

## Kinetics of Complexation of Alkali Earth Metal Ions with 18-Crown-6-Ether in Methanol

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The rates of complexation of the 18-C-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) with  $K^+$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$  in methanol solution have been determined at 25 °C by a pressure-jump technique. The Eigen Winkler mechanism has been applied to interpret the kinetic data. The results suggest that the rate determining step of the complexation in methanol is the rearrangement of the ligand in the outer sphere ion-dipole pair to form a stable encapsulated complex of the metal ion by the crown ether.

### Introduction

The kinetics and mechanism of complexation of the synthetic macrocyclic polyethers with the metal ions have been extensively studied.<sup>1,2</sup> The most of the studies have focused on the complexation of the monovalent alkali metal ions in nonaqueous solution using nmr techniques.<sup>3-6</sup> Although the ultrasonic absorption kinetic studies on the complexation have been reported elucidating the detailed mechanism in various solvents,<sup>7-11</sup> the relatively less attention has been paid to the complexation reactions of the divalent alkali earth metal ions with the crown ethers.<sup>12</sup>

The two mechanisms for the complexation of crown ethers with the metal ions have been proposed. The one is the so-called Chock mechanism<sup>13</sup> in which a rapid conformational change of the crown ethers is followed by the rate determining formation of the metal ion-crown ether complexation. The other is the so-called Eigen-Winkler mechanism<sup>14</sup> which is widely accepted for fast metal-ligand complex formation reactions. In this mechanism the outer sphere complex formation between the metal ion and crown ether by the diffusion controlled approach of the two counter species, precedes the rate determining inner sphere complex formation by the ligand rearrangement desolvation of the cation.

The conclusion has been derived from the kinetic study of  $Ba^{2+}$  with 18-crown-6 in DMF by comparison of it with the corresponding reaction in water, that removal of water molecules from the primary solvation area of the cation in water and rearrangement of crown ether around the cation are respectively the rate-determining steps in the solvents. Chen and Petrucci,<sup>8</sup> in Ultrasonic kinetic study of complexation of 18-crown-6 with alkali metal ions in methanol solution, have observed the conformational change of the ligand alone. However, the rate of the conformational change of the crown ether is much faster than that of the complexation between the metal ion and the crown ether.

In order to find out what process is the rate determining step of the complexation of the divalent alkali earth metal ions with the synthetic polyethers in the methanol solution,

we have carried out the kinetic investigation of the complexation with the pressure jump apparatus. The formation constants of 18-crown-6 with metal ions in methanol solution increase with respect to the aqueous solution. Thus, the pressure-jump technique is able to use for the study of the complexation in methanol solution.

### Experimental

18-crown-6 (Aldrich Co, 98%) was recrystallized from acetonitrile solution. The inorganic ions in the form of chloride salts were all analytical reagent grade.  $KCl$ ,  $MgCl_2 \cdot 6H_2O$ ,  $BaCl_2 \cdot 2H_2O$ ,  $CaCl_2$ , and  $SrCl_2 \cdot 6H_2O$  were dried in the oven at 150 °C. 18-crown-6 stock solution was prepared by dissolving it in methanol and standardized by drying and weighting method. The stock solutions of the metal ions were prepared by dissolving each salt in methanol. The stock solutions of the metal ions were standardized by the Volhard method.<sup>15</sup> The absolute methanol used is Merck reagent grade.

The stability constant of the 1:1 complexes of 18-C-6 with  $Sr^{2+}$  ion which has not been reported in the literature were measured by the conductometric method which has been previously described in details.<sup>16</sup> The conductance measurements were performed on a conductivity apparatus (Yellow Springs, Model 31) with a dropping cell whose cell constant is 0.942  $cm^{-1}$ .

The kinetic data for the complexation reactions were obtained by the pressure-jump technique.<sup>17,18</sup> The pressure-jump apparatus constructed is modified from that described elsewhere.<sup>18</sup> The rise time of the apparatus measured by a 0.2M nickel sulphate solution was found to be less than 50  $\mu sec$ . The temperature of the reaction cell was controlled within  $\pm 0.1$  °C with a circulated constant temperature bath.

The apparatus is illustrated in Figure 1. Two conductivity cells which are constructed of stainless steel are connected to the wheaton bridge. Each cell has a stainless steel electrode shielded with a teflon supportor from the stainless steel body. One contains the electrolyte solution being studied and the other is filled with the reference  $KCl$  solution. The conductance of the reference solution is adjusted to be equal to that of the solution under investigation before placement in

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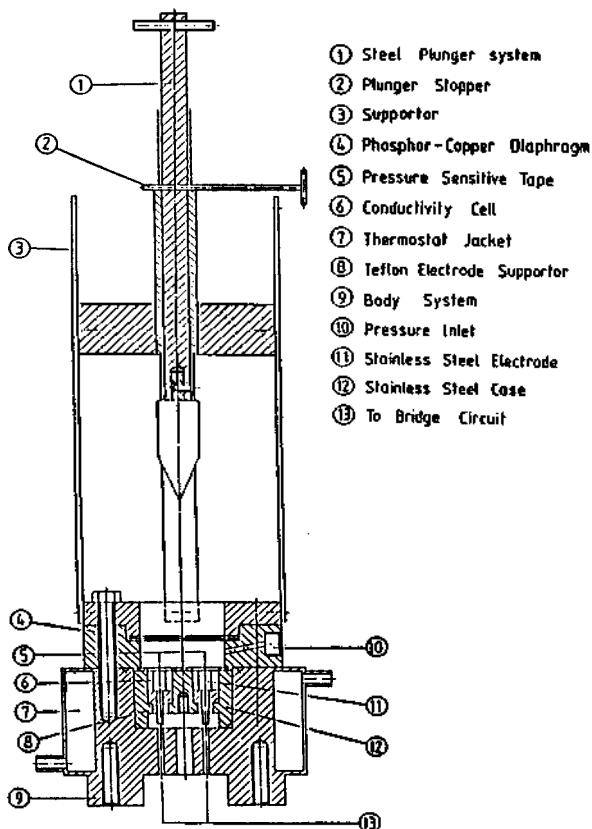


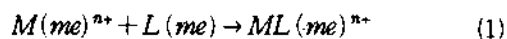
Figure 1. Schematic diagram of pressure-jump apparatus.

the cell. The conductivity cell is sealed by pressure sensitive tape and a pressure of about 30 atmospheres is applied to. After the sudden release of pressure by the rupture of phosphorus-bronze diaphragm by a steel plunger, the relaxation effect is traced by means of a bridge circuit. The signal is stored on the Hewlett Packard, Type 1223A storage oscilloscope.

## Results and Discussion

Figure 2 shows a typical relaxation curve for the methanol solution of  $\text{Ba}^{2+}$  and 18-C-6 of which equilibrium concentrations are  $2.30 \times 10^{-6}\text{M}$  in each. The relaxation time of this solution was calculated to be 347 usec. A relaxation time characterized by a single relaxation step was observed for the system.

The interaction of the metal ion with 18-C-6 in methanol solution would be expressed as



where  $M(me)$  and  $L(me)$  represent the metal ion with the charge of  $n$  and 18-C-6 ligand solvated by the methanol, respectively. The rate constants of the complex formation reaction are related to the relaxation time,  $\tau$  by equation (2)

$$\frac{1}{\tau} = k_f f^2 (\bar{C}_M n^+ + \bar{C}_L) + k_r \quad (2)$$

when  $k_f$  and  $k_r$  are the forward and reverse rate constants of the complexation, respectively. In equation (2),  $\bar{C}_M n^+$  and  $\bar{C}_L$  represent the equilibrium concentrations of the metal ion and 18-C-6 ligand, respectively, and  $f$  is the mean coefficient of the species. The activity coefficients were estimated from



Figure 2. Typical relaxation trace of  $\text{Ba}^{2+}$ -18-C-6 at  $25^\circ\text{C}$ ,  $\bar{C}_M n^+ + \bar{C}_L = 2.0 \times 10^{-6}\text{M}$ , Sweep:  $200 \mu\text{sec/div}$ . Relaxation time measured:  $347 \mu\text{sec}$ .

Table 1. Experimental Conditions and Relaxation Times for 18-C-6 Complexation with Various Metal Ions at  $25^\circ\text{C}$  and  $u=0$

cations	$\bar{C}_M \times 10^5$ (M)	$\bar{C}_L \times 10^5$ (M)	$\frac{1}{\tau} \times 10^{-3}$ ( $\text{sec}^{-1}$ )	$(f^2 \bar{C}_M n^+ + \bar{C}_L) + \frac{1}{K_{eq}}$ $\times 10^5$
$\text{K}^+$	2.29	3.75	3.52	5.99
	1.95	2.92	2.75	4.86
	1.64	2.29	2.30	3.96
	1.21	1.53	1.72	2.80
$\text{Ca}^{2+}$	15.6	17.2	3.68	43.5
	10.8	11.8	2.90	34.7
	7.56	8.12	2.54	28.5
	5.59	5.97	2.29	24.8
$\text{Sr}^{2+}$	5.02	5.60	3.83	9.28
	3.58	3.86	2.79	6.86
	2.53	2.67	2.43	5.01
	2.03	2.12	1.92	4.11
$\text{Ba}^{2+}$	0.46	0.48	4.70	0.89
	0.33	0.33	4.43	0.64
	0.23	0.23	2.88	0.46
	0.19	0.19	2.25	0.38

the Davies equation.<sup>19</sup> Introducing the formation constant  $K_{eq}$  of the complex, equation (2) can be rewritten as

$$\frac{1}{\tau} k_r (f^2 (\bar{C}_M n^+ + \bar{C}_L) + \frac{1}{K_{eq}}) \quad (3)$$

where  $K_{eq} = k_f/k_r$ .

The forward rate constant of the complexation could be obtained by the linear regression analysis of the equation (3) and the reverse rate constant could be calculated from the relationship,  $k_r = k_f/K_{eq}$ . The literature values of  $K_{eq}$ <sup>20</sup> for the various metal complexes of 18-C-6 were used for the calculation of the equilibrium concentrations of the species and the reverse rate constant. The accurate value of  $K_{eq}$  for  $\text{Sr}^{2+}$  complex of 18-C-6 could not be found in the literature. Thus we have measured it to be  $\log K_{eq} = 5.64$  by the conductometric method. This value is well agreed with the inferior limit ( $>5.5$ ) reported<sup>20</sup> for  $\text{Sr}^{2+}$ -18-C-6 complex in methanol. The relaxation data of the complex formation reactions are given in Table 1. Table 2 shows the rate constants and formation constants of the complexation of  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  by 18-C-6 in methanol solution at  $25^\circ\text{C}$ .

The Eigen-Winkler mechanism of complexation reaction

**Table 2. Rate Constants and Formation Constants of 18-C-6 Complexation with Various Metal Ions at 25°C and  $\mu \rightarrow 0$** 

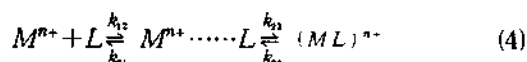
cations	$k_f \times 10^{-7} (\text{M}^{-1}\text{sec}^{-1})$	$k_r \times 10^{-2} (\text{sec}^{-1})$	$\log K_{eq}^a$
K <sup>+</sup>	5.58 ± 0.23	0.49 ± 0.03	6.06 ± 0.03
Ca <sup>2+</sup>	0.74 ± 0.05	10.2 ± 0.80	3.86 ± 0.02
Sr <sup>2+</sup>	3.50 ± 0.39	0.80 ± 0.09	5.64 ± 0.40 <sup>b</sup>
Ba <sup>2+</sup>	48.8 ± 7.0	0.45 ± 0.06	7.04 ± 0.08

Errors indicated are a standard deviation, <sup>a</sup>Ref. 20, <sup>b</sup>This work.

**Table 3. Kinetic Data for the Complexation Reactions of 18-C-6 with Various Metal Ions at 25°C and  $\mu \rightarrow 0$** 

cations	$K_{12} (\text{M}^{-1})$	$k_{23} (\text{sec}^{-1})$	$k_{32} (\text{sec}^{-1})$
K <sup>+</sup>	0.25	$2.23 \times 10^8$	$5.12 \times 10^1$
Ca <sup>2+</sup>	0.35	$2.11 \times 10^7$	$1.21 \times 10^3$
Sr <sup>2+</sup>	0.35	$1.00 \times 10^8$	$1.02 \times 10^2$
Ba <sup>2+</sup>	0.35	$1.40 \times 10^9$	$5.55 \times 10^1$

of the metal ion with 18-C-6 in methanol is described as



The first step is the diffusion collision between the metal ion and the ligand crown ether to form the outer sphere complex. The second step is the rate determining formation of the complex in which the metal ion is encapsulated in the ligand cavity. The forward and reverse rate constants are related to the rate constants of the individual steps as

$$k_f = K_{12} k_{23} \quad \text{and} \quad k_r = k_{32} \quad (5)$$

where  $K_{12} = k_{12}/k_{11}$

If  $K_{12}$  is estimated,  $k_{23}$ , which reflects the rate of the inner sphere complex formation, can be calculated.  $K_{12}$  would be estimated as identifying it with the Fuoss constant. The Fuoss equation derived on statistical ground<sup>21</sup> is

$$K_{12} = \frac{4\pi Na^3}{3000} e^b \quad (6)$$

where  $b = \frac{Zeu}{\epsilon a^2 kt}$

In the above equation,  $N$  is the Avogadro's number,  $a$  is the closest approach between the metal ion and dipole,  $\mu$  is the dipole to be separated from the metal ion,  $\epsilon$  is the dielectric constant of the solvent,  $k$  is the Boltzman constant, and  $e$  is the electronic charge. Using reasonable parameters such as  $\mu = 1.68 \times 10^{-18}$  esu-cm,<sup>22</sup>  $\epsilon = 32.6$  and  $a = 4\text{Å}$ , it is estimated  $K_{12} = 0.25$  and  $0.35$  for monovalent and divalent cations, respectively.

Table 3 summarizes the equilibrium and kinetic data of each individual step of complexation reactions of some alkali and alkali earth metal ion with 18-C-6. The value of  $k_{23}$  for K<sup>+</sup> is well agreed with that reported in the literature<sup>8</sup>. The literature value of  $k_{23}$  for K<sup>+</sup> determined by the Ultrasonic absorption technique<sup>8</sup> is  $1.8 \times 10^8 \text{sec}^{-1}$ . It is noted that the rate constant of the complexation increases in the order of  $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$  in the series of the alkali metal ions. This order would reflect the size effect on the complexation reaction. The ionic radius of the cations increases in same order.

By making a kinetic comparison between K<sup>+</sup> and Ba<sup>2+</sup>

systems, where the ionic radii of the cations are similar, the size effect on the complexation would be eliminated. These two metal ions have similar ionic radii<sup>2</sup> as 1.35 Å for Ba<sup>2+</sup> and 1.38 Å for K<sup>+</sup>. Since the solvent molecule is more strongly bound to Ba<sup>2+</sup> ions than to K<sup>+</sup> ion, the rate constant ( $k_{23}$ ) for the complexation of K<sup>+</sup> should be larger than that for Ba<sup>2+</sup> if the desolvation of the metal ion were the rate determining step for the complexation process with 18-C-6. On the contrary, the experimental result shows that the rate of the complex formation reaction of Ba<sup>2+</sup> is much faster than that of K<sup>+</sup>. Therefore, the rate determining process might be something else other than the desolvation of the metal ion.

The ratio of  $k_{23}$  between Ba<sup>2+</sup> and K<sup>+</sup> is  $k_{23}^{\text{Ba}}/k_{23}^{\text{K}} = 6.3$ . This ratio is approximately agreed with the value (8.0) estimated considering the charge effect between the cations on the theoretical basis<sup>10</sup>. This would mean that  $k_{23}$  reflects the rearrangement of the ligand on the complexation process. A similar result has been obtained in the study of the complexation of 18-C-6 in DMF solvent system<sup>10</sup>. There is also a kinetic evidence obtained by the Ultrasonic relaxation study, that the rate constant for the inner sphere complex formation step ( $k_{23}$ ) reflects the rearrangement of the 18-C-6 ligand around the cation to form a wrapped configuration with oxygen atoms of the ligand toward the metal ion in methanol in contrast to the complexation in water. In water solvent, it has been generally known that the rate of desolvation from the outer sphere complex controls the overall rate of the complex formation.

Once the complex is formed, the reverse rate constant ( $k_r = k_{32}$ ) becomes an exclusive function of decapsulating out of the metal ion from the crown ether cavity. This means that the ratio of the cation and cavity radii would be an important factor for the rate of decomplexation. Since the ratio of the cation and cavity radii is close to unity in both K<sup>+</sup> and Ba<sup>2+</sup> complexes with 18-C-6, the K<sup>+</sup> and Ba<sup>2+</sup> complexes should be the most difficult to be decapsulated. The cavity radius<sup>2</sup> of 18-C-6 is 1.34-1.43 Å. As listed in Table 3, the reverse rate constants ( $k_{32}$ ) for K<sup>+</sup> and Ba<sup>2+</sup> complexes are the smallest and comparable magnitude each other.

In conclusion, we are suggesting that the rate determining step of the complexation of 18-C-6 is the rearrangement of the ligand in the outer sphere ion-dipole pair to form a stable encapsulated complex of the metal ion by the ligand in methanol solvent as well as in DMF solvent. It is interesting to note that the permittivities of these two solvents are very close each other ( $\epsilon = 36.6$  for DMF and 32.6 for methanol).

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## Hydrophobic Interaction between Rhodamine 6G and Tetraphenylborate Anions

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The hydrophobic interaction occurring between rhodamine 6G and tetraphenylborate anions has been investigated with surfactants by absorption and fluorescence studies. In the order of tetraphenylborate, tetrakis(4-fluorophenyl)borate, and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate the hydrophobicity is found to be increased.

### Introduction

Tetraphenylborate (TPB<sup>-</sup>) anion has been used to investigate the nature of interaction with cationic dyes, such as methylene blue, rhodamine 6G, and crystal violet.<sup>1-5</sup> The ion aggregates associated between dye cation and TPB<sup>-</sup> show characteristic absorption behavior at longer wavelengths and cause fluorescence intensity to decrease with respect to the dye blank. The spectral variations are attributed to the hydrophobic interaction originated from water structure to minimize the disturbance of dye cation and TPB<sup>-</sup> to water and to maximize water-water bonding.<sup>6</sup> The ion pairs have commonly applied to analytical chemistry, especially for the separation of ions by extraction and precipitation.<sup>7</sup> TPB<sup>-</sup> is generally known as an effective precipitating reagent for K<sup>+</sup> and NH<sub>4</sub><sup>+</sup>.<sup>8</sup> Several attempts have been made to improve physico-chemical properties of TPB<sup>-</sup> as an agent for precipitation and solvent extraction in aqueous solutions.<sup>9</sup> The strongly electron-withdrawing trifluoromethyl substitution, in particular, highly increased the lipophilicity and decreased the solubility of ion pair to promote the extraction into organic solvents.<sup>9</sup> However, studies on absorption or fluorescence behavior owing to the hydrophobic interaction have attracted little attention yet.

In the present paper, therefore, analyses on the absorption and fluorescence spectral changes of rhodamine 6G with TPB<sup>-</sup>, tetrakis(4-fluorophenyl)borate, and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anions are reported for the

purpose of understanding the difference of the hydrophobicity of three borates. Among them, TFPB<sup>-</sup> is expected to enhance the formation of ion aggregates most due to the trifluoromethyl substitution.

### Experimental

Rhodamine 6G (Aldrich, GR) was used as a cationic source, Rh6G<sup>+</sup>. Sodium tetraphenylborate (Fluka AG, GR) sodium tetrakis(4-fluorophenyl)borate (Aldrich, GR), and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Dojindo, GR) as sources of boron complex anions, TPB<sup>-</sup>, TFB<sup>-</sup>, and TFPB<sup>-</sup>, respectively, were dissolved in distilled water and stored in polyethylene bottles. TFPB<sup>-</sup> is dissolved in small amount of methanol and diluted with distilled water because of its low solubility. Triton X-100 (Merck) and cetyltrimethylammonium bromide (CTAB) (BDH chemicals Ltd.) of reagent grade were used as received. Ionic strength and pH were adjusted with NaCl (Shinyo, GR) and a CH<sub>3</sub>COOH-CH<sub>3</sub>COONa buffer, respectively. Visible spectra were taken on a Shimadzu UV-240 spectrophotometer and fluorescence emission spectra were recorded on a Hitachi 650-60 spectrofluorimeter.

### Results and Discussion

Figure 1 shows the absorption spectra of  $4.0 \times 10^{-6}$ M Rh6G<sup>+</sup> and the spectral variation caused by the increase of