Extraction of U(VI) and Th(IV) with a novel extractant N,N′-tetrahexylmalonamide (THMA) in toluene*

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Abstract

The dependence of THMA extraction behaviour for U(VI) and Th(IV) on nitric acid concentration, THMA concentration and molecular structure of extracted complex has been studied. For nitric acid solutions of 3.0 mol/L a coordinative mechanism may possibly dominate in the extraction of metal cations. The complex composition of $UO_2(NO_3)_2(THMA)_2$, $Th(NO_3)_4(THMA)_2$ and $Th(NO_3)_4(THMA)_3$ are proved.

Keywords Malonamide, Solvent extraction, Uranyl nitrate, Thorium nitrate, N, N′-tetrahexylmalonamide (THMA)

1 Introduction

Malonamides have been suggested as possible coextractants in a transmutation process and have been investigated early in 1987.[1] The chemical properties of the malonamides depend on the nature of the substituents bound with the nitrogen and on the groups attached to the central carbon atom. It has been shown that the molecular structure of the diamides has a great influence on the metal extraction.[2,3] Enhanced extraction into the organic phase was observed when the carbon chain on the methylene carbon was lengthened to increase the hydrophobic nature of the extractant. The malonamides are completely incinerable extractants and suitable for both actinides and lanthanides to form ion-pairs or coordination compounds with the metal-containing species. In order to study the effect of substituents attached to the nitrogen atom, a novel extractant N,N′-tetrahexylmalonamide (THMA) was synthesized and investigated for U(VI) and Th(IV). Preliminary experiment indicates that the solubility of extracted species corresponding to THMA is higher than that to N,N′-tetrabutylmalonamide and there is no third phase formation under the conditions studied. The results will conduce to the optimization of the malonamide conformation.

2 Experimental

2.1 Materials

THMA was synthesized and purified at our laboratory. The purity of the new malonamide, characterized by IR, ^{1}HNMR and elemental analysis, was high enough (over 98%) to be used in extraction experiments.

2.2 Procedure and apparatus

The malonamide in toluene was vigorously shaken with the aqueous phase for 15 min to reach equilibrium, and after phase disengagement by centrifugation, aliquots of aqueous phase were taken to do Arsenazo-III spectrophotometry analysis for U(VI) and chlorophosphoazo-mA analysis for Th(IV). Then, the amounts of U(VI) or Th(IV) in the organic phase could be calculated.

IR spectra of the extractant and extracted species of U(VI) collected by using a Bio-Rad FTS spectrometer were over 16 scans at a resolution of 2 cm^{-1} using air as background. The samples were presented to the spectrometer by brushing the solution on sodium chloride flats. To ensure reasonable results the solvent must be removed by evaporation before collecting IR spectra.

3 Results and discussion

3.1 Dependence of distribution ratios on

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nitric acid concentration

The extraction distribution ratios, D_U and D_{Th}, under the conditions of 0.20 mol/L THMA in toluene and 5.0×10^{-3} mol/L U(VI) or Th(IV) in aqueous phase, as a function of aqueous nitric acid concentration are plotted in Fig.1. It shows that the values of D_U increase with the increase in nitric acid concentration, however, Wang You-Shao[2] pointed out that there is an inflection at higher nitric acid concentration which usually can be attributed to the competition extraction of nitric acid from aqueous phase. By comparison with the monoamide extraction[4], it can be seen that the higher extraction efficiency of THMA for U(VI) is resulted from the chelate effect. The stability of a metal chelate is greater than that of an analogous monochelated metal complex. For THMA, stable U(VI) chelates can be formed by the structure of six-member rings. However, an inflection of the plots of D_{Th} vs C_{HNO_3} is observed in Fig.1. This behavior may be attributed to the higher stability of the complex between Th(IV) and NO_3^- in aqueous phase compared with that for UO_2^{2+}.

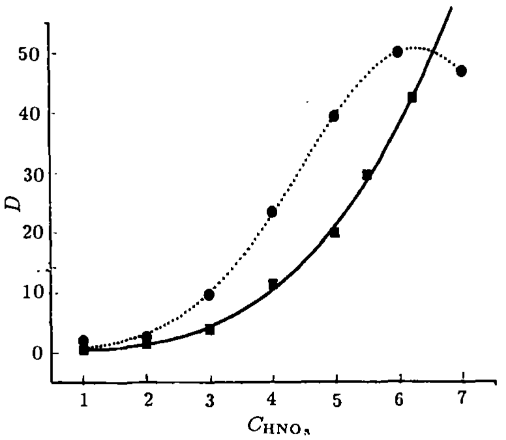

Fig.1 Dependence of distribution ratios of U(VI) (■) and Th(IV) (•) on nitric acid concentration

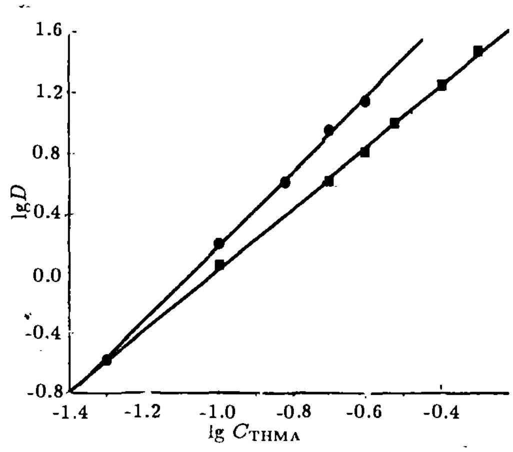

Fig.2 Dependence of distribution ratios of U(VI) (■) and Th(IV) (•) on THMA concentration in toluene

3.2 Dependence of distribution ratios on THMA concentration

The dependence of distribution ratios on THMA concentration, examined at 5.0×10^{-3} mol/L U(VI) and Th(IV) in 3.0 mol/L HNO_3, is shown in Fig.2. The plots of $\lg D_U$ vs $\lg[THMA]_{(o)}$ gives a slope of 2.04 which indicates that two THMA molecules coordinate to one UO_2^{2+}, and $UO_2(NO_3)_2(THMA)_2$ can be determined by the stoichiometry of extracted complex. This is in good agreement with earlier study performed with TBMA in a diluent composed of 50% 1,2,4-trimethylbenzene and 50% kerosene[5]. The coordination mechanism of uranyl ion extraction by THMA may be represented by

$$UO^{2+}_{2(w)} + 2NO^-_{3(w)} + 2THMA_{(o)} = UO_2(NO_3)_2(THMA)_{2(o)} \tag{1}$$

where subscript "o" refers to the species presented in organic phase, for above reaction the equilibrium constant, K_{ex}, is

$$K_{ex} = \frac{[UO_2(NO_3)_2(THMA)_2]_{(o)}}{[UO_2^{2+}]_{(w)}[NO_3^-]^2_{(w)}[THMA]^2_{(o)}} \tag{2}$$

The value of K_{ex} for U(VI) with THMA in toluene is calculated to be 16.37 $mol^{-4}\cdot L^4$.

However, a slope of 2.49 for Th(IV) was obtained, which indicates that two kinds of extracted species, $Th(NO_3)_4(THMA)_2$ and $Th(NO_3)_4(THMA)_3$, are formed in the system. The extraction mechanism can be expressed as followings:

$$Th^{4+}_{(w)} + 4NO^{-}_{3(w)} + 2THMA_{(o)} = Th(NO_3)_4(THMA)_{2(o)} \tag{3}$$

$$Th^{4+}_{(w)} + 4NO^{-}_{3(w)} + 3THMA_{(o)} = Th(NO_3)_4(THMA)_{3(o)} \tag{4}$$

3.3 Conformation of $UO_2(NO_3)_2(THMA)_2$

In comparison between IR spectra of THMA and $UO_2(NO_3)_2(THMA)_2$ it can be seen that the carbonyl(C=O) stretching vibration of the extracted complex is shifted from 1636 cm^{-1} to 1582.3 cm^{-1}, and another new peak located at about 1622 cm^{-1} can be only attributed to C=O stretching vibration. In other words, two carbonyls within a THMA molecule are not equally coordinated to an uranyl ion, namely, the six-member ring formed by THMA and UO_2^{2+} is asymmetrical. The appearance of the characteristic bands at 1030, 1270 and 1497 cm^{-1} implies that NO_3^- coordinates to UO_2^{2+} directly in the extracted complex. Then, the conformation of $UO_2(NO_3)_2(THMA)_2$ can be represented as in Fig.3.

3.4 Separation factor of Th(IV) and U(VI) with THMA

Separation factor between Th(IV) and U(VI) ($\beta_{Th/U} = \frac{D_{Th}}{D_U}$) is influenced by both concentrations of nitric acid and THMA, and it can be seen from Table 1 that the separation factors are not high under the present experimental conditions.

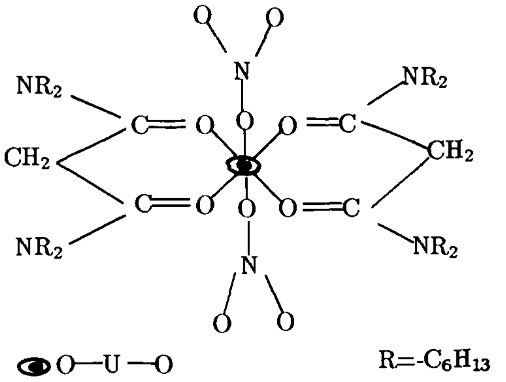

Fig.3 The structure of U(VI) -THMA complex

Table 1 Separation factor between Th(IV) and U(VI)

C_{HNO_3}	2	3	4	5	C_{THMA}	0.10	0.20	0.25
$\beta_{Th/U}$	1.79	2.52	2.05	1.98	$\beta_{Th/U}$	1.40	2.17	2.15

In summary, THMA is an useful extractant for U(VI) and Th(IV). The separation factor between them is not high as compared with monoamides[4]. The stoichiometry of extracted complex is established to be $UO_2(NO_3)_2(THMA)_2$ for U(VI), $Th(NO_3)_4(THMA)_2$ and $Th(NO_3)_4(THMA)_3$ for Th(IV).

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