Equilibrium and Kinetic Studies on Complex Formation Reaction between Crown Ethers and Bivalent Transition Metal Ions

Hideto Matsuyama,* Takeo Arimura, Yoshikazu Miyake, and Masaaki Teramoto
Department of Chemistry and Materials Technology, Faculty of Engineering and Design,
Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606

(Received January 5, 1991)

Synopsis. The complex formation reaction between crown ethers and bivalent transition metal ions was investigated. Although the obtained equilibrium constants were generally small, there was a case where the constant was larger than that for the crown ether–alkali metal system. From kinetic studies the reactions were found to obey the Eigen's mechanism.

It is well known that crown ethers can stably capture various metal ions in their cavities. A number of studies on such complex formations were carried out for an interest in the reaction itself, or for the purpose of metal separation or analysis.[1] However, the target metal has been restricted mostly to alkali and alkaline earth metals so far. Further, relatively few studies have been reported on the kinetics of complex formation reaction although they are important to elucidate the reaction mechanism.

In this work we attempted to investigate both equilibria and kinetics of the complex formation reaction between crown ethers, not containing N or S, and bivalent transition metal ions, for which little information is available in the literature.

Experimental

Materials. Benzo-15-crown-5 (B15C5) and dibenzo-18-crown-6 (B_218C6), purchased from Nacalai Tesque, Inc., were employed in this work. The metal ions used were Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Metal solutions were prepared by dissolving their perchlorates in acetonitrile or methanol.

Equilibrium and Kinetic Experiments. Equilibrium constants were determined spectrophotometrically. An example of the metal-induced spectral change is shown in Fig. 1. In the case of reactions of Zn^{2+} or Co^{2+} with B15C5 in acetonitrile, the equilibrium constants were directly determined by using the molar absorption coefficients of the complexes since the equilibrium constants were large enough to evaluate these coefficients accurately. In other cases where the equilibrium constants were small, they were determined as follows. The metal concentration was adjusted to be much higher than the crown ether concentration so that the former was approximately constant before and after the complex formation. Thus, the absorbance (Abs) obtained by substracting the metal ion absorbance from the total absorbance is given by

$$Abs=\varepsilon_1[\mathrm{C}]+\varepsilon_2[\mathrm{MC}^{2+}] \tag{1}$$

Here [C] and $[\mathrm{MC}^{2+}]$ are the concentrations of crown ether and the complex, respectively, and ε_1 and ε_2 are molar absorption coefficients. The total concentration of crown ether, $[\mathrm{C}]_t$, and the equilibrium constant, K_M, are given by Eqs. 2 and 3.

$$[\mathrm{C}]_t=[\mathrm{C}]+[\mathrm{MC}^{2+}] \tag{2}$$

$$K_M=[\mathrm{MC}^{2+}]/([\mathrm{C}][\mathrm{M}^{2+}]) \tag{3}$$

where M^{2+} denotes a metal ion. Combination of Eqs. 1—3 gives the following formula:

$$\frac{-1}{Abs/[\mathrm{C}]_t-\varepsilon_1}=\frac{1}{\varepsilon_1-\varepsilon_2}+\frac{1}{K_M(\varepsilon_1-\varepsilon_2)}\cdot\frac{1}{[\mathrm{M}^{2+}]} \tag{4}$$

K_M can hence be determined from a plot of $-1/(Abs/[\mathrm{C}]_t-\varepsilon_1)$ against $1/[\mathrm{M}^{2+}]$. An example of such plots is shown in Fig. 2. Linear relations were observed in all cases: this ensures the formation of 1 : 1 complexes assumed in Eq. 3. Almost the same equilibrium constants were obtained at two or three wavelengths near 280 nm in every case.

The rate of complex formation was measured with a stopped flow apparatus (Otsuka Electronics Co., Ltd., RA-401) by following the temporal change in absorbance at 280 nm. To simplify the analysis, the metal concentration was

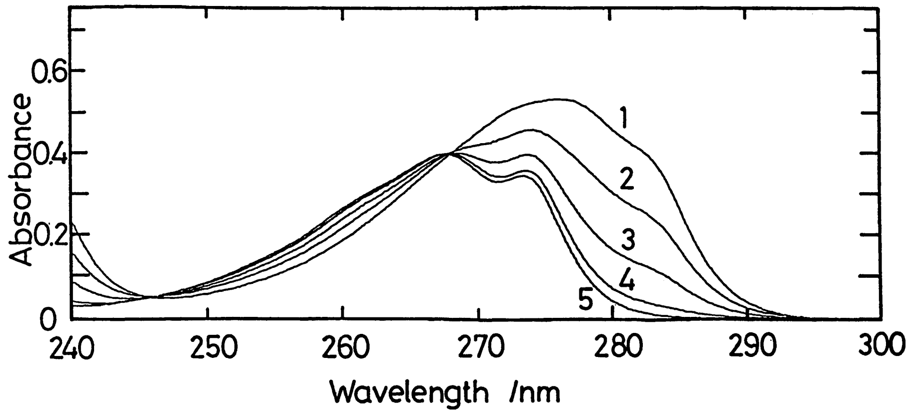

Fig. 1. UV absorption spectra of B15C5 in the absence and presence of Zn^{2+}. Solvent: acetonitrile. $[\mathrm{B15C5}]=2.0\times10^{-4}$ mol dm^{-3}.
1: $[\mathrm{Zn}^{2+}]=0$, 2: $[\mathrm{Zn}^{2+}]=8.8\times10^{-5}$ mol dm^{-3}, 3 : 1.8×10^{-4} mol dm^{-3}, 4 : 3.5×10^{-4} mol dm^{-3}, 5 : 3.5×10^{-3} mol dm^{-3}.

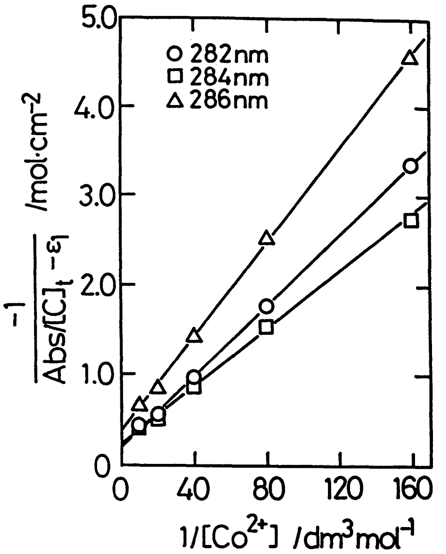

Fig. 2. Relation between $-1/(Abs/[C]_t-\varepsilon_1)$ and $1/[Co^{2+}]$ at various wavelengths. Crown ether: B_218C6, Solvent: acetonitrile, $[C]_t=2.0\times10^{-4}$ mol dm^{-3}.

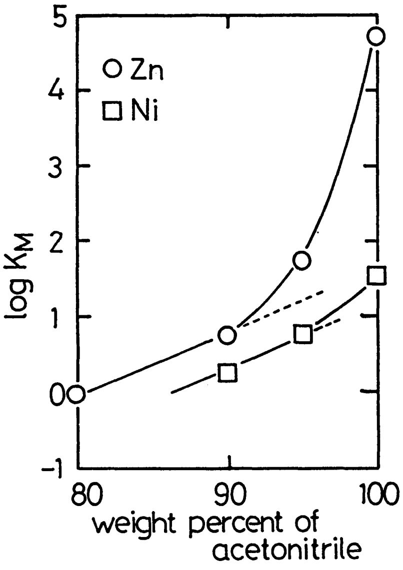

Fig. 3. Equilibrium constant in various acetonitrile–water mixtures. Crown ether: B15C5.

always sufficiently higher than that of crown ether.

All the experiments were carried out at 298 K.

Results and Discussion

Equilibrium Constant. The equilibrium constants obtained are listed in Table 1. The values of K_M with B15C5 in methanol are three orders-of-magnitude smaller than that for the Na^+–B15C5 system in methanol.[2] One of the reasons for this result is that "soft" transition metal ions do not easily form a complex with "hard" crown ether.[3] The sequence of K_M, $Co^{2+}<Ni^{2+}<Cu^{2+}>Zn^{2+}$, follows the Irving–Williams order,[4] which generally holds for the equilibrium constants of transition metals. A similar tendency was observed also with B_218C6 in acetonitrile.

However, the sequence of K_M for B15C5 in acetonitrile is quite different from those in the above two systems. The value of K_M for Zn^{2+} is especially large and is larger than that of Na^+–B15C5 system (3.5×10^4 at 295 K[5]). The ionic radius of Zn^{2+} is the largest among the four metal ions[6] and is closest to the 15C5 cavity radius.[1] One of the causes for the unusual K_M sequence in this solvent may be the metal–crown ether size fitting. However, further investigation is necessary to settle this problem.

Figure 3 shows the values of K_M in various acetonitrile–water mixtures. The value of K_M decreases as the water content increases. This suggests that an increase in the water content leads to an increase in the hydration number of the metal ion, thereby enhancing the total strength of the metal ion solvation and suppressing the complex formation. In the region of higher water content, the variation of $\log K_M$ for Zn^{2+} was found to parallel that for Ni^{2+}, though the number of data points is limited. This indicates that the linear free energy relationship[7] holds between the complex formation of Zn^{2+} and that of Ni^{2+}. On the other hand, as the water content decreases, the $\log K_M$ value for Zn^{2+} gradually deviates from the parallel relation, probably in accordance with the anomaly for the complex formation of Zn^{2+} in pure acetonitrile mentioned above.

Rate of Complex Formation. The reaction between a crown ether and a metal ion is expressed as Eq. 5.

$$M^{2+}+C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MC^{2+} \tag{5}$$

The pseudo-first-order rate constant, k_p with respect to [C] is given by

$$k_p=k_1[M^{2+}]+k_1/K_M \tag{6}$$

The relations between k_p and the metal concentration are shown in Fig. 4. In line with Eq. 6, linear relations were obtained. The obtained complex formation rate constants, k_1, and K_M thus obtained are listed in Table 2. Good agreement is seen between the K_M values obtained from this kinetic study and those from the equilibrium study mentioned above.

If the reaction obeys the Eigen's mechanism,[8] the complex formation rate constant, k_1, is given by $K_{os}k_{sol}$ (K_{os}: equilibrium constant of the outer complex, k_{sol}: rate constant of solvent exchange). Since the value of

Table 1. Equilibrium Constants, K_M/dm^3 mol^{-1}

Crown ether	Solvent	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
B15C5	Methanol	3.4 ± 0.5	7.8 ± 0.8	$4.9\pm0.3\times10^1$	1.9 ± 0.3
B15C5	Acetonitrile	$1.1\pm0.1\times10^3$	$3.5\pm0.4\times10^1$	$4.8\pm0.3\times10^2$	$5.4\pm0.6\times10^4$
B_218C6	Acetonitrile	$1.4\pm0.1\times10^1$	$3.8\pm0.6\times10^1$	$2.9\pm0.1\times10^2$	$2.2\pm0.2\times10^1$

Table 2. Rate and Equilibrium Constants

	k_1	K_M[a)]	K_M[b)]	k_1/K_{os}[c)]	k_{sol}[d)]
	$dm^3\,mol^{-1}\,s^{-1}$	$dm^3\,mol^{-1}$	$dm^3\,mol^{-1}$	s^{-1}	s^{-1}
Ni	7.0×10^2	4.1×10^1	3.5×10^1	2.2×10^3	2.0×10^3[e)]
Zn	1.7×10^6	4.9×10^4	5.4×10^4	5.3×10^6	3.0×10^7[f)]

Crown ether: B15C5, Solvent: acetonitrile

a) Obtained from kinetic studies. b) Obtained from equilibrium studies. c) Equilibrium constant of outer complex, estimated from Fouss's equation[12)] by using 5×10^{-10} m as minimum separation distance between molecules. d) Rate constant of solvent exchange. e) Rate constant of acetonitrile exchange, cited from Ref. 9. f) Rate constant of water exchange, cited from Ref. 10.

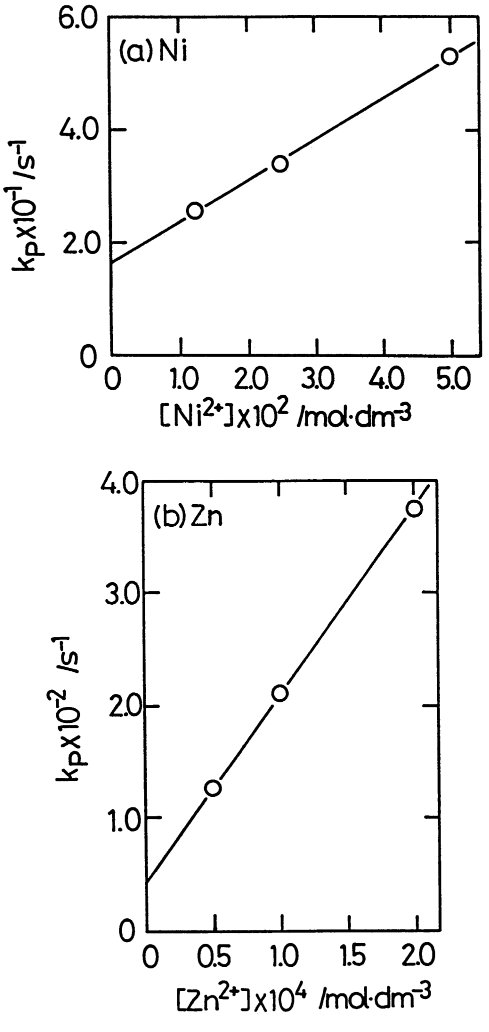

Fig. 4. Relation between k_p and metal concentration. Crown ether: B15C5, Solvent: acetonitrile. (a) $[B15C5]=2.0\times10^{-3}$ mol dm^{-3}, (b) $[B15C5]=7.0\times10^{-6}$ mol dm^{-3}.

k_1/K_{os} for Ni^{2+} is almost in accord with the rate constant for acetonitrile exchange,[9)] we conclude that the reaction obeys the Eigen's mechanism. As far as we know, the rate of exchange of acetonitrile molecules coordinated to Zn^{2+} in the bulk of the solution has not been reported. Although the value of k_1/K_{os} for Zn^{2+} is somewhat smaller than the rate constant of water exchange,[10)] it is presumed that the reaction for Zn^{2+} also obeys the Eigen's mechanism because the rates of water exchange are 3—16 times those of acetonitrile exchange for other bivalent transition metals.[11)]

Maynard et al.[13)] studied the 18-crown-6 ether complexation of alkali metal ions in nonaqueous solvents, and speculated that the reactions consisted of succesive steps involving both ion desolvation and ligand rearrangement, and also that the rearrangement of the macrocyclic ligand was the slowest step. However, the reaction in the present case obeyed the Eigen's mechanism and therefore an ion desolvation should be the rate-determining step. Because the ion desolvation rates for bivalent transition metals are much slower than those for alkali metals, the rate of ligand rearrangement may become faster relatively.

References

1) R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, and J. J. Christensen, *Chem. Rev.*, **85**, 271 (1985).

2) D. G. Parsons, M. R. Truter, and J. N. Wingfield, *Inorg. Chim. Acta*, **47**, 81 (1980).

3) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

4) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192.

5) A. Hofmanova, J. Koryta, M. Brezina, and M. L. Mittal, *Inorg. Chem. Acta*, **28**, 73 (1978).

6) "Landolt-Börstein Zahlenwerte und Funktionen," I. Band, Atom—und Molekularphysik, 4. Teil, Kristalle, Springer-Verlag (1955).

7) P. R. Wells, "Linear Free Energy Relationships," Academic Press, New York (1968).

8) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).

9) S. F. Lincoln and R. J. West, *Aust. J. Chem.*, **26**, 255 (1973).

10) F. Fittipaldi and S. Petrucci, *J. Phys. Chem.*, **71**, 3414 (1967).

11) H. Ohtaki, M. Tanaka, and S. Funahashi, "Youekihannou no Kagaku," Gakkai Syuppan Senta (1977).

12) R. M. Fouss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

13) K. J. Maynard, D. E. Irish, E. M. Eyring, and S. Petrucci, *J. Phys. Chem.*, **88**, 729 (1984).