

An NMR Study on Complexation of Ortho-Xylyl-17-Crown-5 with ^7Li and ^{23}Na Ions in Acetonitrile

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Complexation of ortho-xylyl-17-crown-5 (X17C5) with alkali metal ions in acetonitrile was studied by ^7Li and ^{23}Na NMR spectroscopy. The complex formation constants of X17C5 with LiI, LiSCN, NaI, and NaSCN were determined by investigating the changes in the chemical shifts as a function of the concentration ratio of X17C5 to metal ion. It was found that X17C5 forms 1:1 complex with Li^+ and Na^+ ions and the log K_f 's for the complexation with LiI, LiSCN, NaI, and NaSCN were determined to be 2.88, 2.43, 2.53, and 2.30, respectively. In particular, the kinetics of complexation of X17C5 with Na^+ was investigated by the method of ^{23}Na NMR lineshape analysis. Activation energies were determined from Arrhenius plot of the resultant rate constant data to be 25.4 kJ/mol for NaI and 15.1 kJ/mol for NaSCN. Other kinetic parameters were also calculated by employing the Eyring equation. The decomplexation rates measured were $1.82 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for NaI and $1.50 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for NaSCN. It is concluded that the decomplexation mechanism is predominantly a bimolecular cation exchange for both cases.

Introduction

Since Pedersen's first discovery of macrocyclic crown ethers,¹ tremendous number of research papers have been published on the synthesis of new classes of crown ethers as well as on their thermodynamics of complexation with various cations in different solvent environments. This great interest in the crown ethers mainly arose from the hope that their ability of forming complexes with metal ions might profitably be exploited for industrial purposes. For examples, the crown ethers can be utilized for the phase-transfer catalysis, the development of ion-selective electrode, the separation of the metal cations, the study of ion transport across the membrane, and so on.²

The thermodynamics of macrocyclic crown ethers have been extensively studied and the bulk of those data on numerous classes of macrocycles is excellently summarized in a recent review article by Izatt *et al.*,³ where they point out that the researches on the complexation kinetics, however, have been relatively rare. It is only since 1970's that several research groups have begun studying on the complexation kinetics employing various methods including NMR spectroscopy.⁴

Two different approaches are presently being employed in the NMR study of metal complexation processes; one is to use ^1H and ^{13}C NMR experiments of host molecules⁵ and the other is to directly observe the NMR spectra of guest metal ions. In this work we report some results, such as complex formation constant, activation energy, and decomplexation mechanism, etc., obtained from multinuclear NMR study of the complexation of ortho-xylyl-17-crown-5 (X17C5, shown in Figure 1) with Na^+ and Li^+ ions in acetonitrile solution. This crown ether, first synthesized by Reinhoudt,⁷ has the structure resembling that of benzocrown ether but its ring is expected to be more flexible due to the presence of benzyl protons.

Theory

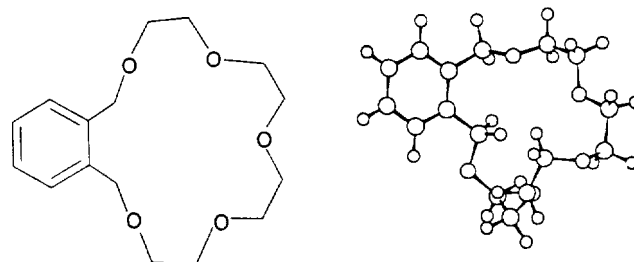


Figure 1. Ortho-xylyl-17-crown-5 and its ball and stick model optimized by MM2 calculation.⁶

The complex formation constant involved two species (metal ion and host crown compound) can be expressed as follows:

$$K_f = \frac{[\text{M}^+\text{L}]}{[\text{M}^+][\text{L}]} \quad (1)$$

where $[\text{ML}^+]$, $[\text{M}^+]$, and $[\text{L}]$ denote, respectively, the concentration of metal-crown-complex, metal ion, and host crown. Along with Eq. (1), they also satisfy the following mass-balance equations

$$[\text{M}^+]_t = [\text{M}^+] + [\text{M}^+\text{L}] \quad (2)$$

and

$$[\text{L}]_t = [\text{L}] + [\text{M}^+\text{L}], \quad (3)$$

where the subscript t stands for the total concentration. The chemical shift of a metal nucleus in a rapidly exchanging system can be expressed by

$$\delta_{\text{obs}} = \chi_f \delta_f + \chi_c \delta_c \quad (4)$$

with $\chi_f = [\text{M}^+]/[\text{M}^+]_t$ and $\chi_c = [\text{M}^+\text{L}]/[\text{M}^+]_t$,

where δ_{obs} represents observed chemical shift of metal ion in the sample solution, and δ_f and δ_c denote the chemical shift of free and complexed metal ion, respectively. Com-

binning Eqs. (1) through (4), we can easily derive the following expression:

$$\delta_{obs} = \frac{1}{2} \left\{ \left(1 - \frac{1}{\rho} - \frac{1}{K_f[M^+]_f} \right) + \left[\left(1 - \frac{1}{\rho} - \frac{1}{K_f[M^+]_f} \right)^2 + \frac{4}{K_f[M^+]_f} \right]^{1/2} \right\} \times (\delta_f - \delta_c) + \delta_c \quad (5)$$

where $\rho = [L]_f/[M^+]_f$. The complex formation constant K_f can be obtained by numerically fitting the observed $\delta_{obs} - \rho$ curve with that calculated from Eq. (5).

Rate constant, a fundamental kinetic information for an exchanging system, can be obtained from NMR lineshape analysis. Two major factors affecting the lineshapes are the transverse relaxation time, T_2 , and exchange rate, and both factors can be simultaneously taken into account if we employ the modified Bloch equations.⁸ For the uncoupled two site (A and B) exchange system the NMR lineshape is represented the following expression:

$$v = -C \left\{ P \left[1 + \tau \left(\frac{\rho_B}{T_{2A}} + \frac{\rho_A}{T_{2B}} \right) \right] + QR \right\} / (P^2 + R^2), \quad (6)$$

where

$$P = \tau \left[\frac{1}{T_{2A}T_{2B}} - 4\pi^2(\Delta\nu)^2 + \pi^2(\delta\nu)^2 \right] + \frac{\rho_A}{T_{2A}} + \frac{\rho_B}{T_{2B}},$$

$$Q = \tau [2\pi\Delta\nu - \pi\delta\nu(\rho_A - \rho_B)],$$

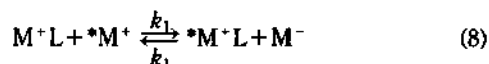
$$R = 2\pi\Delta\nu \left[1 + \tau \left(\frac{1}{T_{2A}} + \frac{1}{T_{2B}} \right) \right] + \pi\delta\nu \tau \left(\frac{1}{T_{2B}} - \frac{1}{T_{2A}} \right) + \pi\delta\nu(\rho_A - \rho_B),$$

$$\delta\nu = \nu_A - \nu_B \quad \Delta\nu = \frac{1}{2}(\nu_A + \nu_B) - \nu,$$

$$\text{and } \tau = \frac{\rho_A}{k_B} = \frac{\rho_B}{k_A}$$

with ν_X , ρ_X , k_X , and T_{2X} denoting the chemical shift, population, exchange rate, and transverse relaxation time at the site X, respectively. The exchange between free (more strictly, solvated) metal ion and complexed metal ion which is of interest in the present work can be most conveniently described by considering this uncoupled two site exchange case. Thus we can deduce exchange mean lifetimes from numerical fitting of experimental data with Eq. (6). The activation parameters can be easily found by plotting the mean lifetime vs inverse temperature with the help of Arrhenius and Eyring equations.⁸

In nonaqueous solutions the rate of complexation is generally diffusion controlled, and the complexation sensitivities are governed by the decomplexation rates, k_d .⁹ Two decomplexation mechanisms are proposed; unimolecular dissociation mechanism [Eq. (7)] and bimolecular cation exchange mechanism [Eq. (8)].¹⁰⁻¹²



From the above equations, the following expression can be derived:

$$\frac{1}{\tau} = k_1[M^+]_f + \frac{k_{-2}[M^+]_f}{[M^+]_f} \quad (9)$$

If we plot $1/\tau[M^+]_f$ versus $1/[M^+]_f$, we can obtain k_1 from the intercept and k_{-2} from the slope and thus can determine which mechanism is more dominant. The exchange mean lifetimes τ in Eq. (9) can be obtained from lineshape analysis at several different total metal-ion concentrations, $[M^+]_f$.

Experimentals

All inorganic salts, purchased from Merck and Aldrich, were dried in a high vacuum line at 343 K for more than 12 hours and stored in the desiccator. Ortho-xylol-17-crown-5 was prepared according to the procedure described by Reinhoudt⁷ and acetonitrile was distilled under reduced pressure before use. All the NMR measurements were carried out on a Varian VXR-200S NMR spectrometer operating at a frequency of 52.92 MHz for ²³Na and 77.74 MHz for ⁷Li.

Chemical Shift Measurements. As external reference 0.05 M NaCl/D₂O solution was used and all the measurements were performed at 20.0 ± 0.1 °C. The concentrations of salts were fixed at 0.022, 0.020, 0.021, and 0.019 M for NaI, NaSCN, LiI, and LiSCN, respectively. The concentrations of crown were varied from 0 to 0.040 M for NaI, to 0.047 M for NaSCN, to 0.041 M for LiI, and to 0.043 M for LiSCN with ρ varying from 0 to ~2. All the NMR data given are the average of three independent measurements.

Lineshape Analysis. Acetone-d₆ was used as external lock. In order to obtain the activation parameters the sample of $\rho \sim 0.4$ was chosen and lineshape was observed at several temperatures and analyzed. Transverse relaxation times were calculated from linewidth according to the relation, $1/T_2 = \pi\Delta\nu_{1/2}$. Longitudinal relaxation times were measured by the conventional inversion recovery method and by comparing these with transverse relaxation time data we have confirmed that alkali metal spectra satisfy the extreme narrowing condition.

Results and Discussion

Complex Formation Constants. The variations of the chemical shifts as a function of ρ , i.e., the concentration ratio of crown to metal ion, are shown in Figure 2. It seems evident from the behavior of chemical shifts that X17C5 forms eventually a 1:1 complex with Li⁺ and Na⁺. The least-square fitting based on Eq. (4) was carried out using a computation program and thus obtained complex formation constants are shown in Figure 2. It shows that X17C5 forms complexes weakly with alkali metal ions compared to other similar crown systems.³

The counter anion effect is not so obvious but we can see that iodide ion induces more stable alkali metal complex with X17C5 than thiocyanate. Both iodide and thiocyanate are known to form contact ion pairs with alkali metal ions, but the latter is known to form stronger ion pair with alkali metal ion than the former.^{10,13} As a result, alkali metals with thiocyanate anions seemed to form less stable complexes.

Another important thing we can point out is that Li⁺ forms a little more stable complex with X17C5 than Na⁺. The size of cations are estimated to be 136 pm for Li⁺ and 190-196

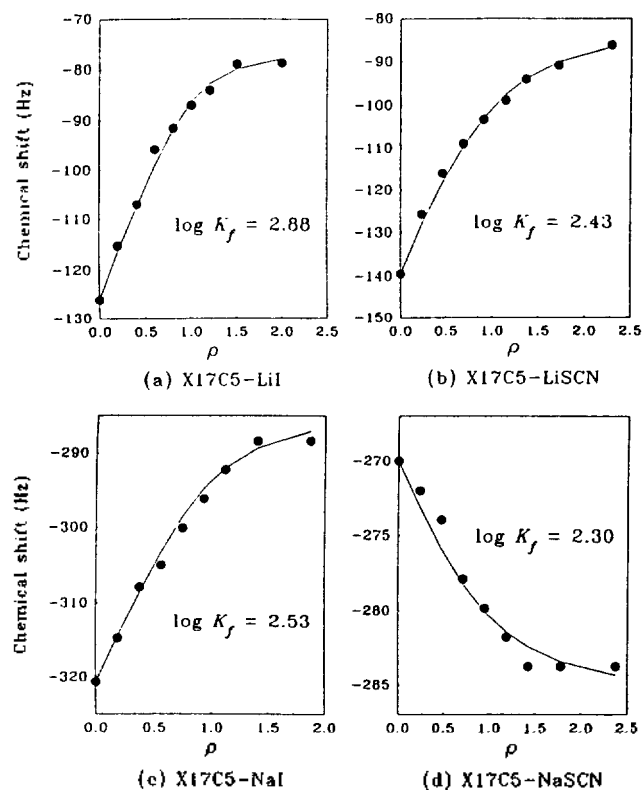


Figure 2. Plots of ${}^7\text{Li}$ and ${}^{23}\text{Na}$ chemical shifts versus ρ in various systems.

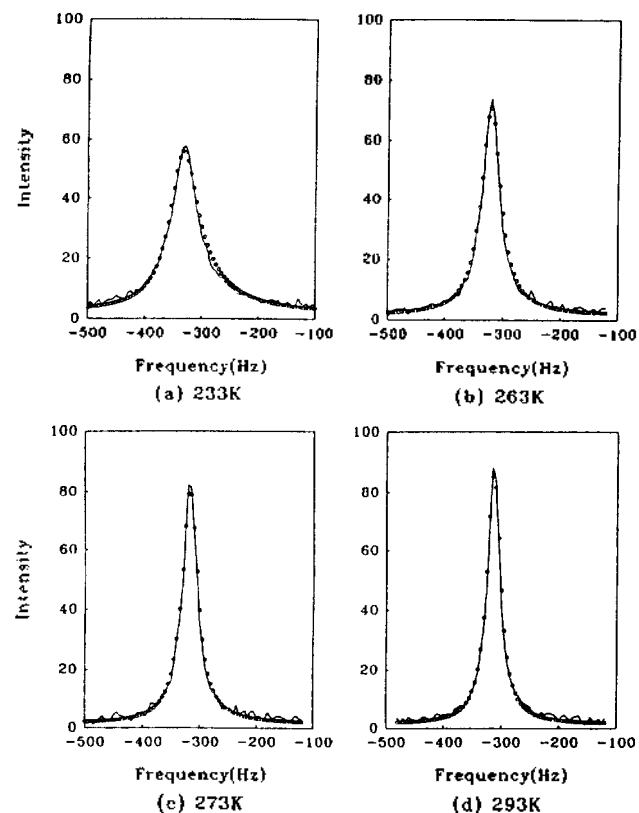


Figure 3. Illustrative examples of ${}^{23}\text{Na}$ NMR lineshape analysis for X17C5-NaI system ($\rho=0.374$). Solid line and small circles represent experimental and calculated data, respectively.

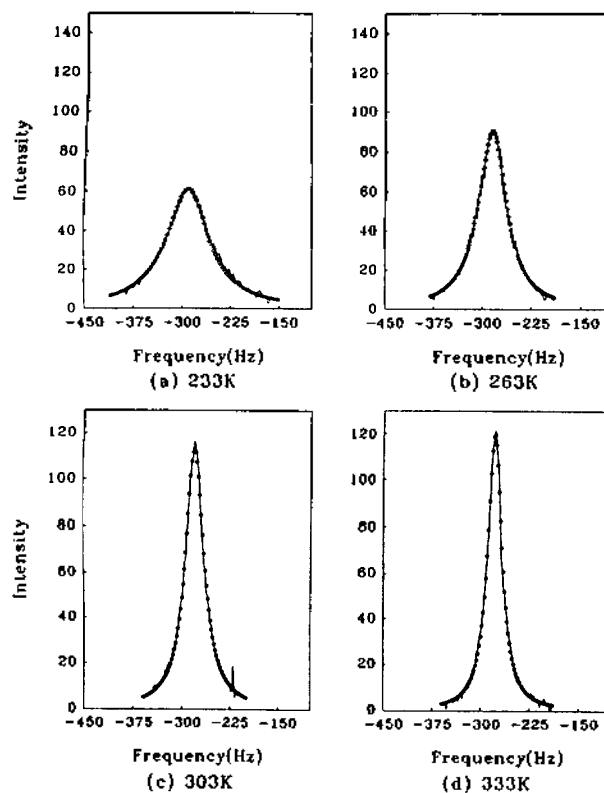


Figure 4. Illustrative examples of ${}^{23}\text{Na}$ NMR lineshape analysis for X17C5-NaSCN system ($\rho=0.475$). Solid line and small circles represent experimental and calculated data, respectively.

pm for Na^+ .¹⁴ And the size of the X17C5 is estimated to be ~ 220 pm.¹⁵ According to size-fit concept¹⁶ Na^+ should be expected to form a stronger complex than Li^+ , but our result is contradictory to this. A previous observation¹⁷ that the more flexible large crown ethers form the more stable complex with small cations owing to the ability of altering their conformation to accommodate these cations may also be applied to this case. It seems that flexible polyether ring enables X17C5 to complex more strongly with Li^+ .

Kinetics. The lineshape fittings according to Eq. (6) are shown in Figure 3 and 4. The Arrhenius plots for X17C5-NaI and -NaSCN systems are shown in Figure 5. The activation energy values obtained from these plots are 25.4 and 15.1 kJ/mol, respectively. The other kinetic parameters are summarized in Table 1. From these results we can see that the entropy contribution is very important, especially in NaSCN system. The plot of $1/\tau[\text{Na}^+]_t$ vs $1/[\text{Na}^+]_f$ for the cases of NaI and NaSCN are shown in Figure 6, which shows that the exchange rate increases only negligibly with the decrease in concentration of free sodium cation in both cases. We see from this that the cation exchange mainly follows the bimolecular exchange mechanism in these two cases and the decomplexation rates of X17C5-NaI and -NaSCN systems are found to be 1.82×10^4 and $1.50 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$. That the activation energy for X17C5-NaI system is higher than that for X17C5-NaSCN system is in agreement with the previous result that NaI forms more stable complex than NaSCN.

The conclusions we have drawn from this study are believed to be consistent with the widely accepted views in

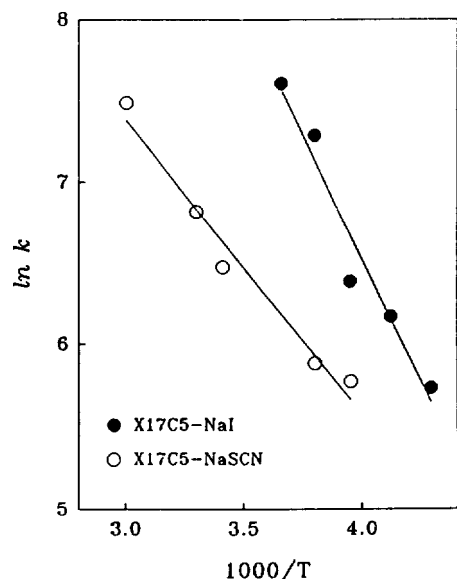


Figure 5. Arrhenius plots for X17C5-NaI and -NaSCN systems.

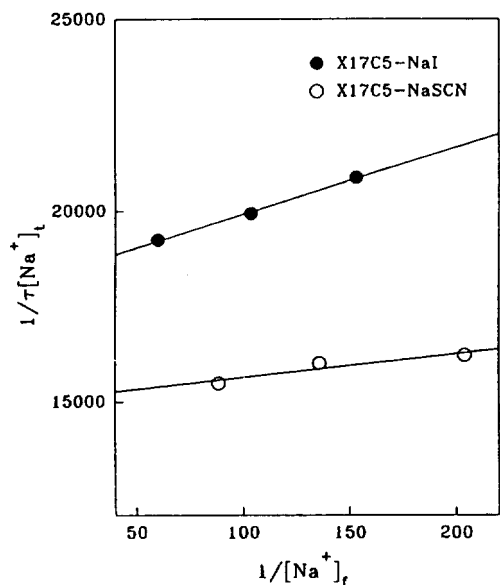


Figure 6. Plots of $1/\tau[\text{Na}^+]_t$ versus $1/[\text{Na}^+]_i$ for X17C5-NaI and -NaSCN systems at 333 and 303 K, respectively.

the following two respects. One is the effect of the solvent. Strasser *et al.*^{10(b)} reported that the nature of the solvent plays an important role in determining the mechanism. They compared NaBPh₄-18C6-propylene carbonate system with NaSCN-18C6-methanol system, where propylene carbonate has distinctively high dielectric constant (65.0) but has somewhat low donor number (15.1) while methanol has intermediate value of dielectric constant (32.6) and donor number (20.0). The result was that the former follows the bimolecular exchange mechanism while the latter obeys to the dissociative exchange mechanism. In their report it was concluded that unimolecular dissociative mechanism is predominant in the solvents which have both high donor numbers and high dielectric constants while bimolecular cation exchange mechanism prevails in the solvents having low donor numbers

Table 1. Kinetic parameters for exchange of sodium ion with X17C5

| Salt | k_{293} ($\text{M}^{-1}\text{s}^{-1}$) | E_a (kJ/mol) | ΔH^\ddagger (kJ/mol) | ΔS^\ddagger (J/mol K) | ΔG^\ddagger_{293} (kJ/mol) |
|-------|---|-------------------|---------------------------------|----------------------------------|---------------------------------------|
| NaI | 1.84×10^4 | 25.4 | 22.9 | -97.5 | 51.5 |
| NaSCN | 1.50×10^4 | 15.1 | 13.8 | -184.2 | 67.8 |

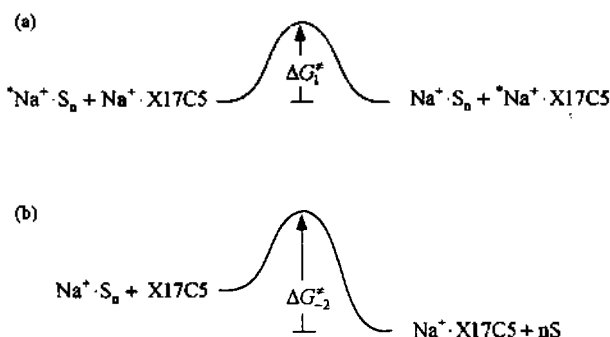


Figure 7. Activated free energy profiles for (a) the bimolecular exchange, (b) the dissociative mechanism.

but high dielectric constants. This can be easily understood when we think of the free energy diagram for the dissociation step (shown in Figure 7).^{10(b)} In the bimolecular mechanism the entering and leaving cations are equally solvated by solvent molecules that whatever the solvent may be ΔG^\ddagger calculated is not affected by their solvating ability. But in the dissociative mechanism solvated Na^+ and complexed Na^+ have different energies so that the solvating ability of a solvent has large influence on the magnitude of ΔG^\ddagger_2 . Therefore a solvent with high dielectric constant generally favors bimolecular mechanism because it lowers the free energy of activation by reducing charge-charge repulsion in the transition state, and a solvent with both high dielectric constant and high donor number generally favors dissociative mechanism because it effectively lowers ΔG^\ddagger_2 . In the case of acetonitrile, it has relatively high dielectric constant of 37.5 and comparatively low donor number of 14.1.¹⁸ Although its dielectric constant is not so high enough to lower ΔG^\ddagger_1 , it is expected to follow bimolecular mechanism owing to its low solvating ability.

The other is the nature of the counter anions.^{10(b)} In the transition state of the bimolecular mechanism the leaving of complexed Na^+ and the entering of solvated Na^+ occurs simultaneously. Therefore two Na^+ ions come close together and their charge-charge repulsion becomes important. When counter anions form strong ion pairs with cations, this charge-charge repulsion is considerably reduced that exchange *via* bimolecular mechanism becomes much easier. Both NaI and NaSCN form contact ion pairs which helps the bimolecular mechanism.

It seems that these two factors work hand in hand to allow the Na^+ -X17C5 system to undergo exchange process *via* bimolecular mechanism. This can also be confirmed by the free energy consideration. In their report, Strasser *et al.* presented a figure¹⁹ which shows the close relationship

between ΔG^{\ddagger}_2 and Gutmann donor number. If we assume that the dissociative mechanism is predominant in acetonitrile, the figure of Strasser *et al.* tells us that ΔG^{\ddagger}_2 will be about 79 kJ/mol. This is 12-28 kJ/mol larger than observed ΔG^{\ddagger} value, which indicates that dissociative mechanism is improbable.

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Topological Analysis on the Spinodal Decomposition and Interfacial Tension of Polymer-Solvent Systems

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A topological theory has been introduced to extend the theory of Balsara and Nauman to evaluate the entropy of inhomogeneous polymer solutions. Previous theories have considered only the terms about the displacement of junction points, while the present theory has obtained a more complete expression for the entropy by adding the topological interaction terms between strands. There have been predicted the characteristics of the spinodal decomposition and the interfacial tension of polymer solutions from the resultant expression. It is exposed that the theoretically predictive values show good agreement with the experimental data for polymer solutions.

Introduction

Topological theories have recently played a great role in studying various physical properties including the elasticity of polymers. The theories which have systematically studied the rubber elasticity so far are the phantom network theo-

ries¹⁻⁶ headed by Flory *et al.* and the topological network theories⁷⁻¹² headed by Iwata *et al.* Since phantom network theories have dealt with the energies of rubber elasticity as only functions of the end-to-end distance between junction points, and have not considered the effect of interaction between chains by entanglement, these have recently retrogra-