March, 1986] Bull. Chem. Soc. Jpn., 59, 733—735 (1986) 733

Thermodynamic Study on Solvent Extraction of Alkali Metal Picrates with 18-Crown-6 into $CHCl_3$

Yasuyuki TAKEDA* and Akio TANAKA
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-chō, Chiba 260
(Received October 11, 1985)

Enthalpy (ΔHex) and entropy changes (ΔSex) for overall extractions of alkali metal (Na, K, Rb, and Cs) picrates with 18-crown-6 (18C6), and those ($\Delta H_{D,L}$ and $\Delta S_{D,L}$) for distribution of 18C6 itself were determined between $CHCl_3$ and water, all the extracted complexes being 1:1:1 complexes. The ΔHex and ΔSex values of 18C6 for all the alkali metals are negative. The $\Delta H_{D,L}$ and $\Delta S_{D,L}$ values of 18C6 are both positive. Enthalpy (ΔHex′) and entropy changes (ΔSex′) for ion-pair extractions of 18C6-alkali metal ion complexes with picrate anions were calculated. All the ΔHex′ and ΔSex′ values are negative except for ΔSex′ value of Na (positive). The ion-pair extractions were discussed from the thermodynamic point of view.

In order to evaluate complexing power and selectivity of newly-synthesized crown compounds for metal ions, solvent extraction has been widely used. Numerous data have been reported for their extraction ability and selectivity toward metal ions. However, only a few thermodynamic parameters regarding solvent extraction with crown compounds have been presented.[1] Thermodynamic quantities provide very valuable information on extraction mechanisms on molecular grounds. Further investigation of extraction processes from the thermodynamic point of view is important for understanding in detail solute-solvent interactions of crown compounds and their complexes and for designing crown compounds with high extractability and selectivity.

In the present study, enthalpy and entropy changes for the overall extraction of alkali metal picrates with 18-crown-6 (18C6), and those for distribution of 18C6 have been determined between $CHCl_3$ and water. Extraction processes of alkali metal picrates with 18C6 were discussed from the standpoint of thermodynamics.

Experimental

18-Crown-6 (Nisso Co., Ltd.) was recrystallized from acetonitrile and, prior to use, dried at 80 °C in a vacuum. Chloroform, picric acid, NaOH, and KOH were analytical grade reagents. Rubidium and caesium hydroxides were reagent-grade. Chloroform was washed three times with distilled water. The other reagents were used without further purification.

The experimental procedures were almost the same as those described in previous papers.[2,3] Extractions were conducted at 15, 20, 25, 30, and 32±0.3 °C. Concentrations of 18C6, alkali metal hydroxides, and picric acid were 9.5×10^{-6}—6.3×10^{-3} M (1 M=1 mol dm^{-3}), 4.2×10^{-3}—1.8×10^{-2} M, and 2.1×10^{-4}—4.0×10^{-4} M, respectively. Extractions were carried out at pH 10.0—11.3.

The Distribution Coefficient of 18C6. Experimental procedures were similar to those in the previous paper.[2] The concentration range of 18C6 was from 2.0×10^{-3} M to 7.5×10^{-2} M. Experiments were carried out at 15, 20, 25, 30, and 32±0.3 °C. Each distribution coefficient value of 18C6 is the average of about ten measurements.

Results

In an equilibrium between a chloroform solution of a crown ether (L) and an aqueous solution of an alkali metal ion (M^+) and a picrate ion (A^-), the equilibrium constants are defined as

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

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

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

$$K\mathrm{ex}' = [\mathrm{MLA}]_o/[\mathrm{ML}^+][\mathrm{A}^-], \tag{4}$$

where the subscript "o" and the lack of subscript denote the organic and aqueous phases, respectively. The overall extraction equilibrium constant (Kex) can be written as

$$K\mathrm{ex} = K_{ML}K\mathrm{ex}'K_{D,L}^{-1}. \tag{5}$$

The distribution ratio of the alkali metal is represented by

$$D = [\mathrm{MLA}]_o/[\mathrm{M}^+]. \tag{6}$$

Combination of Eqs. 1 and 6 leads to

$$D = K\mathrm{ex}[\mathrm{L}]_o[\mathrm{A}^-]. \tag{7}$$

A plot of log (D/[A^-]) against log $[L]_o$ shows a straight line with a slope of 1 in every case, indicating that Kex can be described by Eq. 1. The values of $[L]_o$ and [A^-] in Eq. 7 were calculated by

Table 1. Summary of Extraction Equilibrium Constants for 18C6 and Its Complexes with Alkali Metal Picrates between $CHCl_3$ and H_2O

Temp/°C	$K_{D,L}$	log Kex			
		Na	K	Rb	Cs
15	4.7_7	3.69	6.53	6.12	5.10
20	5.4_4	3.58	6.28	5.87	4.85
25	6.1_1	3.46	6.06	5.64	4.61
30	6.8_5	3.30	5.84	5.40	4.40
32	7.1_9	3.23	5.75	5.33	4.32

Table 2. Extraction Equilibrium Constants for 18C6 and Its Complexes with Alkali Metal Picrates at 25 °C

$\log K_{D,L}$		$CHCl_3$ 0.78_6		C_6H_6[2] -1.19_8		CH_2Cl_2[4] 1.0	
	$\log K_{ML}$	$\log K$ex	$\log K$ex′	$\log K$ex	$\log K$ex′	$\log K$ex	$\log K$ex′
Na	0.80[5]	3.47	3.46	3.39	1.39	3.89	4.09
K	2.03[5,6]	6.07	4.83	5.97	2.74	6.20	5.17
Rb	1.56[5]	5.65	4.88	5.43	2.67	5.96	5.40
Cs	0.99[5]	4.62	4.42	4.38	2.19	5.17	5.18

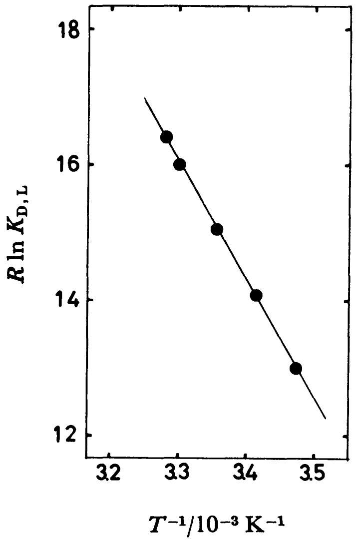

Fig. 1. $R \ln K_{D,L}$ vs. T^{-1} plots for 18C6 between $CHCl_3$ and water.

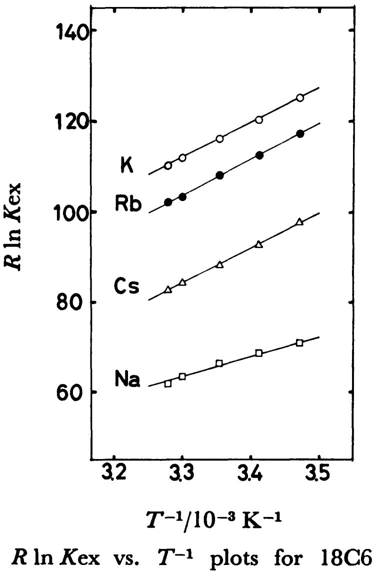

Fig. 2. $R \ln K$ex vs. T^{-1} plots for 18C6-alkali metal picrate complexes between $CHCl_3$ and water.

$$[L]_o = ([L]_t - [MLA]_o)/(1 + K_{D,L}^{-1}), \quad (8)$$

$$[A^-] = [HA]_t - [MLA]_o, \quad (9)$$

where the subscript "t" refers to the total concentration. Equilibrium constants are summarized in Tables 1 and 2.

Table 3. Thermodynamic Quantities for Extraction of 18C6 and Its Complexes with Alkali Metal Picrates

$\Delta H_{D,L}$/kJ mol^{-1} = $17._5$		$T\Delta S_{D,L}$/kJ mol^{-1} = $22._0$ (at 25 °C)	
		ΔH/kJ mol^{-1} [a]	
	ΔHex	ΔH_{ML}	ΔHex′
Na	$-45._7$	−9.41[5]	$-18._8$
K	$-76._4$	−25.01[6]	$-33._9$
Rb	$-79._1$	−16.0[5]	$-45._6$
Cs	$-76._5$	−15.9[5]	$-43._1$
		$T\Delta S$/kJ mol^{-1} (at 25 °C)[b]	
	$T\Delta S$ex	$T\Delta S_{ML}$	$T\Delta S$ex′
Na	$-26._0$	−4.6[5]	0.6
K	$-41._8$	−13.22[6]	$-6._6$
Rb	$-46._9$	−7.1[5]	$-17._8$
Cs	$-50._1$	−10[5]	$-18._1$

a) ΔHex $= -\Delta H_{D,L} + \Delta H_{ML} + \Delta H$ex′, b) ΔSex $= -\Delta S_{D,L} + \Delta S_{ML} + \Delta S$ex′, where subscripts "ex, D,L, ML, and ex′" refer to reactions represented by Eqs. 1—4, respectively.

From Figs. 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. Enthalpy change (ΔH) and entropy change (ΔS) for Eqs. 1 and 2 were calculated from these data. The thermodynamic parameters are listed in Table 3.

Discussion

Values of $\log K_{D,L}$ at 25 °C of 15-crown-5 (15C5) and benzo-15-crown-5 (B15C5) for $CHCl_3$/water system are 0.91[7] and 2.4[8a], respectively. The contribution of an ether oxygen atom to $\log K_{D,L}$ (π_O) at 25 °C for $CHCl_3$/water system can be calculated from $\log K_{D,L}$ values of 15C5 and 18C6 by using the contribution of a methylene group to extraction constants of ion-pairs (π_{CH_2}), π_{CH_2} being 0.47.[9] Values of π_O are −0.76 for 15C5 and −0.81 for 18C6 (15C5: (0.91−0.47×10)÷5, 18C6: (0.786−0.47×12)÷6). The values are nearly identical. The π_O value is −0.79 on the average. The contribution of a benzo group to $\log K_{D,L}$ ($\pi_{C_6H_4}$) can also be calculated from $\log K_{D,L}$ values of B15C5 and dibenzo-18-crown-6 (DB18C6) ($\log K_{D,L}$=3.9[8b] at 25 °C) by means of the values of π_{CH_2} and π_O. Values of $\pi_{C_6H_4}$ are 2.5_9 for B15C5 and 2.4_4 for DB18C6 (B15C5: 2.4−{0.47×8+(−0.79×5)}, DB18C6: [3.9−{0.47×8+(−0.79×6)}]÷2). They are nearly equal. The $\pi_{C_6H_4}$ value is 2.5_1 on the average. From these empirical parameters, log $K_{D,L}$ values at 25 °C between $CHCl_3$ and H_2O for several crown ethers can be estimated.

In the case of 18C6, the orders of log *K*ex and log *K*ex′ for $CHCl_3$ system and that of log K_{ML} are K>Rb>Cs>Na, Rb≥K>Cs>Na, and K>Rb>Cs>Na, respectively (Table 2). The extraction selectivity of 18C6 for alkali metal ions shows the size-fit correlation and is completely consistent with the selectivity in water, whereas it is not always in agreement with the ion-pair-extraction selectivity.

For 18C6, log *K*ex′ value sequences of a given alkali metal are CH_2Cl_2>$CHCl_3$>C_6H_6 (Table 2). This indicates that the extractability of the ion-pair, MLA, decreases with a decrease in dielectric constant (CH_2Cl_2 8.93,[10] $CHCl_3$ 4.9,[11] C_6H_6 2.3[11] at 25 °C).

It is interesting to compare the ion-pair extractability of K(18C6)A into $CHCl_3$ with that of tetrabutylammonium picrate (Bu_4NA). The log *K*ex′ value of K(18C6)A at 25 °C is about one order of magnitude smaller than the ion-pair extraction constant ($K_{ex,ip}=[Bu_4NA]_o/[Bu_4N^+][A^-]=5.75$[9] at 25 °C) of Bu_4NA, although the size of K(18C6)A is nearly identical with that of Bu_4NA.[12] From shapes and sizes of K(18C6)A and Bu_4NA, it seems that the difference in ion-association constants in water between them is not so large. Thus, the data indicate that solute-water interaction of $K(18C6)^+$ is much stronger than that of Bu_4N^+.

It is seen from Table 3 that $\Delta H_{D,L}$ and $\Delta S_{D,L}$ values of 18C6 are both positive and the $T\Delta S_{D,L}$ value at 25 °C is larger than the $\Delta H_{D,L}$ value. Consequently, the fact that 18C6 is more soluble in $CHCl_3$ than in water is completely due to entropy contribution. The explanation for the positive values of $\Delta H_{D,L}$ and $\Delta S_{D,L}$ of 18C6 is the same as that provided in the previous paper.[3]

The Δ*H*ex and Δ*S*ex values of 18C6 for all the alkali metals are negative. Tables 2 and 3 show that the second largest −Δ*H*ex value of K is canceled by the second smallest −*T*Δ*S*ex value, resulting in the greatest log *K*ex, and that the smallest −Δ*H*ex and −*T*Δ*S*ex values of Na balance each other, leading to the smallest log *K*ex. The Δ*H*ex′ value plays a major role in determining the magnitude of Δ*H*ex, whereas the $\Delta S_{D,L}$ value plays a major role in determining the magnitude of Δ*S*ex.

The *K*ex′ value of 18C6 for the $CHCl_3$ system (at 25 °C) decreases in the order, Rb≈K>Cs>Na (Table 2). The largest Δ*H*ex′ and Δ*S*ex′ values of Na cancel each other, resulting in the lowest ion-pair extractability; the second greatest Δ*H*ex′ and Δ*S*ex′ values of K balance each other, leading to the highest ion-pair extractability (Table 3).

All the Δ*H*ex′ and Δ*S*ex′ values are negative except for the Δ*S*ex′ value of Na. Although sizes of these 18C6-alkali metal ion complexes are much the same,[12] both Δ*H*ex′ and Δ*S*ex′ values vary with the alkali metal ion trapped in the 18C6 cavity. This reflects differences in chemical nature of the alkali metal ions in the cavity. The Δ*H*ex′ and Δ*S*ex′ values of Na are much larger than those of the other alkali metals. A possible explanation for the very large Δ*H*ex′ and Δ*S*ex′ values of Na is as follows. The 18C6-Na^+ complex may be most strongly hydrated in an aqueous phase due to the highest charge density of Na^+ and much smaller size of Na^+ compared to that of the 18C6 cavity. The strong interaction between Na^+ in cavities of 18C6 and its analog and solvent molecules was observed in the previous works.[12,13] When the Na^+ complex is extracted into $CHCl_3$ phase, a large amount of water molecules attached to the complex have to be released. This may be responsible for the very large Δ*H*ex′ and Δ*S*ex′ values fo Na.

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