March, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***56***, *931—932 (1983)* 931

Thermodynamic Study on Solvent Extraction of Sodium and Potassium Picrates by Benzo-15-crown-5

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(Received August 20, 1982)

Synopsis. In order to obtain enthalpy and entropy changes for extraction of sodium and potassium picrates by benzo-15-crown-5 (B15C5) between benzene and water, the overall extraction equilibrium constants for the 1:1:1 complexes of B15C5 with the salts were determined at various temperatures. The enthalpy and entropy changes for both the systems are all large and negative.

For the evaluation of complexing ability of a crown ether for various metal ions, solvent extraction is a facile and useful method. Many overall extraction equilibrium constants for various crown ether–metal ion systems have been reported up to date. In some of these works,[1–4] the role of crown ether in the extraction process has been discussed in detail by analyzing the overall extraction equilibrium constant on the basis of constituent equilibria: the stability and extractability of crown ether–metal ion complex, and the distribution coefficient of crown ether itself. For further investigation on the role of crown ether in the extraction process, it is very important to obtain enthalpy and entropy changes for the extraction reaction of a crown ether with a metal ion. However, there is very little data on enthalpy and entropy changes.[5,6]

In the present study, in order to obtain enthalpy and entropy changes for the extraction of sodium and potassium picrates by benzo-15-crown-5 (B15C5) between benzene and water, the overall extraction equilibrium constants for the 1:1:1 complexes of B15C5 with the salts have been determined at various temperatures.

Experimental

The method of purification of B15C5 (Merck Japan Ltd.) has been described in a previous paper.[7] Concentrations of alkali metal hydroxides and picric acid solutions were determined by means of acid and basic titrations, respectively. Analytical-grade benzene was washed twice with distilled water. A benzene phase of B15C5 (1.9×10^{-4}—3.5×10^{-3} M; 1 M=1 mol dm^{-3}), and an aqueous phase of the alkali metal hydroxide (4.6×10^{-3}—1.4×10^{-2} M) and picric acid ($(3.2$—$4.1)\times10^{-3}$ M) in a stoppered glass tube (30 ml) were shaken in a thermostated water bath for 40 min and centrifuged. The initial volume of each phase was 10 ml in all cases. Extractions were conducted at pH 11.1—11.8. 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 at 356 nm by means of a Shimadzu UV-200 spectrophotometer ($\varepsilon=1.45\times10^4$ cm^{-1} M^{-1}). In control experiments, there was no detectable extraction in the absence of B15C5. Extractions for sodium and potassium picrates by B15C5 were conducted at 25, 28, 31, 34, and 37±0.3 °C, and 19, 22, 25, 28, and 31±0.3 °C, respectively.

Results

When an aqueous solution of alkali metal ion (M^+) and picrate ion (A^-) and a benzene solution of crown ether (L) are equilibrated, the equilibrium constants may be defined by

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

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

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

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

where the subscript "o" and the lack of subscript designate 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

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

In the case of $[M^+]\gg[ML^+]$, Eq. 6 becomes

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

Log($D/[A^-]$) *vs.* log$[L]_o$ plots show a linear relationship with a slope of 1 in every case. This indicates that B15C5 forms a 1:1 complex with the alkali metal ion. The values of $[L]_o$ and $[A^-]$ in Eq. 7 were calculated by

$$[L]_o = [L]_t - [MLA]_o, \tag{8}$$

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

where the subscript "t" denotes the total concentration.

As can be seen from Fig. 1, the log K_{ex} *vs.* T^{-1} plots for NaA- and KA-B15C5 systems show a linear relationship. The enthalpy change ($\Delta H°$) and the

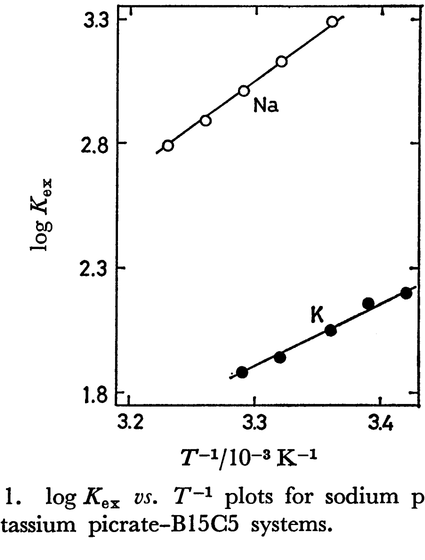

Fig. 1. log K_{ex} *vs.* T^{-1} plots for sodium picrate- and potassium picrate-B15C5 systems.

Table 1. Thermodynamic quantities

Temp/°C	$\log K_{\mathrm{ex}}$	
	Na(B15C5)A	K(B15C5)A
19	—	2.26
22	—	2.16
25	3.29	2.05
28	3.13	1.94
31	3.01	1.88
34	2.89	—
37	2.79	—

	Na(B15C5)A	K(B15C5)A
ΔG°/kJ mol^{-1} (at 25 °C)	−19	−12
ΔH°/kJ mol^{-1}	−74	−50
$T\Delta S^\circ$/kJ mol^{-1} (at 25 °C)	−55	−38

entropy change (ΔS°) were calculated from these data by using the following equations: $\Delta G^\circ = -RT\ln K_{\mathrm{ex}}$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ where ΔG° denotes the free energy change. These thermodynamic quantities are listed in Table 1.

Discussion

It may be seen from Table 1 that overall extraction reactions for B15C5 are all exothermic and the ΔS° values are all negative. For both Na^+– and K^+–B15C5 systems, the very great $-\Delta H^\circ$ value is canceled by the very large $-T\Delta S^\circ$ value, resulting in the small $-\Delta G^\circ$ value and the relatively low preference of Na^+ over K^+. A similar tendency as mentioned above is found in extractions for sodium and potassium picrates–dibenzo-18-crown-6 systems (benzene/water).5) It is interesting that the $-\Delta H^\circ$ and $-\Delta S^\circ$ values of Na^+, which fits much more closely into the B15C5 cavity than K^+, are much greater than those of K^+.

The values of enthalpy ($\Delta H^\circ_{\mathrm{ML}}$) and entropy changes ($\Delta S^\circ_{\mathrm{ML}}$) for the complexation reaction of B15C5 with K^+ in H_2O are −9.75 kJ mol^{-1} and −26 J K^{-1} mol^{-1}, respectively,8) both the $\Delta H^\circ_{\mathrm{ML}}/\Delta H^\circ$ and $\Delta S^\circ_{\mathrm{ML}}/\Delta S^\circ$ ratios being only 0.2. Thus, the contributions of $\Delta H^\circ_{\mathrm{ML}}$ and $\Delta S^\circ_{\mathrm{ML}}$ to ΔH° and ΔS° are small, respectively. Since the $K_{\mathrm{D,L}}$ value scarcely varies (19—21) in the range 19—37 °C, the contributions of enthalpy and entropy changes of this process to ΔH° and ΔS° may be very small, respectively. It thus appears that, for the KA–B15C5 system, the magnitudes of ΔH° and ΔS° are determined primarily by those of enthalpy and entropy changes of the process related to Eq. 4, respectively.

The author wishes to thank Professor Shizuo Fujiwara, Chiba University, for his valuable discussion.

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