Thermodynamic Study of Complex Formation of Benzo-18-crown-6 with K^+, Tl^+, and Pb^{2+} in Water

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Abstract. ΔH^0 and ΔS^0 values of the complex formation in water of benzo-18-crown-6 (B18C6) with K^+, Tl^+, and Pb^{2+} were determined and compared with those of 18-crown-6. The ΔH^0 values of B18C6 are negative. The stability in water of the B18C6-metal ion complex at 25°C is governed largely by the magnitude of the ΔH^0 value. The B18C6-metal ion complex is less stable in water than the corresponding 18C6-metal ion complex. This is due largely to a less favorable enthalpic contribution of the B18C6-metal ion complex compared with the corresponding 18C6-metal ion complex. The two aromatic ether oxygen atoms of B18C6 are responsible for the larger ΔH^0 value of the B18C6-metal ion complex compared with the corresponding 18C6-metal ion complex.

Key words. Benzo-18-crown-6, metal ions, complexation, water, thermodynamics.

1. Introduction

The complexing abilities of various crown ethers in solutions for metal ions have been studied from a thermodynamic point of view. But, on account of poor solubilities and poor complexing abilities for metal ions of most of the crown ethers in water, few papers have been published on the thermodynamic quantities of complex formation of crown ethers with metal ions in water [1].

In this study, in order to obtain more detailed information about stabilities in water of complexes of crown ethers with metal ions, the formation constants of complexes of benzo-18-crown-6 (B18C6) with K^+, Tl^+, and Pb^{2+} were determined in water at various temperatures; the thermodynamic parameters of B18C6 were calculated from these data and compared with those of 18-crown-6 (18C6). The K^+, Tl^+, and Pb^{2+} ions were chosen as being representative of the alkali metal ions, the Tl^+ and Ag^+ group, and of bivalent metal ions, respectively.

2. Experimental

2.1. MATERIALS

Benzo-18-crown-6 was prepared according to the method of Pedersen [2]. The product was recrystallized four times from hexane and dried in a vacuum oven at 30°C. The purity was checked by melting point (mp 44–45°C), elemental analysis, NMR spectroscopy, and conductometry. Extremely pure KCl and analytical grade $TlNO_3$ were purchased from Merck Japan Ltd. They were used without further purification. Analytical grade $Pb(NO_3)_2$ was obtained from Wako Pure Chemicals

Ltd. The purity of $Pb(NO_3)_2$ was determined by EDTA titration. The conductivity of water was less than $3 \times 10^{-7} \Omega^{-1} cm^{-1}$.

2.2. APPARATUS AND PROCEDURE

The conductance measurements were made on a Fuso conductivity apparatus (model 362B) in a water bath thermostated at 15, 20, 30, and $32 \pm 0.005°C$. Two cells with cell constants of 0.059701 and 0.093934 cm^{-1} were used. The experimental procedure to obtain the formation constants of 1 : 1 complexes of B18C6 with K^+ and Tl^+ has been described elsewhere [3].

The emf measurements were made with a Denki Kagaku Keiki ion meter apparatus (model IOC-10) in a water bath thermostated at 15, 20, 30, and $35 \pm 0.05°C$. A Denki Kagaku Keiki 7180 Pb^{2+}-selective electrode and a Denki Kagaku Keiki 4083 Ag|AgCl reference electrode were used for Pb^{2+} measurements. The formation constant of the 1 : 1 complex of B18C6 with Pb^{2+} was obtained according to the method of Frensdorff [4].

The initial concentrations of KCl, $TlNO_3$, $Pb(NO_3)_2$, and B18C6 were (3–4) $\times 10^{-3}$, (2–4) $\times 10^{-3}$, (4–6) $\times 10^{-4}$, and $1 \times 10^{-4} - 3.2 \times 10^{-2}$ M, respectively.

3. Results and Discussion

The formation constants, K_{ML}, of B18C6 complexes with K^+ and Tl^+ were obtained in the same manner as described in the previous study [3], where $K_{ML} = [ML^{m+}]/[M^{m+}][L]$; M^{m+} and L are the metal ion and crown ether, respectively. The analysis of the potentiometric data for obtaining the K_{ML} value of the B18C6 complex with Pb^{2+} was similar to that described by Frensdorff [4]. In this study, it has been assumed that the association between a cation and an anion is negligible on account of the high dielectric constant of water. The log K_{ML} values of the B18C6-metal ion complexes in water at various temperatures are compiled in Table I.

The log K_{ML} vs. T^{-1} plot for each B18C6-M^{m+} complex system gives a linear relationship. The enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from these data and are summarized in Table II.

The complexation reactions of B18C6 with K^+, Tl^+, and Pb^{2+} in water are exothermic. The stability in water of a B18C6-metal ion complex is governed largely by the magnitude of the ΔH^0 value. The same tendency is observed for 18C6. The log K_{ML} value at 25°C of the B18C6 complexes increases in the order $Tl^+ < K^+ < Pb^{2+}$. The most favorable ΔH^0 value of the B18C6-K^+ complex is

Table I. log K_{ML} values of B18C6-M^{m+} complexes in water at various temperatures[a].

	15°C	20°C	25°C [5]	30°C	32°C	35°C
K^+	1.84 ± 0.01	1.80 ± 0.01	1.74	1.685 ± 0.009	1.66 ± 0.01	—
Tl^+	1.75 ± 0.01	1.71 ± 0.01	1.68	1.66 ± 0.01	1.65 ± 0.02	—
Pb^{2+}	3.29 ± 0.02	3.22 ± 0.01	3.19	3.14 ± 0.01	—	3.08 ± 0.02

[a] Each log K_{ML} value is the average of 6–8 measurements. The uncertainties are the standard deviations.

Table II. Thermodynamic quantities of crown ether–metal ion complexes in water at 25°C.

Crown ether	K$^+$ (1.38 Å^a)			Tl$^+$ (1.50 Å^a)			Pb^{2+} (1.19 Å^a)		
	log K_{ML}	ΔH^0 kJ mol^{-1}	$T\Delta S^0$ kJ mol^{-1}	log K_{ML}	ΔH^0 kJ mol^{-1}	$T\Delta S^0$ kJ mol^{-1}	log K_{ML}	ΔH^0 kJ mol^{-1}	$T\Delta S^0$ kJ mol^{-1}
B18C6	1.74 [5]	−18.1	−8.2	1.68 [5]	−9.7	−0.04	3.19 [5]	−17.0	1.2
18C6	2.03 [6]	−25.0 [6]	−13.2 [6]	2.27 [1]	−18.6 [1]	−5.6 [1]	4.27 [1]	−21.6 [1]	2.7 [1]
B15C5	0.38 [1]	−9.75 [1]	−7.6 [1]	—	—	—	—	—	—

^{a} Ionic radius [7].

greatly cancelled by the most unfavorable $T\Delta S^0$ value, resulting in the second largest log K_{ML} value. The most favorable and unfavorable ΔH^0 and $T\Delta S^0$ values are also observed for the 18C6–K$^+$ complex. The enthalpy of hydration, ΔH_h^0, of K$^+$ (-360 kJ mol^{-1}) is nearly equal to that of Tl$^+$ (-364 kJ mol^{-1}) and very much larger than that of Pb^{2+} (-1556 kJ mol^{-1}) [8]. Since K$^+$ fits best into the crown-6 cavity (cavity radius: 1.38 Å [1]), the six donor ether oxygen atoms of the crown-6 adopt the most favorable arrangement around the K$^+$ ion. This is responsible for the smallest ΔH^0 value of the crown-6–K$^+$ complex. A possible explanation for the smallest $T\Delta S^0$ value of the crown-6–K$^+$ complex is as follows. The entropy of hydration, ΔS_h^0, of K$^+$ (-74.1 J K^{-1} mol^{-1}) is nearly equal to that of Tl$^+$ (-69.9 J K^{-1} mol^{-1}) and is very much larger than that of Pb^{2+} (-198 J K^{-1} mol^{-1}) [8]. When a complex-formation reaction occurs between a crown ether and a metal ion in water, most of the water molecules bound to the metal ion and the crown ether are released. Since K$^+$ has the most suitable size for the crown-6 cavity, the structure of the crown-6–K$^+$ complex can be considered to be the most rigid. Consequently, the $T\Delta S^0$ value of the crown-6–K$^+$ complex is the smallest.

The most unfavorable ΔH^0 value and the nearly zero value of $T\Delta S^0$ of the B18C6–Tl$^+$ complex lead to the smallest log K_{ML} value.

The highest stability of the B18C6–Pb^{2+} complex is attributed to the most favorable $T\Delta S^0$ value and the second largest $-\Delta H^0$ value, which is comparable to the $-\Delta H^0$ value of the B18C6–K$^+$ complex. The most favorable $T\Delta S^0$ value and the second largest $-\Delta H^0$ value, which is comparable to the $-\Delta H^0$ value of the 18C6–K$^+$ complex, are also found for the 18C6–Pb^{2+} complex. The interaction of Pb^{2+} with the six donor ether oxygen atoms of the crown-6 may be much stronger than that of K$^+$ owing to the much higher charge density of Pb^{2+} compared with K$^+$. The interaction with water of the crown-6–Pb^{2+} complex may be stronger than that of the corresponding crown-6–K$^+$ complex. But the ΔH^0 value of the crown-6–Pb^{2+} complex is slightly larger than that of the corresponding crown-6–K$^+$ complex. This may be attributed to the smaller ΔH_h^0 value of a free Pb^{2+} ion. Complexation of the crown-6 with Pb^{2+} may cause the greatest conformational change on account of the highest charge density and the smaller size of Pb^{2+} compared with the crown-6 cavity. The crown-6–Pb^{2+} complex may undergo stronger hydration than the corresponding crown-6–K$^+$ and $-$Tl$^+$ complexes. But the $T\Delta S^0$ value of the crown-6–Pb^{2+} complex is positive and the largest. Pb^{2+} undergoes much stronger hydration than K$^+$ and Tl$^+$ [8]. Thus, more water molecules may be released on complexation of the crown-6 with Pb^{2+} compared with K$^+$ and Tl$^+$. This is responsible for the most favorable $T\Delta S^0$ value of the crown-6–Pb^{2+} complex.

The $-\Delta H^0$ value of the B18C6–K$^+$ complex is about twice as large as that of the B15C5–K$^+$ complex, whereas the $T\Delta S^0$ values of the two K$^+$ complexes are almost the same. The higher stability in water of the B18C6–K$^+$ complex is due entirely to more favorable enthalpic contribution compared with the B15C5–K$^+$ complex. The larger $-\Delta H^0$ value of the B18C6–K$^+$ complex compared with the B15C5–K$^+$ complex is attributable to the larger number of donor ether oxygen atoms of B18C6 and the much better size-fit of K$^+$ for the B18C6 cavity.

The B18C6-metal ion complex is less stable in water than the corresponding 18C6-metal ion complex. This is due largely to the less favorable enthalpic contribution of the B18C6-metal ion complex compared with the corresponding 18C6-metal ion complex. The basicity of an aromatic ether oxygen atom is lower than that of an aliphatic ether oxygen atom. 18-Crown-6 has six aliphatic ether oxygen atoms, whereas B18C6 has two aromatic and four aliphatic ether oxygen atoms. The two aromatic ether oxygen atoms are responsible for the larger ΔH^0 value of the B18C6-metal ion complex compared with the corresponding 18C6-metal ion complex.

The $T\Delta S^0$ values of the B18C6–K^+ and –Tl^+ complexes are larger than those of the 18C6–K^+ and –Tl^+ complexes, respectively. But the reverse is true for the crown-6–Pb^{2+} complexes. The larger $T\Delta S^0$ value of the B18C6-univalent metal ion complex is attributable to the higher ligand-ring rigidity of B18C6 owing to the benzo group compared with the case of 18C6. The size of Pb^{2+} is smaller than that of the crown-6 cavity. On account of the more flexible structure of 18C6, the Pb^{2+} ion in the crown-6 complex must be more effectively wrapped by 18C6 than by B18C6. It thus appears from this that more water molecules attached to a free Pb^{2+} ion are released on complexation with 18C6 compared with B18C6. Since Pb^{2+} is much more strongly hydrated than K^+ and Tl^+ [8], in the case of Pb^{2+}, this effect on the entropy change at complexation should surpass the effect of the ligand-ring flexibility, resulting in the smaller $T\Delta S^0$ value of the B18C6–Pb^{2+} complex compared with the 18C6 complex. The above discussion is supported by the data on coextraction of water into nitrobenzene with alkali and alkaline earth metal ions in the presence of B18C6 and 18C6 [9].

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