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Thermodynamics and Coordination Characteristics of the Hydronium–Uranium(VI)–Dicyclohexano-24-crown-8 Extraction Complex

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Abstract

The extraction equilibrium of the hydronium–uranium(VI)–dicyclohexano-24-crown-8 complex was carried out in the crown ether–1,2-dichloroethane–HCl aqueous solution system at different temperatures. The extraction complex has the overall composition $(L)_2\cdot(H_3O^+\cdot xH_2O)_2\cdot UO_2Cl_4^{2-}$ (L = dicyclohexano-24-crown-8). The values of the extraction equilibrium constants (K_{ex}) increase steadily with a decrease in temperature: 13.5 (298 K), 7.96 (301 K), 4.20 (303 K) and 2.07 (305 K). A plot of $\log K_{ex}$ against $1/T$ shows a straight line. The value of the enthalpy change, ΔH°, was calculated from the slope and equals -212 kJ mol^{-1}. The value of the entropy change, ΔS°, was calculated from ΔH° and K_{ex} and equals -690 J K^{-1} mol^{-1}, whereas $\Delta G^\circ = -6.45$ kJ mol^{-1}. Comparing these thermodynamic parameters with those of the dicyclohexano-18-crown-6 isomer **A** [1] ($\Delta S^\circ = -314$ J K^{-1} mol^{-1}, $\Delta H^\circ = -101$ kJ mol^{-1} and $\Delta G^\circ = -8.37$ kJ mol^{-1}), it can be seen that ΔH° and ΔS° are more negative for the former than for the latter, and both are enthalpy-stabilized complexes. The molecular structure of the complex has the feature that there are two $H_5O_2^+$ ions in it, in contrast to the H_3O^+ ions in the dicyclohexano-18-crown-6 isomer **A** complex [1]. Each of the $H_5O_2^+$ ions is held in the crown ether cavity by four hydrogen bonds. The $H_5O_2^+$ ion has a central bond. The uranium atom forms $UO_2Cl_4^{2-}$ as a counterion away from the crown ether. The formation of this complex is in good agreement with more negative entropy change and less negative free energy change, as mentioned above.

Introduction

Dicyclohexano-24-crown-8 (L) is similar to dicyclohexano-18-crown-6 in its ability to extract tetra- and hexavalent uranium, neptunium and plutonium from mineral acid solutions [2–4]. The extraction equilibrium and molecular structure of the hydronium–uranium(VI)–dicyclohexano-18-crown-6 isomer **A** (**Ia**) complex have been studied [1]. The structure analysis of the complex showed the distinct result that in the extraction complex each of the two H_3O^+ cations is anchored in the crown ether cavity by three hydrogen bonds and forms a symmetrical structure, and the uranium atom is surrounded by two oxygen atoms and four Cl^- ions as a $UO_2Cl_4^{2-}$ anion. Accordingly, the process of extraction of uranium(VI) from HCl aqueous solution with **Ia** has been clarified. The purpose of this paper is to report the thermodynamic parameters and molecular structure of the hydronium–uranium(VI)–dicyclohexano-24-crown-8 extraction complex in order to elucidate the effect of the donor number as well as of the cavity size of the crown ether on formation of the hydronium–crown ether complex.

Experimental

Dicyclohexano-24-crown-8 was obtained from the Shanghai Chemical Reagent Institute. Purity was checked by IR and ^{1}H NMR spectrometry (see Figs, 1, 2). Other reagents were of AR grade.

Distribution measurements of the extraction were performed as described previously [5]. The crystalline extraction complex was prepared from the organic phase by a non-polar solvent dilution procedure at 25 °C.

The assay of the extraction complex was carried out by the following procedures. The crystals of the extraction complex were dissolved in 1,2-dichloroethane for assays of UO_2^{2+}, Cl^- and the crown ether. The uranium content was determined by arcenazo spectrophotometry. The chloride ion content was estimated using an ion-selective electrode. The determination of the crown ether was made by extraction-spectrophotometry of LKPi, as described previously [5].

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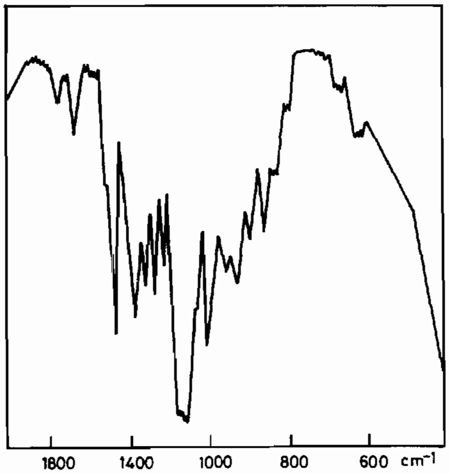

Fig. 1. Infrared spectrum of dicyclohexano-24-crown-8.

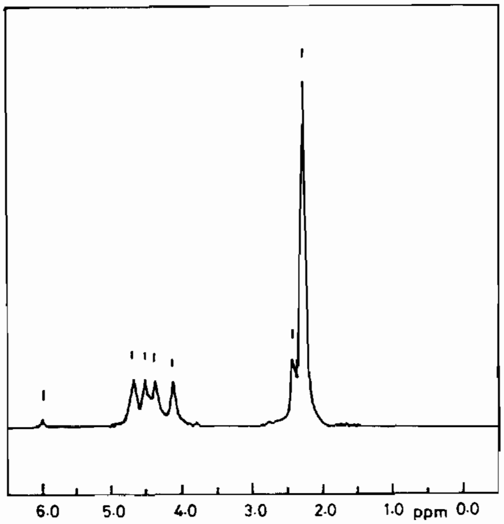

Fig. 2. ^1H NMR of dicyclohexano-24-crown-8.

UV–Vis spectra were recorded using a 7520-type spectrophotometer. IR spectra of the complex and the crown ether were recorded on an IFS-113V IR spectrometer. ^1H NMR spectra were run on an MSL-300 NMR spectrometer.

The crystal structure was determined by the X-ray diffraction method. All intensity data were collected on an Enraf–Nonius CAD-4 diffractometer using Mo Kα radiation. The position parameters of uranium were solved by Patterson and direct methods. All other non-hydrogen atoms were found in a subsequent difference-Fourier synthesis. Crystal data: $(C_{24}H_{44}O_8)_2(H_5O_2^+)_2\cdot UO_2Cl_4^{2-}\cdot C_6H_6$; $M = 1485.3$, light yellow, monoclinic, space group $P2_1/n$, $a = 15.208(7)$, $b = 27.082(2)$, $c = 16.905(1)$ Å, $\beta = 95.38(2)°$, $Z = 4$.

Results and Discussion

Thermodynamic Quantities

The extraction equilibrium of uranium(VI) with dicyclohexano-24-crown-8 from HCl aqueous solution can be written as

$$2\overline{L} + 2H^+(xH_2O) + UO_2^{2+} + 4Cl^- = \overline{L_2\cdot(H^+\cdot xH_2O)_2\cdot UO_2Cl_4^{2-}}$$

where the bar above the symbol designates the organic phase. The extraction equilibrium constant K_{ex} was calculated from the equation:

$$K_{ex} = \frac{D_u\left(1 + \sum_{i=1} \beta_i [Cl^-]^i\right)}{[\overline{L}]^2[H^+]^2[Cl^-]^4}$$

where square brackets represent the molar concentration, D_u is the distribution ratio of uranium, and β_i is the formation constant of $UO_2Cl_i^{(2-i)+}$. The equilibrium concentration of the crown ether in the organic phase $[\overline{L}]$ was calculated as mentioned in ref. 5. In order to obtain the accurate concentration of the crown ether in each phase, the distribution ratios D_L ($D_L = [\overline{L}]/[L]$) of dicyclohexano-24-crown-8 between 1,2-dichloroethane and 3.78 N HCl aqueous solution were determined at different temperatures. The values of D_L were found to be

t(°C)	25.0	28.0	30.2	31.9	35.0
D_L	45.3	56.0	64.3	69.8	81.7

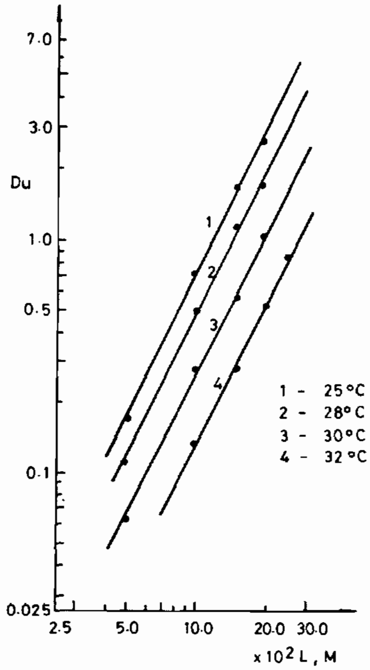

Fig. 3. Distribution ratio of uranium *vs.* concentration of L in the organic phase.

TABLE I. Extraction of UO_2Cl_2 with Dicyclohexano-24-crown-8 in 1,2-Dichloroethane at 25 °C[a]

C_L° [b] $\times 10^2$ (M)	$[\bar{L}]$ [c] $\times 10^2$ (M)	$[\bar{U}]$ [d] $\times 10^3$ (M)	$[U]$ [e] $\times 10^3$ (M)	D_u	K_{ex}
0.503	0.434	0.298	1.66	0.18	13.3
1.05	0.875	0.798	1.16	0.69	13.2
1.57	1.31	1.22	0.737	1.65	13.9
2.07	1.74	1.44	0.512	2.82	13.6
				Average:	13.5

[a] HCl = 3.78 N. [b] C_L°: original concentration of the crown ether in the organic phase. [c] $[\bar{L}]$: equilibrium concentration of the crown ether in the organic phase. [d] $[\bar{U}]$: concentration of uranium in the organic phase. [e] $[U]$: concentration of uranium in the aqueous phase.

As an example we present in Table I a set of measurements of extraction distribution. Other sets of experiments of extraction equilibrium were also carried out at different temperatures. To avoid overcrowding, a summary of all distribution data is given in Fig. 3. The values of the extraction equilibrium constants (K_{ex}) increase steadily with a decrease in temperature. A plot of $\log K_{ex}$ against $1/T$ shows a straight line (Fig. 4). The value of the enthalpy change, ΔH°, was calculated from the slope and equals -212 kJ mol^{-1}. The value of the entropy change, ΔS°, was calculated from ΔH° and K_{ex} and equals -690 J K^{-1} mol^{-1}, whereas $\Delta G^\circ = -6.45$ kJ mol^{-1}. Comparing these thermodynamic parameters with those of the dicyclohexano-18-crown-6 isomer A ($\Delta S^\circ = -314$ J K^{-1} mol^{-1}, $\Delta H^\circ = -101$ kJ mol^{-1}, and $\Delta G^\circ = -8.37$ kJ mol^{-1}), it can be seen that ΔH° and ΔS° are more negative for the former than for the latter and both are enthalpy-stabilized complexes ($\Delta H < 0$ and dominant, $T\Delta S < 0$).

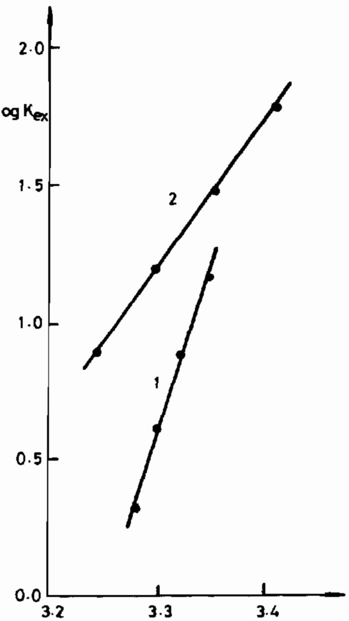

Fig. 4. Plot of $\log K_{ex}$ *vs.* $1/T$: 1 (L), 2 (**Ia**).

Characteristics and Structure of the Crystalline Extraction Complex

The crystals of the extraction complex are light yellow and melt at 98.7–102.3 °C. The complex has the overall composition $(L)_2\cdot(H_3O^+\cdot xH_2O)_2\cdot UO_2Cl_4^{2-}$, which was confirmed by direct assay as follows: (*w*/*w*%) dicyclohexano-24-crown-8 calc. 65.57, found 65.76; UO_2^{2+} calc. 19.23, found 18.89; Cl calc. 9.96, found 10.20 and H^+ calc. 0.142, found 0.140.

The ^{1}NMR signals of the protons within the crown ether cavity and the $H^+\cdot xH_2O$ protons in the complex dissolved in $CDCl_3$ appear at 3.175 and 9.234 ppm respectively. The ratio of the integrated peak is 5.64 (theoretical value = 5.60 for the 1:1 complex of $H_3O^+\cdot H_2O$ with the crown ether). In addition, the cyclohexyl proton resonance appears at 1.299–1.852 ppm (see Fig. 5).

The projection of the complex structure is shown in Fig. 6. The complex structure consists of two $H_5O_2^+$ complex cations and a complex anion $UO_2Cl_4^{2-}$. In the complex anion, the uranyl ion is surrounded by four chloride ions to form a distorted tetragonal bipyramid, about 7.7 Å away from the complex cation $LH_5O_2^+$. This is almost the same as we found in the complex of $(\mathbf{Ia})_2\cdot(H_3O^+)_2\cdot UO_2Cl_4^{2-}$ [1]. But the complex cation (*i.e.* protonated crown ether) shows some distinct features for different crown ethers. In **Ia**–H_3O^+, the H_3O^+ ion is anchored in the crown ether cavity by three stronger hydrogen bonds which have distances of 2.648, 2.618 and 2.685 Å. In the complex cation of the structure reported here we found the presence of the $H_5O_2^+$ ion, which the ^{1}H NMR spectrum mentioned above also revealed, as well as the structure difference between the two $H_5O_2^+$ cation complexes owing to the existence of isomers **A** and **B** in dicyclohexano-24-crown-8. In isomer **A**

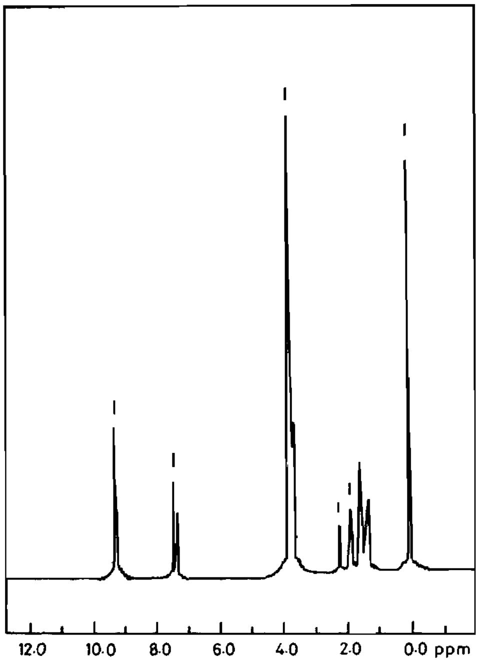

Fig. 5. ^1H NMR spectrum of the hydronium–uranium(VI)–dicyclohexano-24-crown-8 extraction complex.

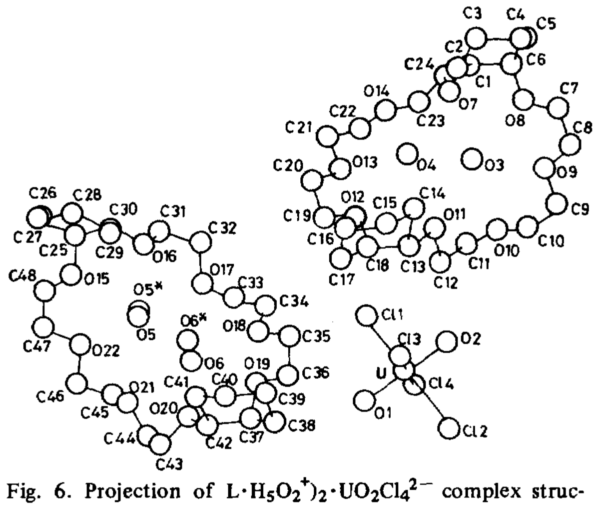

Fig. 6. Projection of $L \cdot H_5O_2^+)_2 \cdot UO_2Cl_4^{2-}$ complex structure. L = dicyclohexano-24-crown-8.

(Fig. 6, right part) the $H_5O_2^+$ ion has a central bond O(3)··H··O(4) with a length of 2.377 Å. The remaining four hydrogen atoms on the $H_5O_2^+$ form weaker hydrogen bonds (O(3)···O(8,10) with distances of 2.879 and 2.846 Å, and O(4)···O(12,14) with distances of 2.910 and 2.845 Å). In isomer **B** (Fig. 6, left part) each of the two oxygen atoms in the $H_5O_2^+$ ion has two disorder positions, which is similar to that shown in the bis(hydroniumdichloropicrate)-1,4,7,10,13,16-hexaoxacyclooctadecane complex [6].

The formation of the $H_5O_2^+$ ion, the steric deformation of dicyclohexano-24-crown-8 in complexation with $H_5O_2^+$, and the weaker bond between $H_5O_2^+$ and the ligand, all taken together, can provide a rationalization for the more negative entropy change and less negative free energy change displayed by the extraction process of the title complex, as mentioned above.

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