Bull. Chem. Soc. Jpn., 57, 1055—1057 (1984)

Thermodynamic Study on Solvent Extraction of Alkali Metal Picrates by 15-Crown-5

Yasuyuki Takeda,* Tsuyoshi Namisaki, and Shizuo Fujiwara
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-chō, Chiba 260

(Received September 22, 1983)

In order to obtain enthalpy (ΔH_1°) and entropy changes (ΔS_1°) for overall extraction reactions of 15-crown-5 (15C5) with alkali metal picrates between benzene and water, and those (ΔH_2° and ΔS_2°) for partition of 15C5 itself, overall extraction equilibrium constants of 1:1:1 complexes of 15C5 with the salts and distribution coefficients of 15C5 were determined at 20, 30, 35, and 40 °C. The ΔH_1° and ΔS_1° values of 15C5 for the alkali metals are all negative. Both the ΔH_2° and ΔS_2° values are positive. In general, the ΔH_2° and ΔS_2° values play a major role in determining the magnitude of ΔH_1° and ΔS_1° values, respectively, except the case of entropy change for the potassium system. Enthalpy (ΔH_4°) and entropy changes (ΔS_4°) for ion-pair extractions of 15C5-alkali metal ion complexes by picrate anions were calculated by using the ΔH_1° and ΔS_1° values, and the literature values for complex-formation reactions of 15C5 with alkali metal ions in water. Both ΔH_4° and ΔS_4° values vary with the alkali metal ion held in the 15C5 cavity. The ΔH_4° and ΔS_4° values for Na^+, Rb^+, and Cs^+ are all negative, whereas those for K^+ are all positive.

15-Crown-5 (15C5) constitutes a most fundamental skeleton along with 12-crown-4 and 18-crown-6 among various crown compounds. Benzo-15-crown-5 (B15C5), which is a derivative of 15C5, is used as a pendant of polymers, a moiety of bis(crown ether)s, and a colorimetric reagent. These compounds are important for analytical chemistry as versatile agents in solvent extraction. Thus, a detailed study on the extraction process of metal ions with 15C5 and B15C5 would be in order.

For the benzene/water system, extraction-selectivity tendencies of 15C5 and B15C5 for alkali metal ions are almost similar to each other, which are consistent with size relationship.[1,2] The extractability of 15C5 for the same alkali metal ion is larger than that of B15C5 except for Li^+.[1,2] For further study on the role of B15C5 in the extraction process, enthalpy and entropy changes for the overall extraction reactions of B15C5 with sodium and potassium picrates have been determined.[3] The enthalpy and entropy changes for both systems are large and negative.[3]

In the present work, enthalpy and entropy changes for the overall extraction reactions of 15C5 with alkali metal picrates, and those for partition of 15C5 itself have been determined between benzene and water. Enthalpy and entropy changes for ion-pair extractions of 15C5-alkali metal ion complexes by picrate anions were calculated by using these thermodynamic quantities and the literature values for complex-formation reactions of 15C5 with alkali metal ions in water.

Experimental

15-Crown-5 (Nisso Co., Ltd.) was used without further purification. Benzene, picric acid, NaOH, and KOH were analytical grade reagents. Rubidium and caesium hydroxides were reagent-grade. Benzene was washed three times with distilled water.

The benzene phase of 15C5 (1.3×10^{-4}—5.8×10^{-2} M; 1 M=1 mol dm^{-3}), and the aqueous phase of the alkali metal hydroxide (6.1×10^{-3}—1.2×10^{-2} M) and picric acid ((4.1—9.7)$\times10^{-3}$ M) in a stoppered glass tube (30 ml) were shaken in a thermostated water bath for 45 min and centrifuged. The initial volume of each phase was 10 ml in all the cases. Extractions were carried out at pH 10.0—11.7. The picrate in the benzene phase was back-extracted into 8 ml of 0.01 M NaOH aqueous solution, and the picrate concentration was determined spectrophotometrically (λ_{max}=356 nm, $\varepsilon=1.45\times10^4$ cm^{-1} M^{-1}). In blank experiments, there was no extraction in the absence of 15C5. Extractions were conducted at 20, 30, 35, and 40±0.3 °C.

The Distribution Coefficient of 15C5. A 13 ml benzene solution containing 15C5 (7.7×10^{-5}—6.0×10^{-4} M) and an equal volume of distilled water in a stoppered glass tube were shaken in a thermostated water bath for 40 min and centrifuged. A portion 12 ml of the benzene phase and an equal volume of aqueous solution (pH 10.5—11.0) containing NaOH (1.1×10^{-1}M) and picric acid (1.0×10^{-1} M) were placed in a stoppered glass tube and shaken. After centrifuging, the picrate in the benzene phase was back-extracted into 10 ml of 0.01 M NaOH aqueous solution, and the picrate concentration was determined spectrophotometrically (λ_{max}= 356 nm, $\varepsilon=1.45\times10^4$ cm^{-1} M^{-1}). Experiments were conducted at 20, 30, 35, and 40±0.3 °C.

Results

When an equilibrium is established between an aqueous phase of alkali metal ion (M^+) and picrate ion (A^-), and a benzene phase of crown ether (L), the equilibrium constants is defined as

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

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

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

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

where the subscript "o" and the lack of subscript denote the organic and aqueous phases, respectively. Thus, K_{ex} can be written as

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

The distribution ratio of the alkali metal may be represented by

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

The substitution of Eq. 1 into Eq. 6 gives

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

Log ($D/[A^-]$) *vs.* log $[L]_o$ plots show a straight line with a slope of 1 in every case. This indicates that the K_{ex} can be described by Eq. 1. The values of $[L]_o$ and $[A^-]$ in Eq. 7 were calculated by

TABLE 1. SUMMARY OF EQUILIBRIUM CONSTANTS

Temp/°C	$K_{D,L}$	log K_{ex}			
		Na^+	K^+	Rb^+	Cs^+
20	0.12_6	4.06	2.68	2.30	2.05
25[1)]	0.15_6	3.90	2.58	2.14	1.90
30	0.16_3	3.80	2.53	2.03	1.81
35	0.20_0	3.68	2.41	1.95	1.65
40	0.22_1	3.52	2.37	1.86	1.57

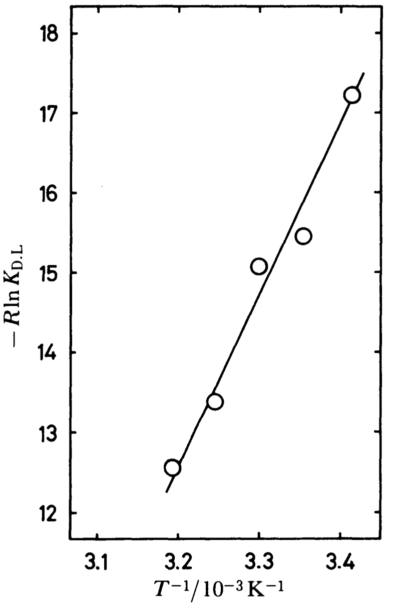

Fig. 1. $-R\ln K_{D,L}$ *vs.* T^{-1} plots for 15C5 between benzene and water.

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

$$[A^-]=[HA]_t-[MLA]_o, \tag{9}$$

where the subscript "t" denotes the total concentration. The equilibrium constants are listed in Table 1.

It can be seen from Figs. 1 and 2 that the $-R\ln K_{D,L}$ *vs.* T^{-1} and $R\ln K_{ex}$ *vs.* T^{-1} plots show a linear relationship. The enthalpy change (ΔH_n°) and the entropy change (ΔS_n°) for Eqs. 1 and 2 were calculated from these data by means of the following equations: $\Delta G^\circ=-RT\ln K$ and $\Delta G^\circ=\Delta H^\circ-T\Delta S^\circ$, where ΔG° and the subscript "*n*" designate the free energy change and the number of equation, respectively. The thermodynamic quantities are summarized in Table 2.

Discussion

As can be seen from Table 2, the $T\Delta S_2^\circ$ value is canceled by the ΔH_2° value, resulting in much greater solubility of 15C5 in water than in benzene. The ΔH_2° and $T\Delta S_2^\circ$ (at 25 °C) values of dibenzo-18-crown-6 (DB18C6) between benzene and water are 8.4 and 25 kJ mol^{-1} respectively.[5)] 15-Crown-5 and DB18C6 are hydrated in an aqueous phase through hydrogen bonds between ether oxygen atoms of the crown ethers and water molecules. When the crown ethers pass over into the benzene phase from the aqueous phase, the water molecules bound to the crown ethers have to be released. The breaking of the hydrogen bonds and the release of the water molecules would lead ΔH_2° and ΔS_2° of both 15C5 and DB18C6 to positive values. The same tendency has been reported for transfer of 18-crown-6 and cryptand 222 from water to methanol (ΔH_2° and $\Delta S_2^\circ>0$).[6)]

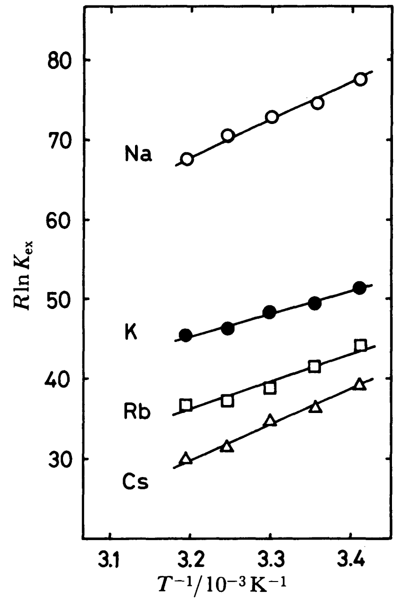

Fig. 2. $R\ln K_{ex}$ *vs.* T^{-1} plots for 15C5-alkali metal picrate systems between benzene and water.

TABLE 2. THERMODYNAMIC QUANTITIES

ΔH_2°/kJ mol^{-1}=$20._9$		$T\Delta S_2^\circ$/kJ mol^{-1} (at 25 °C)=$16._1$	
	ΔH_n°/kJ mol^{-1} [a)]		
	n=1	n=3[4)]	n=4
Na^+	$-45._3$	−6.28	$-18._1$
K^+	$-27._3$	−17	$10._6$
Rb^+	$-37._7$	−7.95	$-8._8$
Cs^+	$-42._5$	−5.4	$-16._2$
	$T\Delta S_n^\circ$/kJ mol^{-1} (at 25 °C)[b)]		
	n=1	n=3[4)]	n=4
Na^+	$-22._9$	−2.2	$-4._6$
K^+	$-12._5$	−13.0	17
Rb^+	$-25._3$	−4.4	$-4._8$
Cs^+	$-31._6$	−0.6	−15

a) $\Delta H_1^\circ=-\Delta H_2^\circ+\Delta H_3^\circ+\Delta H_4^\circ$, b) $\Delta S_1^\circ=-\Delta S_2^\circ+\Delta S_3^\circ+\Delta S_4^\circ$

The ΔH_1° and ΔS_1° values of 15C5 for all the alkali metal ions are negative (Table 2). Both ΔH_1° and ΔS_1° values vary somewhat with the alkali metal ion trapped in the 15C5 cavity. Tables 1 and 2 show that the smallest $-\Delta H_1^\circ$value of K^+ is balanced by the smallest $-T\Delta S_1^\circ$ value, resulting in the second largest log K_{ex} value and the second largest $-\Delta H_1^\circ$ value of Cs^+ is canceled by the largest $-T\Delta S_1^\circ$ value, resulting in the smallest log K_{ex} value.

In general, the ΔH_2° and ΔS_2° values play a major role in determining the magnitude of ΔH_1° and ΔS_1° values, respectively, except the case of entropy change for the potassium system, whereas the ΔH_3° and ΔS_3° values play a minor role except for the potassium system.

Both ΔH_4° and ΔS_4° values vary with the alkali metal ion held in the 15C5 cavity (Table 2). This may be attributed to the fact that, since surface charge of alkali metal ions larger than the 15C5 cavity is not effectively shielded by the 15C5 ring, chemical natures of the 15C5 complexes with alkali metal ions (Na^+, K^+, Rb^+, Cs^+) are different from each other. The $K_{ex'}$ value (at 25 °C) sequences of 15C5 for the alkali mtal ions are $Na^+ \gg K^+ > Rb^+ > Cs^+$. The highest extractability for Na^+-15C5 complex is due to the largest $-\Delta H_4^\circ$ and the second smallest $-T\Delta S_4^\circ$ values. The second greatest $-\Delta H_4^\circ$ value of 15C5 complex with Cs^+ is canceled to a considerable extent by the largest $-T\Delta S_4^\circ$ value. Thus, the 15C5 complex with Cs^+ shows the lowest extractability. It is very interesting that ΔH_4° and ΔS_4° values for 15C5 complexes with Na^+, Rb^+, and Cs^+ are all negative, whereas those for 15C5 complex with K^+ are all positive. For the reaction corresponding to Eq. 4, the number of chemical species is larger for the reactant system than for the product system. This is presumably the dominant factor in determining the ΔS_4° values of 15C5 complexes with Na^+, Rb^+, and Cs^+ to be negative. The fact that, although the ΔH_4° value of the 15C5 complex with K^+ is by far the most unfavorableor ion-pair extraction of the K^+ complex, the extraction efficiency of the K^+ complex is the second largest depends totally on much the greatest $T\Delta S_4^\circ$ value (Table 2). The reason why the ΔH_4° and ΔS_4° values of the 15C5 complex with K^+ are positive and large cannot be clearly explained at the present time. However, it is conceivable that the positive ΔS_4° value of the 15C5 complex with K^+ is due to the difference in the hydration state between the 15C5 complex with K^+ in the aqueous phase and the 15C5 complex with potassium picrate in the benzene phase.

References

1) Y. Takeda and H. Gotō, *Bull. Chem. Soc. Jpn.*, **52**, 1920 (1979).

2) Y. Takeda, Y. Wada, and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, **54**, 3727 (1981).

3) Y. Takeda, *Bull. Chem. Soc. Jpn.*, **56**, 931 (1983).

4) R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, *J. Am. Chem. Soc.*, **98**, 7620 (1976).

5) A. Sadakane, T. Iwachido, and K. Tōei, *Bull. Chem. Soc. Jpn.*, **48**, 60 (1975).

6) M. H. Abraham and H. C. Ling, *Tetrahedron Lett.*, **23**, 469 (1982).