effect on the complexation is very difficult, because many effects are related to one another. But in this study the two main effects, the dipolar and solvation effects, were taken into account. We have separated each effect according to the following model, assuming that each effect is independent of each other.

The structures of the solvated cation and the complex are assumed to be composed of conducting spheres with 1+ charge of radii R_1 and R_2, respectively, in a homogeneous medium of dielectric constant, ϵ. It is also assumed that their radii do not vary, even though these spheres are transferred from the solvent to a vacuum. The complexation reaction involves the following four elementary processes: (1) transfer of the solvated cation from the solvent to the vacuum; (2) desolvation of the solvent molecules in the vacuum; (3) complexation between the cation and the polymer in the vacuum; (4) transfer of the complex from the vacuum to the solvent. The free energy changes of these processes are denoted by ΔG_i, ΔG_d, ΔG_p, and ΔG_c, respectively. The total free energy change of the complexation in the solvent is expressed by

$$\begin{aligned}\Delta G &= E - \mu^{\ominus} \\ &= \Delta G_i + \Delta G_d + \Delta G_p + \Delta G_c \end{aligned} \qquad (12)$$

In an isodonicity solvent mixture system, $\Delta G_d + \Delta G_p$ is a constant. The electrostatic energy, $\Delta G_i + \Delta G_c$, is given by the Born equation[5] as

$$\Delta G_i + \Delta G_c = \frac{N_A e^2}{8\pi\epsilon_0}\left(\frac{1}{R_1} - \frac{1}{R_2}\right)\left(1 - \frac{1}{\epsilon}\right) \qquad (13)$$

In an isodielectric solvent mixture system $\Delta G_i + \Delta G_c + \Delta G_p$ is a constant. Thus, the variation of ΔG is governed only by desolvation energy ΔG_d.

Experimental Section

Reagents. PEO with a nominal molecular weight of 2×10^4 was used throughout this study. Sodium tetraphenylborate was reagent grade and was dried under a vacuum. Potassium tetraphenylborate was prepared by adding 20% aqueous solution of $NaBPh_4$ to 12.7% aqueous solution of potassium chloride. The precipitate was recrystallized three times from 2:1 acetone–water mixture. Triisoamylbutylammonium tetraphenylborate ($TABBPh_4$) was prepared and purified by the method of Fuoss.[6] Acetonitrile (AN) was stirred with calcium hydride and distilled. Propylene carbonate (PC) was stirred with a molecular sieve, 4 Å, and distilled under reduced pressure [87 °C (2 mmHg)]. Nitromethane (NM) was stirred with a molecular sieve, 4 Å, and distilled.

Conductivity Measurements. Conductivity was measured by a GenRad GR-1689 digibridge at 3 kHz in a glass cell controlled to 25 ± 0.02 °C by a silicon oil circulating glass jacket. The measurement was repeated three times, and the reproducibility was good.

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 have a maximum similar to the behavior of polyelectrolytes in added salt systems. The value of the intrinsic viscosity of PEO, $[\eta]$, was obtained by extrapolating the curve to the intercept.

Donicity of the Solvent Mixture. Gutmann's donor number (DN) of a solvent, which is based on the enthalpy of the reaction between $SbCl_5$ and the solvent in 1,2-dichloroethane solution, is an empirical scale of solvent donor ability.[4] DN values of PC and AN are 15.1 and 14.1, respectively, and the donicity difference between AN and PC is very small. Recently donicity of solvent has been reevaluated with various methods. For instance, from the NMR measurement of $NaAlEt_4$, Day et al.[7] suggested that PC is a better donor relative to AN than originally estimated. According to ^{23}Na NMR measurement by Popov,[8] however, AN is a better donor than PC. On the other hand, Persson et al.[9] and Marcus[10] have estimated the donicity difference between AN and PC as small as that estimated by Gutmann. The donicity of solvent depends on the method of estimation, and more studies are needed to estimate exact donicity of solvent. DN is not an absolute scale of solvent donicity, but it can be almost regarded as the scale of solvent donor ability. Since the donicity difference between AN and PC is very small, it is reasonable that the PC–AN solvent mixture is almost regarded as an isodonicity solvent mixture system and that there is little solvent effect of donicity to the complexation between PEO and alkali-metal ions in the PC–AN solvent mixture system.

It was found that there is a linear relationship between the DN and the ^{23}Na NMR chemical shift in many solvents.[11] On the other hand, in the binary solvent mixture system the donicity does not increase linearly with the mole fraction of the higher donicity solvent because of the preferential solvation. Popov et al. proposed a method to estimate the degree of the preferential solvation using the relation between the ^{23}Na NMR chemical shift and the composition of the binary solvent mixture,[12] and Gutmann estimated DN of the solvent mixture by assuming the linear relationship between DN's and Popov's data of the ^{23}Na NMR chemical shift.[13] In this study, DN's of AN–NM solvent mixture system were estimated with this method.

Table I
Properties of the AN–NM Solvent Mixture System

solvent	mole fraction of AN	ϵ	DN
NM	0	36	2.7
AN-1	0.1	36	6.5
AN-2	0.2	36	8.7
AN-3	0.3	36	10.2
AN-5	0.5	36	12.0
AN-8	0.8	36	13.5
AN	1	36	14.1

Table II
Properties of the PC–AN Solvent Mixture System

solvent	mole fraction of PC	ϵ	DN
AN	0	36	14.1
PC-1	0.1	44.8	
PC-3	0.3	47.1	
PC-7	0.7	57.3	
PC	1	64.4	15.1

Dielectric Constant of the Solvent Mixture. In the PC–AN solvent mixture, ϵ of the solvent was estimated at 3 kHz with the aforementioned digibridge using a three-terminal liquid cell. In AN–NM solvent mixture, ϵ values were reported to be about 36,[14] so that this mixture is regarded as an isodielectric constant solvent mixture. The properties of these binary solvent mixtures are summarized in Tables I and II, respectively.

Limiting Ionic Equivalent Conductivities. The degree of the cation binding to PEO was estimated by the conductometry of the solution. Here we define relative conductivity as the conductivity of the solution divided by the conductivity of the pure salt solution. It was assumed that the relative conductivity when all the cation are bound is equal to $\lambda_-^0/(\lambda_+^0 + \lambda_-^0)$ where λ_+^0 and λ_-^0 are limiting ionic equivalent conductivities.[2] The limiting equivalent conductivity of $TABBPh_4$, Λ_t^0, was determined by analyzing the data of conductivities for $TABBPh_4$ with the Fuoss–Onsager equation.[14] λ_-^0 of BPh_4^- was assumed to be $\Lambda_t^0/2$.[6] The limiting equivalent conductivity of alkali metal tetraphenylborate, Λ_a^0, is determined with the same method as $TABBPh_4$. Then λ_+^0 of alkali-metal ion could be estimated by the relationship, $\lambda_+^0 = \Lambda_a^0 - \lambda_-^0$.

Results and Discussion

Effect of the Dielectric Constant of the Solvent. Figure 1 shows the plot of the relative conductivity of the solution against the PEO concentration, C_p. The concentration of $NaBPh_4$ was 2 mM. The conductivity decreased with increasing PEO concentration. This is due to the binding of cation on the PEO chain. The decrease became remarkable with increasing content of AN. It means that the interaction between cation and PEO becomes stronger with decreasing dielectric constant of the solution, since the solvent donicity does not vary with the PC–AN ratio. Determined binding constants are summarized in Table III together with the standard deviation of log K_0, σ, and the intrinsic viscosities of the solution. It is evident that K_0 increases with decreasing ϵ. Since the electrostatic interaction is inversely proportional to ϵ, log K_0 was plotted against ϵ^{-1} in Figure 2. As shown in the figure a linear relationship between them was observed. The slope of the linear relationship between log K_0 vs ϵ^{-1} can be calculated from eq 13 with R_1 = 1.8 Å and R_2 = 3 Å. R_1 was the sum of the crystallographic radius of sodium ion (0.98 Å) and the empirical correction term for solvated cation in modified Born equation

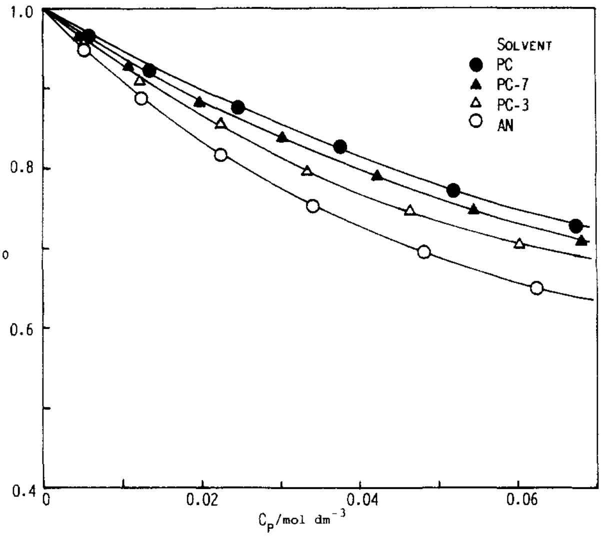

Figure 1. Plots of Λ/Λ_0 vs C_p in NaBPh$_4$-PEO-PC-AN. The concentration of the salt, C_s, is 2 mM.

Table III
Binding Constants for NaBPh$_4$-PEO-PC-AN

solvent	ϵ	10^3C_s, M	K_0	log K_0	σ	$[\eta]$, dL g^{-1}
AN	36	1	310	2.49	0.03	0.619
		2	260	2.41	0.04	0.954
		5	230	2.37	0.05	0.919
PC-1	44.8	1	230	2.36	0.01	0.950
		2	190	2.28	0.02	0.990
		5	160	2.20	0.03	0.904
PC-3	47.1	1	200	2.30	0.03	0.953
		2	160	2.19	0.01	1.057
		5	120	2.07	0.03	1.000
PC-7	57.3	1	170	2.22	0.02	0.927
		2	120	2.06	0.02	1.216
		5	89	1.90	0.03	1.107
PC	64.4	1	130	2.12	0.03	1.118
		2	93	1.97	0.03	1.291
		5	61	1.79	0.03	1.030

(0.82 Å).[15] R_2 was roughly estimated from the crystal structure of PEO-NaI complex determined by the X-ray diffraction method.[16] In Figure 2 the dotted line shows this calculated slope. It is consistent with our experimental data. ϵ of PC was about twice as large as that of AN, but the influence of ϵ to K_0 was not so large. The intrinsic viscosity seems to increase with an increase in ϵ of the solution. This is rather strange because of a decreasing number of bound ions in higher dielectric medium. A possible explanation is that the less effective electrostatic shielding in high dielectric medium results in the increase in the long-range electrostatic potential and the expansion of chain.

Effect of the Donicity of the Solvent. Figure 3 shows the conductivity curves in AN-NM solvent mixture system. The degree of the decrease of the conductivity became larger with increasing content of NM. It means that the interaction between cation and PEO becomes stronger with the decreasing donicity of the solvent. Binding constants in the AN-NM solvent mixture system are summarized in Table IV. K_0 increased remarkably with decreasing DN. Since the cation is a kind of Lewis acid, a decrease of DN of the solvent decreases the solvation and lowers the desolvation energy. This causes an increase of the binding constant. It should be noted that $[\eta]$ increases with decreasing DN, suggesting that the PEO chain is more expanded in a lower donicity solvent. This may be attributed to an increase of the number of bound cations in a lower donicity solvent mixture, since the dielectric constant is kept nearly constant. It means that the repulsive interaction between the ions bound on a PEO chain causes the expansion of the chain. Figure 4 is the plot of log K_0 vs DN. A linear relationship between log K_0 and DN was observed.

Consider a binary solvent mixture of solvent S1 and S2. We assume that DN of S2, $(\text{DN})_2$, is larger than that

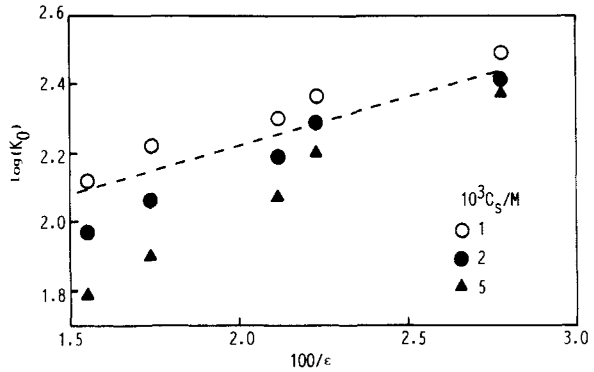

Figure 2. Relationship between log K_0 and ϵ^{-1} in NaBPh$_4$-PEO-PC-AN.

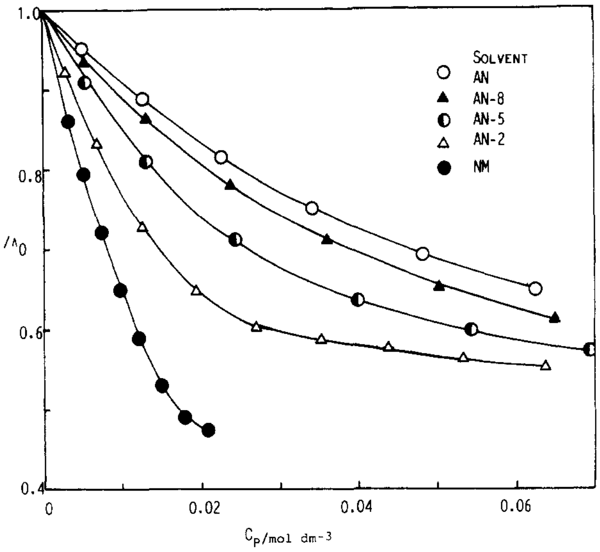

Figure 3. Plots of Λ/Λ_0 vs C_p in NaBPh$_4$-PEO-AN-NM. C_s = 2 mM.

Table IV
Binding Constants for NaBPh$_4$-PEO-AN-NM

solvent	DN	10^3C_s, M	K_0	log K_0	σ	$[\eta]$, dL g^{-1}
NM	2.7	1	65000	4.81	0.14	1.60
		2	45000	4.65	0.07	1.27
		5	10000	4.01	0.09	1.24
AN-1	6.5	1	8000	3.91	0.14	1.93
		2	8600	3.93	0.09	1.49
		5	20000	4.30	0.10	1.13
AN-2	8.7	1	2600	3.41	0.21	1.73
		2	3000	3.47	0.15	1.57
		5	3000	3.47	0.03	0.97
AN-3	10.2	1	1700	3.22	0.12	1.78
		2	2000	3.31	0.12	1.29
		5	1700	3.24	0.02	1.04
AN-5	12.0	1	630	2.80	0.16	1.12
		2	510	2.71	0.19	1.37
		5	510	2.71	0.22	0.94
AN-8	13.5	1	380	2.58	0.05	1.08
		2	330	2.52	0.07	1.14
		5	310	2.49	0.09	0.97
AN	14.1	1	310	2.49	0.03	0.62
		2	260	2.41	0.04	0.95
		5	230	2.37	0.05	0.92

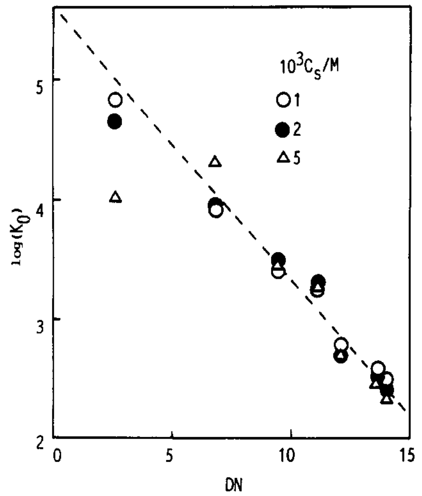

Figure 4. Relationship between log K_0 and DN in NaBPh$_4$–PEO–AN–NM.

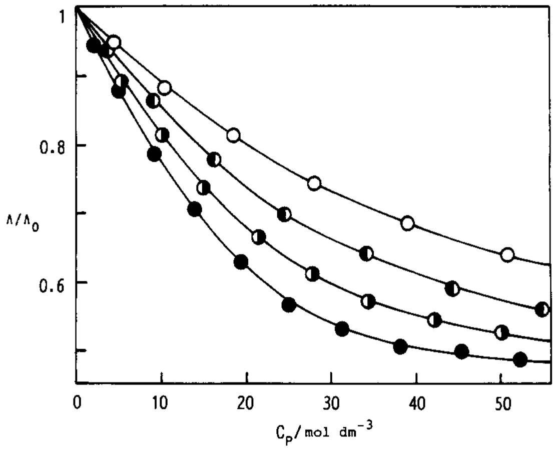

Figure 5. Plots of Λ/Λ_0 vs C_p in KBPh$_4$–PEO–AN–NM. C_s = 2 mM.

Table V
Binding Constants for KBPh$_4$–PEO–AN–NM

solvent	DN	10^3C_s, M	K_0	log K_0	σ	[η], dL g^{-1}
NM	2.7	1	3800	3.58	0.06	1.30
		2	2900	3.46	0.05	1.26
		3	2600	3.35	0.02	1.15
AN-1	6.5	1	2300	3.36	0.06	1.38
		2	1900	3.28	0.04	1.29
		3	1700	3.23	0.03	1.06
AN-2	8.7	1	1200	3.07	0.13	1.81
		2	1100	3.05	0.15	1.36
		3	1600	3.21	0.05	0.91
AN-5	12.0	1	630	2.80	0.12	1.45
		2	630	2.80	0.14	1.02
		3	560	2.75	0.13	1.04
AN	14.1	1	460	2.66	0.07	0.71
		2	420	2.62	0.08	0.68
		3	340	2.53	0.07	0.97

of S1, (DN)$_1$. The difference between DN values is

$$\Delta\mathrm{DN} = (\mathrm{DN})_2 - (\mathrm{DN})_1 \qquad (14)$$

In the S2–S1 solvent mixture, the equilibrium of preferential solvation of solvent molecules to metal ion, M$^+$, is given by the following equilibrium

$$\mathrm{M^+S1 + S2 \rightleftarrows M^+S2 + S1} \qquad (15)$$

Then the standard chemical potential of metal ion in this solvent mixture is expressed by

$$\mu^{\ominus} = \mu_1^{\ominus} + \Delta G_s^{\ominus} \qquad (16)$$

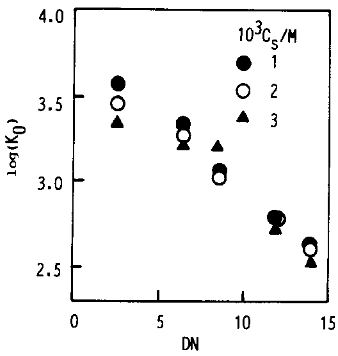

Figure 6. Relationship between log K_0 and DN in KBPh$_4$–PEO–AN–NM.

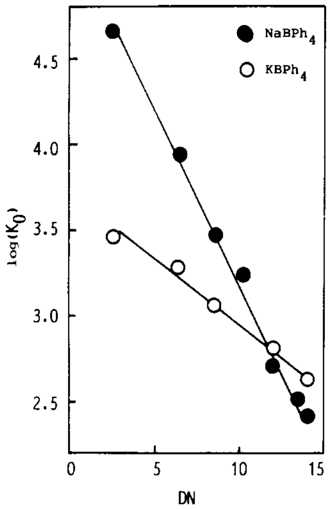

Figure 7. Variation of log K_0 with alkali-metal ions. C_s = 2 mM.

$\mu_1^{\ominus}$ is the standard chemical potential of the metal ion in solvent S1, and $\Delta G_s^{\ominus}$ is the standard free energy change of the equilibrium denoted by eq 15. Substituting eq 16 into eq 10, K_0 is expressed by

$$K_0 = \exp[(\mu_1^{\ominus} + \Delta G_s^{\ominus} - E)/RT]$$

$$\ln K_0 = \ln K_0' + \Delta G_s^{\ominus}/RT$$

$$K_0' = \exp[(\mu_1^{\ominus} - E)/RT] \qquad (17)$$

where K_0' is the binding constant in S1. It may be rational to assume that $-\Delta G_s^{\ominus}$ is proportional to DN; i.e.

$$-\Delta G_s^{\ominus} \propto \mathrm{DN} \qquad (18)$$

Then we can obtain the linear relationship between log K_0 and DN as

$$\log K_0 = \log K_0' - b\mathrm{DN} \qquad (19)$$

where b is a constant. The linear relationship between log K_0 and DN in Figure 4 supports this model based on the preferential solvation. The slope of line can be calculated using $\Delta G_s^{\ominus}$ values, obtained by Popov et al.,[12] assuming that the solvation number, n_s, is a constant. The slope of the dotted line in Figure 4 was obtained with n_s = 4, and it is consistent with our experimental data.

Figure 5 shows the conductivity curves of KBPh$_4$–PEO in the AN–NM solvent mixture system, and the binding constants are summarized in Table V. The influence of DN on the binding constant seemed to be smaller than that for NaBPh$_4$–PEO. Figure 6 is the plot of log K_0 vs DN in this system. As has been mentioned above, DN values are the apparent values estimated from NMR chemical shift. Also in this case, the linear relationship was observed. Thus the complexation of K^+–PEO must be associated with the preferential solvation similar to that of Na^+–PEO. The effect of the cations is shown in Figure 7. The slope of the linear relationship in the K^+–PEO system was smaller than that in the Na^+–PEO system. K_0 of Na^+–PEO was larger than that of K^+–PEO in NM, while the situation is reverse in AN. This may be explained as follows. The ionic radius of Na^+ is smaller than that of K^+, so that the ion–dipole interaction of PEO with Na^+ is stronger than that with K^+. Therefore, in low-donicity NM where the interaction between cation and solvent is small, the interaction of PEO–Na^+ is stronger than that of PEO–K^+. On the other hand, Na^+ is more solvated than K^+ in high-donicity solvent, so that the interaction between PEO and Na^+ becomes weak. As the result of this ion solvation effect, K_0 of Na^+–PEO is smaller than that of K^+–PEO in AN.

Conclusion

The solvent effect of the complexation between PEO and alkali-metal ions was quantitatively correlated with the dielectric constant and the donor number using binary solvent mixtures. The strength of the complexation was found to be mainly governed by the donor number. The cation size effect is also explained from this viewpoint.

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Registry No. AN, 75-05-8; NM, 75-52-5; PC, 108-32-7.

Relaxation in Bead-Jump Polymer Simulations

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ABSTRACT: A new algorithm for the generation of equilibrium configurations of polymers is described. The algorithm involves nonlocal moves and is suitable for end-restricted polymers. It is shown to reproduce the correct equilibrium properties of both ideal and self-avoiding polymers. A naive analysis shows that the equilibration time τ for this algorithm should scale with the polymer length N as $\tau \propto N^2$, with the time measured in terms of the computer steps. Simulations in one, two, and three dimensions indicate that the dynamics is considerably slower than expected both for ideal and self-avoiding polymers, although it is still faster than algorithms involving local moves. A novel "stretch relaxation" mechanism is found to be responsible for this anomalous slowness; its origin, however, has not been clearly identified.

I. Introduction

Increasingly, computer simulations are being used to study statistical properties of polymer liquids.[1-3] Certain important properties, such as scaling behavior with molecular weight, may be simulated with very simple models of the polymer chains. Indeed for such properties, any type of self-avoiding walks with finite mean-square step length is adequate.[4] This has led to a growing interest in how a polymer system may be simulated most efficiently.[5,6] For a dilute polymer liquid the most efficient Monte Carlo algorithm for many purposes is the "slithering snake", or reptation[2,7] dynamics. In this scheme one chooses one of the chain ends at random and transfers a monomer from this end to the other repeatedly. If the transferred monomer touches another, the move is rejected. This scheme applied to an N-bead chain leads to a statistically independent configuration in a computer time of order N^2.

For many situations, however, reptation dynamics is not appropriate. If the system is so concentrated that free-volume effects become important, the time for a successful reptation step may become unmanageably large. In such situations, molecular dynamics[3,8] methods appear to be more practical. Another case where reptation dynamics cannot be used is in polymers whose ends are attached to something. In such cases a common approach[9,10] is to use algorithms involving local moves. In such schemes (which we shall call "local algorithms"), a monomer is chosen at random and is moved to a nearby lattice site while preserving the connectivity of the chain. (Such a move is typically possible for only a fraction of the mono-

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