

Solvent Extraction of Univalent and Bivalent Metal Picrates with 1,2-Bis[2-(2-methoxyethoxy)ethoxy]benzene (Noncyclic Crown Ether) into CHCl_3

YASUYUKI TAKEDA*, WATARU OHSONE, and NAOAKI FUKADA
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho, Chiba 260, Japan

(Received: 13 September 1989; in final form: 15 February 1990)

Abstract. The overall extraction equilibrium constants, K_{ex} , of 1:1: m complexes of 1,2-bis[2-(2-methoxyethoxy)ethoxy]benzene ($\text{AC} \cdot \text{B18C6}$) with uni- and bivalent metal picrates, MA_m , were determined at 25°C between CHCl_3 and water, and thereby the ion-pair complex-formation constants, $K_{\text{MLA},o}$, of $\text{AC} \cdot \text{B18C6}$ with the univalent metal picrates in CHCl_3 were calculated. The $\text{AC} \cdot \text{B18C6}$ is an open-chain analog of benzo-18-crown-6 (B18C6). The equilibrium constants of $\text{AC} \cdot \text{B18C6}$ were compared with those of B18C6 . K_{ex} sequences of $\text{AC} \cdot \text{B18C6}$ for uni- and bivalent metals are $\text{TI}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+$ and $\text{Pb}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+}$, respectively. The same extraction-selectivity was observed for B18C6 , but the extractability of $\text{AC} \cdot \text{B18C6}$ for the same cation is much lower than that of B18C6 ; the extraction selectivity of $\text{AC} \cdot \text{B18C6}$ for alkali metals is lower than that of B18C6 . The $K_{\text{MLA},o}$ sequence of $\text{AC} \cdot \text{B18C6}$ is $\text{K}^+ > \text{Rb}^+ > \text{TI}^+ > \text{Cs}^+ \approx \text{Na}^+$, which is consistent with that of B18C6 . But $K_{\text{MLA},o}$ of $\text{AC} \cdot \text{B18C6}$ is much smaller than the corresponding $K_{\text{MLA},o}$ of B18C6 ; the selectivity of $\text{AC} \cdot \text{B18C6}$ among alkali metal picrates in CHCl_3 is lower than that of B18C6 . This reflects the difference in the structures between $\text{AC} \cdot \text{B18C6}$ (acyclic and flexible) and B18C6 (cyclic and rigid).

Key words. Noncyclic crown ether, metal picrates, solvent extraction.

1. Introduction

1,2-Bis[2-(2-methoxyethoxy)ethoxy]benzene ($\text{AC} \cdot \text{B18C6}$) is a noncyclic counterpart of benzo-18-crown-6 (B18C6). Their structures are shown in Figure 1.

In a previous paper [1], in order to study the macrocyclic effect (enhanced stabilities of complexes of cyclic crown compounds with cationic species), the formation constants and limiting ionic molar conductivities of 1:1 $\text{AC} \cdot \text{B18C6}$ -

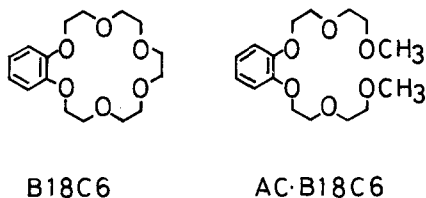


Figure 1.

* Author for correspondence.

alkali metal ion complexes in nonaqueous solvents were determined at 25°C and were compared with those of B18C6 complexes. The selectivity order of AC · B18C6 for the alkali metal ions, except for Na⁺, is consistent entirely with that of B18C6 (K⁺ > Rb⁺ > Cs⁺). But the selectivity of AC · B18C6 for the alkali metal ions is lower than that of B18C6, and the AC · B18C6-alkali metal ion complex is less stable than the corresponding B18C6 complex. These findings reflect the difference in the structures between flexible AC · B18C6 and rigid B18C6. It was shown from the data on mobilities of the AC · B18C6 complexes that the alkali metal ion in the AC · B18C6 complex is coordinated by the two arms and the alkali metal ion in the AC · B18C6 complex is more effectively screened than that in the B18C6 complex.

In this study, the overall extraction equilibrium constants of uni- and bivalent metal picrates with AC · B18C6 between CHCl₃ and water were determined at 25°C and thereby the ion-pair complex-formation constants of AC · B18C6 with the metal picrates in CHCl₃ were calculated. The equilibrium constants of AC · B18C6 were compared with those of B18C6 [2]. The macrocyclic effect on the metal ion-extraction process and on the ion-pair complex-formation reaction in CHCl₃ was discussed.

2. Experimental

2.1. MATERIALS

The preparation of AC · B18C6 was described in the previous paper [1]. CHCl₃, picric acid, LiOH, NaOH, KOH, TlNO₃, Ca(NO₃)₂, Sr(NO₃)₂, Ba(NO₃)₂, and Pb(NO₃)₂ were analytical-grade reagents. Rubidium and caesium hydroxides were reagent-grade. CHCl₃ was washed four times with distilled water. The purities of all the metal nitrates were determined by EDTA titration. The concentrations of solutions of the hydroxides and picric acid were determined by neutralization titration.

2.2. EXTRACTION OF METAL PICRATES WITH AC · B18C6

The experimental procedures were similar to those previously described [3]. Extractions were conducted at 25 ± 0.2°C. Concentrations of AC · B18C6, metal salts, and picric acid were 5.2 × 10⁻³–7.2 × 10⁻²M (1M = 1 mol dm⁻³), 9.4 × 10⁻³–2.2 × 10⁻¹M, and 1.2 × 10⁻³–1.4 × 10⁻²M, respectively. The extractions of alkali metal ions were performed at pH 10.5–11.1 and those of the other metal ions at pH 2.2–3.0. The concentrations of alkali metals extracted into CHCl₃ were determined by a UV-spectrophotometer, and those of the other metals by an atomic absorption spectrophotometer. No Ca²⁺ was extracted with AC · B18C6 into CHCl₃.

2.3. THE DISTRIBUTION COEFFICIENT OF AC · B18C6

A 36 mL CHCl₃ solution of AC · B18C6 (2.3 × 10⁻²–1.0 × 10⁻¹M) and an equal volume of distilled water in a 100 mL separatory funnel were agitated in a

thermostated water bath at $25 \pm 0.2^\circ\text{C}$ for 2 h and centrifuged. A 30 mL portion of the aqueous phase and an equal volume of CHCl_3 were placed in a 100 mL separatory funnel, shaken, and centrifuged. A 24 mL portion of the CHCl_3 phase was transferred to a beaker and left until evaporation was complete. The residue in the beaker was dissolved in 4 mL CHCl_3 and the concentration of the $\text{AC} \cdot \text{B18C6}$ was determined spectrophotometrically at 276 nm. The logarithm of the distribution coefficient value of $\text{AC} \cdot \text{B18C6}$ is 3.40 ± 0.04 , which is the average of 25 measurements.

3. Results

When an equilibrium occurs between an aqueous phase of a metal ion, M^{m+} , and a picrate ion, A^- , and a CHCl_3 phase of $\text{AC} \cdot \text{B18C6}$, L, the equilibrium constants are defined as

$$K_{\text{ex}} = [\text{MLA}_m]_{\text{o}} / [\text{M}^{m+}][\text{L}]_{\text{o}}[\text{A}^-]^m, \quad (1)$$

$$K_{\text{D,L}} = [\text{L}]_{\text{o}} / [\text{L}], \quad (2)$$

$$K_{\text{ex}}(\text{HA}) = [\text{HA}]_{\text{o}} / [\text{H}^+][\text{A}^-], \quad (3)$$

$$K_{\text{ML}} = [\text{ML}^{m+}] / [\text{M}^{m+}][\text{L}], \quad (4)$$

$$K_{\text{ex,ip}} = [\text{MLA}_m]_{\text{o}} / [\text{ML}^{m+}][\text{A}^-]^m, \quad (5)$$

where the subscript 'o' and the lack of a subscript denote the organic and the aqueous phase, respectively. K_{ex} can be written as

$$K_{\text{ex}} = K_{\text{ML}} K_{\text{ex,ip}} K_{\text{D,L}}^{-1}. \quad (6)$$

The distribution ratio of the metal is represented by

$$D = [\text{MLA}_m]_{\text{o}} / ([\text{M}^{m+}] + [\text{ML}^{m+}]). \quad (7)$$

In the case of $[\text{M}^{m+}] \gg [\text{ML}^{m+}]$, Eq. 7 is transformed into

$$D = K_{\text{ex}}[\text{L}]_{\text{o}}[\text{A}^-]^m. \quad (8)$$

For every metal ion system, the $\log(D/[\text{A}^-]^m)$ vs. $\log[\text{L}]_{\text{o}}$ plot shows a straight line with a slope of 1. This indicates that $\text{AC} \cdot \text{B18C6}$ forms a 1:1 complex with the metal ion. The values of $[\text{L}]_{\text{o}}$ and $[\text{A}^-]$ of Eq. 8 were calculated from Eqs. 9 and 10, respectively.

$$[\text{L}]_{\text{o}} = [\text{L}]_{\text{t}} - [\text{MLA}_m]_{\text{o}}, \quad (9)$$

$$[\text{A}^-] = ([\text{HA}]_{\text{t}} - m[\text{MLA}_m]_{\text{o}}) / \{1 + (K_{\text{HA}} + K_{\text{ex}}(\text{HA}))[\text{H}^+]\}, \quad (10)$$

where the subscript 't' denotes the total concentration. The $K_{\text{ex}}(\text{HA})$ value was spectrophotometrically determined to be 87.1 ± 0.4 using the association constant of picric acid ($K_{\text{HA}} = 1.9_5$ [4]). Equilibrium constants are summarized in Table I, together with those from the literature.

Table I. Equilibrium constants at 25°C

Crown ether	$\log K_{D,L}$	Cation	Ionic radius (\AA) ^a	$\log K_{ex}$	$\log K_{MLA_m,o}$ ^b
AC · B18C6	3.40 ± 0.04	Li ⁺	0.74	-0.43 ± 0.01	—
		Na ⁺	1.02	0.55 ± 0.01	3.47
		K ⁺	1.38	1.65 ± 0.01	4.22
		Rb ⁺	1.49	1.60 ± 0.01	4.04
		Cs ⁺	1.70	1.30 ± 0.01	3.48
		Tl ⁺	1.50	2.50 ± 0.02	3.83
		Sr ²⁺	1.13	2.53 ± 0.01	—
		Ba ²⁺	1.36	3.96 ± 0.02	—
		Pb ²⁺	1.19	4.86 ± 0.03	—
		B18C6	2.569 [2]	Na ⁺	
K ⁺				5.11 [2]	7.68
Rb ⁺				4.61 [2]	7.05
Cs ⁺				3.84 [2]	6.02
Tl ⁺				5.23 [2]	6.56
Sr ²⁺				6.62 [2]	—
Pb ²⁺				9.18 [2]	—

^aR. D. Shannon and C. T. Prewitt: *Acta Crystallogr.* **B25**, 925 (1969).

^b $K_{MLA_m,o} = K_{ex}/K_{ex}(MA_m)$.

4. Discussion

4.1. THE DISTRIBUTION COEFFICIENT OF AC · B18C6

Contributions of methyl (π_{CH_3}) and methylene (π_{CH_2}) groups to extraction constants of ion pairs and those of an ether oxygen atom (π_o) and a benzo group ($\pi_{C_6H_4}$) to $\log K_{D,L}$ at 25°C for the $CHCl_3$ /water system are 0.82 [5], 0.47 [5], -0.79 [6], and 2.5₄ [2], respectively. From these empirical parameters, the $\log K_{D,L}$ value of AC · B18C6 at 25°C between $CHCl_3$ and water can be estimated to be 3.2₀ ($2.5_4 + 0.47 \times 8 + 0.82 \times 2 + (-0.79) \times 6 = 3.2_0$). This is nearly equal to the experimental $\log K_{D,L}$ value of AC · B18C6 (3.40). The $K_{D,L}$ value is one of the most important fundamental-equilibria which govern the extractability of a crown ether for a cation (Eq. 6). Therefore, the $\log K_{D,L}$ value is required in order to understand the mechanism of extraction of metal salts with a crown ether on molecular grounds. Unknown $\log K_{D,L}$ values at 25°C of crown ethers between $CHCl_3$ and water can be estimated by use of the empirical parameters.

4.2. EXTRACTION OF METAL IONS WITH AC · B18C6

The $\log K_{ex}$ value of AC · B18C6 for univalent metal ions decreases in the order $Tl^+ > K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$, which is completely consistent with the case of B18C6 (Table I); namely, extraction-selectivity tendencies of AC · B18C6 and B18C6 for the univalent metal ions are identical. However, the difference in $\log K_{ex}$ values of AC · B18C6 between neighboring alkali metal ions in the periodic table is

smaller than that of B18C6. The difference between the largest and the smallest $\log K_{\text{ex}}$ values of AC·B18C6 among alkali metal ions is smaller than that of B18C6. This shows that the extraction selectivity of AC·B18C6 for alkali metal ions is lower than that of B18C6. The extraction selectivity for Tl^+ among K^+ and Rb^+ is higher for AC·B18C6 than for B18C6, whereas that among Na^+ and Cs^+ is the reverse. A possible explanation for the smallest $\log K_{\text{ex}}$ value of the AC·B18C6– Li^+ complex among the univalent metal ions is as follows. Since Li^+ undergoes the strongest hydration and the AC·B18C6– Li^+ complex may undergo the greatest entropy-destabilization on account of the smallest size of Li^+ , the stability of the AC·B18C6– Li^+ complex in water can be expected to be the lowest among the univalent metal ions. Since the AC·B18C6– Li^+ complex may be hydrated most strongly, the $\log K_{\text{ex,ip}}$ value of the AC·B18C6– Li^+ complex can be expected to be the smallest among the univalent metal ions. Consequently, the smallest $\log K_{\text{ex}}$ value of the AC·B18C6– Li^+ complex is attributed to the smallest $\log K_{\text{ML}}$ and $\log K_{\text{ex,ip}}$ values.

The $\log K_{\text{ex}}$ value sequence of bivalent metal ions with AC·B18C6 is $\text{Pb}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+}$ (Table I). For alkaline earth metal ions, the larger the size of the metal ion, the more extractable with AC·B18C6 it is. Although Pb^{2+} and Sr^{2+} are nearly equal in size, AC·B18C6 shows a higher extraction-selectivity for Pb^{2+} than for Sr^{2+} . The same tendency as that described above is observed for B18C6.

The extractability of AC·B18C6 for the same metal ion is much lower than that of B18C6. The $\log K_{\text{D,L}}$ value of AC·B18C6 that of B18C6 and $\log(K_{\text{ML}}K_{\text{ex,ip}})$ of AC·B18C6 for the same metal ion is smaller than that of B18C6, resulting in the much lower extractability of AC·B18C6 compared with B18C6.

4.3. STABILITY OF AC·B18C6 COMPLEXES WITH METAL PICRATES IN CHCl_3

The ion-pair extraction equilibrium constant of a metal picrate is defined as $K_{\text{ex,ip}}(\text{MA}_m) = [\text{MA}_m]_0 / [\text{M}^{m+}][\text{A}^-]^m$. $\log K_{\text{ex,ip}}(\text{MA}_m)$ values of Na^+ , K^+ , Rb^+ , Cs^+ , and Tl^+ between CHCl_3 and H_2O at 25°C are -2.92 [7], -2.57 [7], -2.44 [7], -2.18 [7], and -1.33 [8], respectively. $K_{\text{MLA}_m,0}$ refers to the formation constant of a $1:1:m$ complex of AC·B18C6 or B18C6 with the metal picrate in a CHCl_3 solution. The $\log K_{\text{MLA}_m,0}$ values at 25°C are listed in Table I. The $\log K_{\text{MLA}_m,0}$ value of an AC·B18C6–alkali metal picrate complex in CHCl_3 is larger by 0.4–2.0 than the $\log K_{\text{ML}}$ value of the corresponding AC·B18C6–alkali metal ion complex in acetonitrile, propylene carbonate, or methanol [1], where $K_{\text{ML}} = [\text{ML}^+]/[\text{M}^+][\text{L}]$. A similar relation is found to hold between $\log K_{\text{MLA}_m,0}$ and $\log K_{\text{ML}}$ of the B18C6–alkali metal system [9]. $K_{\text{MLA}_m,0}$ is the ion-pair complex formation constant of AC·B18C6 or B18C6 with the metal picrate in CHCl_3 . Since the reaction is an ion-pair complex formation reaction, the picrate anion, as well as the solvent CHCl_3 , has a great effect on the stability of the MLA_m complex compared with the reaction in the polar solvents between a free metal ion and AC·B18C6 or B18C6. The interaction between M^+ and L may be stronger than that between MA and L; the interaction between ML^+ and the polar solvents may be stronger than that between MLA and CHCl_3 , where

$L = AC \cdot B18C6$ or $B18C6$. The solvation of the charged species M^+ in the polar solvents may be stronger than that of the neutral species MA in $CHCl_3$. It thus appears that the larger $\log K_{MLA,o}$ value compared to the corresponding $\log K_{ML}$ value is attributed to the stronger solvation of M^+ in the polar solvents than that of MA in $CHCl_3$.

The $\log K_{MLA,o}$ sequences of $AC \cdot B18C6$ and $B18C6$ with the univalent metal ions are $K^+ > Rb^+ > Tl^+ > Cs^+ \approx Na^+$ and $K^+ > Rb^+ > Tl^+ > Cs^+ > Na^+$, respectively. The selectivity orders of $AC \cdot B18C6$ and $B18C6$ for the univalent metal picrates in $CHCl_3$ are the same. The difference in $\log K_{MLA,o}$ values of $AC \cdot B18C6$ between neighboring alkali metals in the periodic table is smaller than that of $B18C6$ (Table I). The difference between the largest and the smallest $\log K_{MLA,o}$ values of $AC \cdot B18C6$ among alkali metals is smaller than that of $B18C6$. The selectivity of $AC \cdot B18C6$ among alkali metal picrates in $CHCl_3$ is lower than that of $B18C6$.

The $AC \cdot B18C6$ -univalent metal picrate complex is much less stable in $CHCl_3$ than the corresponding $B18C6$ complex. The difference in $\log K_{MLA,o}$ values of an alkali metal between $AC \cdot B18C6$ and $B18C6$ increases in the order $Na^+ < Cs^+ < Rb^+ < K^+$. This indicates that cyclization of $AC \cdot B18C6$ enhances the selectivity among the alkali metals. From the above discussion, the selectivity of $AC \cdot B18C6$ for the alkali metal ions in water must be lower than that of $B18C6$, and the $AC \cdot B18C6$ -alkali metal ion complex must be less stable in water than the corresponding $B18C6$ complex, these being factors which determine the lower extraction selectivity and the lower extractability of $AC \cdot B18C6$ for the alkali metal ions than those of $B18C6$, respectively.

When a complexation reaction occurs in $CHCl_3$ between $AC \cdot B18C6$ and an alkali metal picrate, the alkali metal must be accommodated in the pseudocavity formed by two flexible arms at the *ortho* position of $AC \cdot B18C6$. Thus, the two flexible arms adopt the most favorable conformation according to the size of the alkali metal ion at the complexation reaction. Thus $B18C6$ hardly alters its conformation on complexation with an alkali metal picrate in $CHCl_3$ compared with $AC \cdot B18C6$. This is responsible for the lower selectivity of $AC \cdot B18C6$ for the alkali metals in $CHCl_3$ than that of $B18C6$. The flexible structure of $AC \cdot B18C6$ causes entropy-destabilization of the $AC \cdot B18C6$ -alkali metal picrate complex in $CHCl_3$, resulting in the lower stability of the $AC \cdot B18C6$ complex compared with the corresponding $B18C6$ complex.

Although the sizes of Tl^+ and Rb^+ are almost the same, the $\log K_{MLA,o}$ values of the thallium picrate- $AC \cdot B18C6$ and $-B18C6$ complexes are smaller than those of the rubidium picrate- $AC \cdot B18C6$ and $-B18C6$ complexes, respectively (Table I). The difference in $\log K_{MLA,o}$ values of $AC \cdot B18C6$ between Rb and Tl is smaller than that of $B18C6$. This may be attributed to the difference in the structures between $AC \cdot B18C6$ (acyclic and flexible) and $B18C6$ (cyclic and rigid).

References

1. Y. Takeda, S. Sakamoto, N. Ohashi, and N. Fukada: *Bull. Chem. Soc. Jpn.* **61**, 2707 (1988).
2. Y. Takeda and M. Nishida: *Bull. Chem. Soc. Jpn.* **62**, 1468 (1989).
3. Y. Takeda: *Bull. Chem. Soc. Jpn.* **52**, 2501 (1979).

4. *Dissociation Constants of Organic Acids in Aqueous Solution*, G. Kortün, W. Vogel, and K. Andrussov (Eds.) Butterworths, London (1961).
5. H. Matsunaga and T. Yotsuyanagi: *Nippon Kagaku Kaishi* (1982) 785.
6. Y. Takeda and A. Tanaka: *Bull. Chem. Soc. Jpn.* **59**, 733 (1986).
7. K. Kimura, T. Maeda, and T. Shono: *Talanta* **26**, 945 (1979).
8. T. Maeda, K. Kimura, and T. Shono: *Fresenius Z. Anal. Chem.* **298**, 363 (1979).
9. Y. Takeda, Y. Ohyagi, and S. Akabori: *Bull. Chem. Soc. Jpn.* **57**, 3381 (1984).