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FURTHER STUDY OF EXTRACTION EQUILIBRIUM OF URANIUM(VI) WITH DICYCLOHEXANO-18-CROWN-6 AND ITS APPLICATION TO SEPARATING URANIUM AND THORIUM

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In our publication (1), the extraction of uranium with dicyclohexano-18-crown-6 (mixed isomers) has been described. The extraction equilibrium of uranium(VI) from aqueous hydrochloric acid solution with dicyclohexano-18-crown-6 isomer A (Ia) and isomer B (Ib) in 1,2-dichloroethane is presented in this paper. The extracted species are found to be 1:2 (metal/crown) for Ia and 2:3 for Ib from slope analysis and direct determination of extracted complexes. The extraction equilibrium constants (Kex) have been determined at 25 °C, and equal 29.5 for the former and 0.208 for the latter. It is concluded that Ia has stronger coordinate ability for uranium than Ib. The different orientation of the lone pairs of the oxygen atoms in both isomers will be taken into account for interpreting above results. The extraction of uranium(VI) with dicyclohexano-18-crown-6 (mixed isomers) or Ia from aqueous hydrochloric acid solution is effective and selective. In 0.1M crown ether-1,2-dichloroethane-6N HCl system, the separation factor U(VI)/Th(IV) exceeds 1000. The result can be taken in separating uranium and thorium.

Introduction

After comparing the extractability of a series of crown ethers, it is concluded that dicyclohexano-18-crown-6 is better one for extracting tetra- and hexavalent uranium from HNO_3 and HCl media. The extraction of uranium with dicyclohexano-18-crown-6 (mixed isomers) has been described in several publications (e.g. 1,2,3), however in which the different ligating properties for uranium were not considered between isomers.

It is well known that when dicyclohexano-18-crown-6 is made by the catalytic hydrogenation of the benzo-analogue, two of the possible five isomers of dicyclohexano-18-crown-6 are produced, and have been identified structurally as the cis-syn-cis - isomer A (Ia) and cis-anti-cis - isomer B (Ib), and the two isomers have markedly different coordinate properties towards mono- and divalent cations.

The purpose of this paper is to report the extraction equilibrium of uranium(VI) from aqueous hydrochloric acid solution with dicyclohexano-

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The equilibrium concentrations of uranium(VI) in each phase were determined by 2-(5-Bromo-2-pyridylazo)-5-diethylamino phenol spectrophotometry. For determination of dicyclohexano-18-crown-6 isomer A and isomer B in two phases, 0.2 ml of aqueous solution or organic solution was taken, the acid neutralized with aqueous potassium hydroxide solution, 2 ml 5.0×10^{-3} M potassium dichloropicrate solution added and the crown ether extracted as dicyclohexano-18-crown-6.$KPiCl_2$ into an equal volume of 1,2-dichloroethane. The organic phase was colorless after the third extraction. The extracted dicyclohexano-18-crown-6.$KPiCl_2$ was then determined spectrophotometrically at 395 nm ($_{395} = 4.77 \times 10^3$ mol^{-1} cm^{-1}).The acidity in the aqueous phase was determined by titration with sodium hydroxide solution using phenolphthalein as indicator. The acidity in organic phase was determined by back extracting 0.2 ml of the organic phase into 20 ml distilled water and measuring the aqueous phase with a type PH2 pH-meter.

Results and discussion

1. Distribution of crown ether between two phases

Dicyclohexano-18-crown-6 isomer A and isomer B have higher solubility in aqueous solution (Ia$\sim$0.053 M; Ib$\sim$0.018 M) (6), and stronger bonding with hydronium ion in acidic medium. Therefore, in order to get accurate concentration of crown ether in each phase for investigating the extraction equilibrium of uranium in crown ether - 1,2-dichloroethane - HCl - aqueous solution system, the distribution of crown ether between two phase should be considered. Previous experiments showed that distribution ratios D_L ($D_L = [\overline{L}] / [L]$) of Ia and Ib between 1,2-dichloroethane and 4N HCl aqueous solution were equal to 29.4 and 37.9 respectively at 25°C. A decrease in distribution ratio with increasing HCl concentration in aqueous solution was obtained. In 6N HCl aqueous solution the distribution ratios were found to be 3.68 for Ia and 4.94 for Ib. Evidently, the complexation of hydronium ion with Ia or Ib increases the solubility of crown ether in aqueous phase, so D_L is decreased. In the calculation of extraction equilibrium constants, considering the extraction of uranium, the equilibrium concentration of crown ether in organic phase L can be represented by following equation:

$$[\overline{L}] = \left(C_L^o - \frac{Du}{Du + 1} C_u^o \cdot n \right) \cdot \frac{D_L}{D_L + 1}$$

where C_L^o - original concentration of crown ether in organic phase; Du - distribution ratio of uranium; C_u^o - original concentration of uranium in aqueous phase; n - molecular ratio of crown ether to uranium in extracted complex.

2. Composition of extracted complex and equilibrium constant

The composition of extracted complex was determined by slope analysis and derect assay of extracted complex. The results of slope analysis were showed in Fig. 3. The dependence of log Du vs. log$\overline{[L]}$ was a straight line with a slope of 2 for Ia and 1.5 for Ib. For direct assay of extracted complex, the organic phase was diluted by benzene to get the crystalline product of extracted complex, in which the contents of uranium, crown ether and hydrochloric dcid were determined. The results of assay corresponded to the formulas $(\text{Ia})_2\text{UO}_2\text{Cl}_2\cdot2\text{HCl}$ for Ia and $(\text{Ib})_3(\text{UO}_2\text{Cl}_2)_2\cdot4\text{HCl}$ for Ib, and were coindent with slope

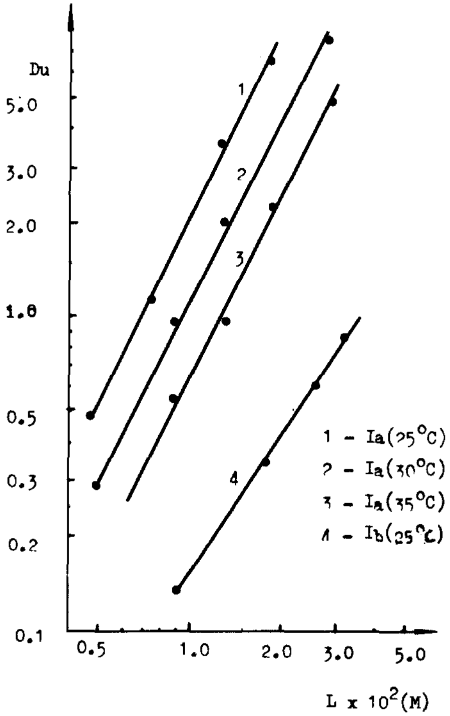

Fig. 3. Distribution ratio of uranium versus concentration of Ia (or Ib) in organic phase

analysis. Therefore, the extraction equilibrium can be written as

$$UO_2^{2+} + nL + 2H_3O^+ + 4Cl^- = (L)n(H_3O^+)_2\ UO_2Cl_4^{2-}$$

where the bar above the quantity designates the organic phase. The corresponding extraction constant Kex can be calculated by

$$Kex = \frac{Du\ (\ 1 + \beta_1[H_3O^+]\ )}{[L]^n \cdot [H_3O^+]^2 \cdot [Cl^-]^4}$$

In above equation, square brackets represent the molar concentration, and β_1 is the formation constant of UO_2Cl^+. The extraction concentration constants Kex for Ia and Ib are given in Table 1, and indicate that Ia has stronger coordinate ability towards uranium than Ib. It should be an important reason for interpreting above results that both isomers have different lone pair orientation of the oxygen atoms in cyclic cavity. (7) Two of lone pair orientation are trigonal for Ia, but none for Ib. Calculated electronegativities of the lone pairs suggest that metal ion being along the extention of the bisector of C-O-C, 'trigonal', be more stable than other possible directions in 18 - membered cyclic ether complexes. A convincing explanation of the difference between the uranium complexes of Ia and Ib requires a further study of the structure of both complexes.

3. Separation of uranium and thorium

In preliminary experiments, the separation factors of extracting uranium and thorium with crown ethers have been determined in picric acid system, and presented in Table 2, from which it may be seen that dicyclohexano-18-crown-6 does not have higher efficiency of separating uranium and thorium than other crown ethers. However, the extraction of uranium(VI) from aqueous hydrochloric acid solution with dicyclohexano-18-crown-6 (mixed isomers) or Ia is effective and selective. In 0.1M crown ether-1,2-dichloroethane- 6N HCl system, the separation factor U(VI)/Th(IV) exceeds 1000. An example of extraction separating uranium and thorium quantitatively can be offered as following: 6N HCl solution contained 0.0225 M UO_2Cl_2 and trace amount of ^{234}thorium was extracted with an equal volume of 0.1 M dicyclohexano-18-crown-6 (or Ia) in 1,2-dichloroethane. The uranium was transfered to organic phase completely. To remove any ^{234}thorium in organic phase, the extract was washed with

Table 1
Extraction of UO_2Cl_2 with Ia and Ib in 1,2-dichloroethane at 25 °C

C_L^o $(M\times10^2)$	$\overline{[L]}_t$ $(M\times10^2)$	$\overline{[L]}$ $(M\times10^2)$	$[L]_t$ $(M\times10^4)$	C_u^o $(M\times10^4)$	$\overline{[U]}$ $(M\times10^4)$	$[U]$ $(M\times10^4)$	Du	Kex
				L = Ia				
0,526	0.510	0.466	1.59	6.67	2.20	4.47	0.493	29.3
0.820	0.795	0.723	2.46	6.67	3.57	3.10	1.15	29.4
1.39	1.35	1.24	4.21	6.95	5.44	1.51	3.61	30.3
1.95	1.89	1.77	6.02	6.95	6.04	0.91	6.68	29.2
								av 29.5
				L = Ib				
0.686	0.686	0.660	1.74	6.95	0.550	6.40	0.086	0.207
0,914	0.891	0,879	2.32	6.67	0.783	5.89	0,133	0.208
1.76	1.72	1.69	4.46	6.67	1.71	4.96	0.345	0.206
2.59	2.52	2.49	6.57	6.67	2.56	4.11	0.623	0.205
3.20	3.12	3.07	8.10	6.95	3.26	3.68	0.885	0.212
								av 0.208

[HCl] = 3.88 N ; $\overline{[L]}_t$ - total concentration of crown ether in organic phase ; $[L]_t$ - total concentration of crown ether in aqueous phase ; $\overline{[U]}$ - concentration of uranium in organic phase ; $[U]$- concentration of uranium in aqueous phase.

Table 2
Separation factors of extracting uranium and thorium at 25 °C

Crown ether	D_u	D_{Th}	$\beta_{Th/U}$
4-methybenzo-15-crown-5	0.174	2.98	17.1
Dicyclohexano-18-crown-6 (mixed isomers)	0.415	2.23	5.37
18-crown-6	0.581	7.67	13.2
Dibenzo-18-crown-6	0.113	1.39	12.3

Organic solvent - 1,2-dichloroethane ; aqueous phase - 0.04 M HPi ; D_u - distribution ratio of uranium(VI) ; D_{Th} - distribution ratio of thorium(IV) ; $\beta_{Th/U}$ - separation factor of extracting uranium and thorium.

6N HCl aqueous solution two times. Meanwhile, the raffinate, in which ^{234}thorium was left, was equilibrated with fresh organic phase once again to remove uranium (if any). In this way the high yeild and purity can be obtained not only for uranium, also for thorium.

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