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Thermodynamic Study of Solvent Extraction of Monovalent Metal Picrates with Benzo-18-crown-6 into Chloroform

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Abstract. Thermodynamic parameters (ΔH^0_{ex} and ΔS^0_{ex}) for the overall extractions of monovalent metal (Na, K, Rb, and Tl) picrates with benzo-18-crown-6 (B18C6), and those ($\Delta H^0_{D,L}$ and $\Delta S^0_{D,L}$) for the distribution of B18C6 were determined between chloroform and water. All the extracted B18C6 complexes were $1:1:1$ complexes (B18C6 : metal ion : picrate anion). The ΔH^0_{ex} and ΔS^0_{ex} values for all the metals are negative. Every extraction of the metal picrate with B18C6 is completely enthalpy driven. The $\Delta H^0_{D,L}$ and $\Delta S^0_{D,L}$ values of B18C6 are both positive, and the partition of B18C6 is entirely entropy driven. Enthalpy ($\Delta H^0_{ex,ip}$) and entropy changes ($\Delta S^0_{ex,ip}$) for ion-pair extractions of B18C6–metal ion complexes with picrate anions were calculated. All the $\Delta H^0_{ex,ip}$ and $\Delta S^0_{ex,ip}$ values are negative, and the ion-pair extractions are completely enthalpy driven.

Key words. Solvent extraction, thermodynamics, benzo-18-crown-6, monovalent metal picrates, chloroform.

1. Introduction

In our previous paper [1], the role of benzo-18-crown-6 (B18C6) in the metal ion-extraction process from water to chloroform was studied from the equilibrium standpoint; namely, the overall extraction equilibrium constant values were analyzed by constituent equilibria, e.g. the distribution constant of B18C6, the formation constant in water and the ion-pair extraction constant with a picrate anion of the B18C6–metal ion complex. The distribution of B18C6 governs the extractability of B18C6 for metal ions, and the stability in water and the ion-pair extractability of the B18C6 complex govern both the extractability and selectivity of B18C6 for metal ions. The enthalpy and entropy changes of complex formation of B18C6 with some metal ions in water have been determined [2]. Therefore, in the present study, in order to further investigate the role of B18C6 in the extraction process, the enthalpy and entropy changes for the overall extraction of metal picrates with B18C6 and for the distribution of B18C6 have been determined between chloroform and water. The distribution behavior of B18C6 and the extraction of metal picrates with B18C6 are discussed on molecular grounds from the thermodynamic point of view.

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2. Experimental

2.1. MATERIALS

Chloroform, picric acid, LiOH·H$_2$O, NaOH, KOH, RbOH, and TlNO$_3$ were analytical grade reagents. Chloroform was purified by distillation and washed three times with distilled water. Benzo-18-crown-6 was prepared according to the method of Pedersen [3]. The product was recrystallized four times from hexane and dried in a vacuum oven at 35°C. Its purity was checked by melting point (m.p. 44–45°C) and elemental analysis.

2.2. EXTRACTION OF METAL PICRATES WITH B18C6

The experimental procedures were almost the same as those described in previous papers [1, 4]. Extractions were performed at pH 11.2–12.0 and at 15, 20, 30, and 32 ± 0.2°C. For the TlNO$_3$ system, LiOH·H$_2$O was added to the aqueous phase to prevent the picric acid from distributing into the CHCl$_3$ phase. Under these experimental conditions scarcely any picrate was extracted into the CHCl$_3$ phase in the absence of TlNO$_3$. Concentrations of B18C6, metal salts, and picric acid were $(1.2-6.5) \times 10^{-4}$ M$(1$ M $= 1$ mol dm$^{-3})$, 1.4×10^{-2}–2.2×10^{-1} M, and $(1.3-6.1) \times 10^{-3}$ M, respectively.

2.3. DISTRIBUTION COEFFICIENT OF B18C6

The experimental procedures were almost the same as those described in our previous paper [1]. Experiments were conducted at 15, 20, 30, and 32 ± 0.2°C. The concentration range of B18C6 was from 2.7×10^{-2} M to 1.7×10^{-1} M. The distribution coefficient values of B18C6 are listed in Table I.

3. Results

When an equilibrium is reached between an aqueous phase of a monovalent metal ion (M$^+$) and a picrate ion (A$^-$), and a CHCl$_3$ phase of a crown ether (L), the

Table I. Summary of $K_{D,L}$ values of B18C6 between CHCl$_3$ and H$_2$O[a]

Temp./°C	$K_{D,L}$
15	333 ± 5
20	350 ± 5
25	371[b]
30	393 ± 6
32	408 ± 4

[a] Each $K_{D,L}$ value is the average of 11–13 measurements. The uncertainties are the standard deviations.
[b] Ref. [1].

equilibrium constants are defined as

$$K_{ex} = [MLA]_o/[M^+][L]_o[A^-] \tag{1}$$

$$K_{D,L} = [L]_o/[L] \tag{2}$$

$$K_{ML} = [ML^+]/[M^+][L] \tag{3}$$

$$K_{MLA} = [MLA]/[ML^+][A^-] \tag{4}$$

$$K_{D,MLA} = [MLA]_o/[MLA] \tag{5}$$

where the subscript 'o' and the lack of subscript denote the organic and the aqueous phase, respectively. The overall extraction equilibrium constant (K_{ex}) can be written as

$$K_{ex} = K_{D,L}^{-1} K_{ML} K_{MLA} K_{D,MLA}. \tag{6}$$

The distribution ratio of the metal is represented by

$$D = [MLA]_o/([M^+] + [ML^+] + [MLA]). \tag{7}$$

In the case when $[M^+] \gg [ML^+] + [MLA]$, Equation 7 is transformed into

$$D = K_{ex}[L]_o[A^-]. \tag{8}$$

Plots of $\log(D/[A^-])$ vs. $\log[L]_o$ give a straight line with a slope of 1 in every case. This indicates that the B18C6 forms a 1:1 complex with the M^+ ion.

From the mass balances, $[M^+]$, $[L]_o$, and $[A^-]$ are given by

$$[M^+] = ([M]_t - [MLA]_o)/(1 + K_{ML}K_{D,L}^{-1}[L]_o +$$
$$+ K_{ML}K_{D,L}^{-1}K_{MLA}[L]_o[A^-]) \tag{9}$$

$$[L]_o = ([L]_t - [MLA]_o)/(1 + K_{D,L}^{-1} + K_{ML}K_{D,L}^{-1}[M^+] +$$
$$+ K_{ML}K_{D,L}^{-1}K_{MLA}[M^+][A^-]) \tag{10}$$

$$[A^-] = ([HA]_t - [MLA]_o)/\{1 + (K_{HA} + K_{ex}(HA))[H^+] +$$
$$+ K_{ML}K_{D,L}^{-1}K_{MLA}[M^+][L]_o\} \tag{11}$$

where $K_{HA} = [HA]/[H^+][A^-]$, $K_{ex}(HA) = [HA]_o/[H^+][A^-]$, and the subscript 't' denotes the total concentration. For the K^+ and Tl^+ systems, it is assumed that the $K_{ML}K_{D,L}^{-1}K_{MLA}[L]_o[A^-]$ term of Equation 9, the $K_{ML}K_{D,L}^{-1}K_{MLA}[M^+][A^-]$ term of Equation 10, and the $(K_{HA} + K_{ex}(HA))[H^+]$ and $K_{ML}K_{D,L}^{-1}K_{MLA}[M^+][L]_o$ terms of Equation 11 are negligible compared with 1 under these experimental conditions [5]. For the Na^+ and Rb^+ systems it is assumed that the $K_{ML}K_{D,L}^{-1}[L]_o(1 + K_{MLA}[A^-])$ term of Equation 9, the $K_{ML}K_{D,L}^{-1}[M^+](1 + K_{MLA}[A^-])$ term of Equation 10, and the $(K_{HA} + K_{ex}(HA))[H^+]$ and $K_{ML}K_{D,L}^{-1}K_{MLA}[M^+][L]_o$ terms of Equation 11 are negligible compared with 1 under these experimental conditions [5]. Thus, the K_{ex} value of each system was determined by using the corresponding $[M^+]$, $[L]_o$, and $[A^-]$ values. Equilibrium constants are compiled in Table II.

From Figures 1 and 2, $R \ln K_{D,L}$ vs. T^{-1} and $R \ln K_{ex}$ vs. T^{-1} plots are found to be linear in every system. The enthalpy and entropy change for Equations 1 and

Table II. Thermodynamic parameters for extraction of monovalent metal picrates with B18C6 and 18C6 between $CHCl_3$ and water

	$\log K^0_{D,L}$ [a]	$\Delta H^0_{D,L}$ [b]	$T\Delta S^0_{D,L}$ [a,b]
B18C6	2.569 [c]	8.6_3	$23._3$
18C6 [d]	0.78_6	$17._5$	$22._0$

B18C6

	$\log K_{ex}$ [a,c]	ΔH^0_{ex} [b]	$T\Delta S^0_{ex}$ [a,b]	$\log K_{ML}$ [a,e]	ΔH^0_{ML} [b,f]	$T\Delta S^0_{ML}$ [a,b,f]	$\log K_{ex,ip}$ [a,c]	$\Delta H^0_{ex,ip}$ [b]	$T\Delta S^0_{ex,ip}$ [a,b]
Na^+	3.02	$-51._8$	$-34._9$	1.38	–	–	4.21	–	–
K^+	5.11	$-71._4$	$-41._9$	1.74	-18.1	-8.2	5.94	$-44._6$	$-10._4$
Rb^+	4.61	$-72._1$	$-45._8$	1.15	–	–	6.03	–	–
Tl^+	5.23	$-75._0$	$-45._1$	1.68	-9.7	-0.04	6.12	$-56._6$	$-21._7$

18C6

	$\log K_{ex}$ [a,c]	ΔH^0_{ex} [b]	$T\Delta S^0_{ex}$ [a,b]	$\log K_{ML}$ [a,e]	ΔH^0_{ML} [b,f]	$T\Delta S^0_{ML}$ [a,b,f]	$\log K_{ex,ip}$ [a,c]	$\Delta H^0_{ex,ip}$ [b]	$T\Delta S^0_{ex,ip}$ [a,b]
K^+	6.07[d]	$-76._4$ [d]	$-41._8$ [d]	2.03[g]	-25.01[g]	-13.22[g]	4.83[d]	$-33._9$ [d]	$-6._6$ [d]

[a] at 25°C. [b] $kJ\ mol^{-1}$. [c] Ref. [1]. [d] Ref. [8]. [e] Ref. [9]. [f] Ref. [2]. [g] Ref. [10].
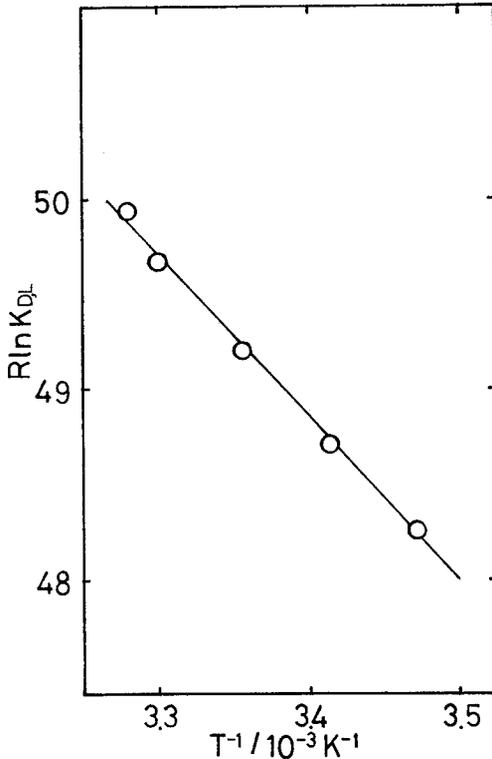
Fig. 1. $R \ln K_{D,L}$ vs. T^{-1} plots for B18C6 between $CHCl_3$ and water.

2 were calculated from these data. The thermodynamic parameters are summarized in Table II [7].

4. Discussion

4.1. DISTRIBUTION OF B18C6

It has been reported that contributions of a methylene group to ΔH^0 and ΔS^0 of ion-pair extraction of tetraalkylammonium picrates ($\Delta H^0_{ex,ip}(CH_2)$ and $\Delta S^0_{ex,ip}(CH_2)$) between $CHCl_3$ and water are 0.93 kJ mol^{-1} and 14 J K^{-1} mol^{-1}, respectively, and that contributions of an ether oxygen atom to $\Delta H^0_{D,L}(\Delta H^0_D(o))$ and $\Delta S^0_{D,L}(\Delta S^0_D(o))$ between $CHCl_3$ and H_2O are 0.9_6 kJ mol^{-1} and $-15._8$ J K^{-1} mol^{-1}, respectively [4]. By using these values, contributions of a benzo group to $\Delta H^0_{D,L}(\Delta H^0_D(C_6H_4))$ and $\Delta S^0_{D,L}(\Delta S^0_D(C_6H_4))$ between $CHCl_3$ and H_2O can be calculated from the $\Delta H^0_{D,L}$ and $\Delta S^0_{D,L}$ values of B18C6 if the additivity of the functional group contribution holds; namely, $\Delta H^0_D(C_6H_4) = \Delta H^0_{D,L} - \Delta H^0_{ex,ip}$ $(CH_2) \times 10 - \Delta H^0_D(o) \times 6$ and $\Delta S^0_D(C_6H_4) = \Delta S^0_{D,L} - \Delta S^0_{ex,ip}(CH_2) \times 10 - \Delta S^0_D$ (o) $\times 6$. The $\Delta H^0_D(C_6H_4)$ and $\Delta S^0_D(C_6H_4)$ values are -6.4 kJ mol^{-1} and 33 J K^{-1}, respectively. The vaporization enthalpy change of a hydrocarbon increases with an increase in the number of carbon atoms. The large positive vaporization enthalpy
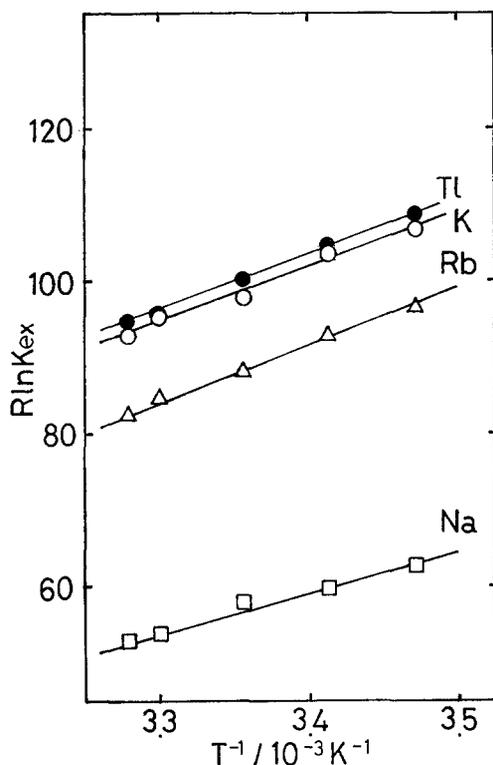
Fig. 2. $R \ln K_{ex}$ vs. T^{-1} plots for B18C6–monovalent metal picrate complexes between $CHCl_3$ and water.

change of a hydrocarbon having a large number of carbon atoms cancels the negative hydration enthalpy change of the hydrocarbon, resulting in the increasing dissolution enthalpy change of the hydrocarbon with an increase in the number of carbon atoms. This is responsible for the negative $\Delta H_D^0(C_6H_4)$ value. For the distribution of benzene and its derivatives from water to nonpolar organic solvents, negative enthalpy changes are also found [11]. The $\Delta S_D^0(C_6H_4)$ value is positive and about 2.4 times as large as the $\Delta S_{ex,ip}^0(CH_2)$ value. This is attributed to stronger hydrophobic hydration of the benzo group compared with the methylene group.

   Partition of B18C6 from water to chloroform is entirely entropy driven. $T\Delta S_{D,L}^0$ values of B18C6 and 18C6 at 25°C are nearly equal. The much higher lipophilicity of B18C6 compared with 18C6 is completely due to the large negative $\Delta H_D^0(C_6H_4)$ value. The effect of hydrophobic hydration of the benzo and methylene groups overcomes that of interaction between ether oxygen atoms and water, resulting in positive $\Delta S_{D,L}^0$ values of B18C6.

4.2. EXTRACTION OF METAL PICRATES WITH B18C6

The ΔH_{ex}^0 and ΔS_{ex}^0 values of B18C6 for all the metals are negative. The ΔH_{ex}^0 value is much smaller than the corresponding $T\Delta S_{ex}^0$ value. Every extraction of the metal

picrate with B18C6 is entirely enthalpy driven. The same is true for the case of 18C6 [8]. The least favorable ΔH_{ex}^0 value of Na$^+$ is balanced by the most favorable $T\Delta S_{ex}^0$ value, leading to the smallest log K_{ex} value; namely, the lowest extractability depends completely on the most unfavorable ΔH_{ex}^0 value. The highest extractability of Tl$^+$ depends completely on the most favorable ΔH_{ex}^0 value. For the B18C6–K$^+$ and –Tl$^+$ systems, the $\Delta H_{ex,ip}^0$ value plays a major role in determining the magnitude of ΔH_{ex}^0, but the $\Delta S_{D,L}^0$ value plays a major role in determining the magnitude of ΔS_{ex}^0.

In the cases of B18C6–K$^+$ and –Tl$^+$ complexes, the $\Delta H_{ex,ip}^0$ and $\Delta S_{ex,ip}^0$ values are negative, and the $\Delta H_{ex,ip}^0$ value is much smaller than the corresponding $T\Delta S_{ex,ip}^0$ value. Thus, ion-pair extraction of B18C6–K$^+$ and –Tl$^+$ complexes with picrate anion is entirely enthalpy driven. The $\Delta H_{ex,ip}^0$ and $\Delta S_{ex,ip}^0$ values of K$^+$ are larger than those of Tl$^+$. This indicates that B18C6 does not effectively shield the cation in the cavity from picrate anions and solvents. The higher log $K_{ex,ip}$ value of Tl$^+$ compared with K$^+$ is perfectly attributable to the more favorable $\Delta H_{ex,ip}^0$ value. The larger log $K_{ex,ip}$ value of the B18C6–K$^+$ complex is due to the more favorable $\Delta H_{ex,ip}^0$ value compared with the 18C6–K$^+$ complex. The enthalpy and entropy change of partition of neutral crown ethers between chloroform or benzene and water are both positive (Table II) [4, 8, 12, 13]. It follows from this that the enthalpy and entropy changes of partition of the neutral M(B18C6)A complex (M = K or Tl) between chloroform and water are also positive. Thus, from the fact that the $\Delta H_{ex,ip}^0$ and $\Delta S_{ex,ip}^0$ values of the M(B18C6)$^+$ complex (M = K or Tl) are negative, the enthalpy and entropy change of ion-pair formation of the M(B18C6)A complex in water may be both negative. The same also holds for the case of the K(18C6)A complex.

References and Notes

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