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Extraction of americium and lanthanides by dialkyldithiophosphinic acid and f-f absorption spectra of the extraction complexes

Zhu Yongjun, Xu Jingming*, Chen Jing, Chen Yingzhong

Institute of Nuclear Energy Technology, Tsinghua University, Beijing 102201, China

Abstract

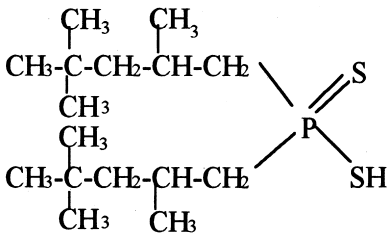
A dialkyldithiophosphinic acid, HBTMPDTP (R2PSSH, R: trimethylpentyl group), has been found to be an effective extractant for separating trivalent americium from lanthanides in nitrate solution. A simple six-stage extraction process can separate >99.99% Am from fission product lanthanides and >99% lanthanides from Am. The f-f absorption spectra of Am^{3+} and Nd^{3+} extracted into HBTMPDTP were measured. Red shift of the spectra of sulfur coordinated complexes is obvious. Intensity of hypersensitive absorption peaks increases drastically and some splittings occur. Absorption spectra of different inner coordination configurations were calculated and compared with experimental ones. The most probable inner coordination configuration of Am- and Nd-HBTMPDTP extraction complexes are both 8-sulfur coordinated cubic symmetries. © 1998 Elsevier Science S.A.

Keywords: Americium; Lanthanides; Extraction; Separation; Extraction complex; f-f absorption spectra

1. Introduction

Since the 1970s, partitioning-transmutation (P-T) of highly active waste (HAW) produced in the reprocessing of nuclear fuel has been studied worldwide. The nuclides which have to be separated from HAW include residual U, Pu, minor actinides (Np, Am, Cm) and long-lived fission products. Several partitioning processes have been proposed [1]. A difficult problem in partitioning is to separate trivalent Am from lanthanides. Because the ionic structure and radius of trivalent Am is very close to those of lanthanides (Eu and Nd), their chemical behaviour in solution is very similar.

Bis(2,4,4-trimethylpentyl)dithio-phosphinic acid (HBTMPDTP) has been found to be an effective extractant to separate Am from lanthanides in nitrate solution. Its molecule formula is as follows



The commercial product Cyanex301 from CYTEC Co. Canada contains about 80 wt.% of HBTMPDTP. The extraction of Am, Eu and Nd was studied by using purified Cyanex301.

The f-f shift absorption spectra of f-element complexes in ultraviolet and visible regions have been studied in the Institute of Nuclear Energy Technology (INET) for determining the structure of the extraction complexes [2]. The coordination symmetries of the 4f or 5f element complex can be deduced from the comparison of calculated results with the measured spectra. This method was applied to study the most probable coordination structure of sulfur coordinated Am- and Nd-HBTMPDTP complexes.

2. Experimental

2.1. Reagents

Extractant: Cyanex301 was purified by ammonium salt recrystallization in benzene [3]. The purified product was examined by ^{31}P-NMR, IFS and potentiometric titration. The HBTMPDTP content in the purified product was higher than 99 wt.%.

Diluent: hydrogenated kerosene from Jin Zhou Refinery. ^{241}Am was obtained from the Chinese Institute of Atomic Energy, radioactive tracer ^{152,154}Eu from irradia-

*Corresponding author. Fax: +86 10 69771464; e-mail: inezxw@mail.tsinghua.edu.cn

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tion of spectroscopic pure Eu_2O_3 in the reactor of INET. The other reagents are all analytically pure.

2.2. Extraction

The organic phase (HBTMPDTP/kerosene) and aqueous phase containing Am and lanthanide nitrate were mixed for 30 min. The Am and lanthanides concentration in the separated phases were measured, respectively. The tracer ^{241}Am and ^{152,154}Eu were measured by a well-type γ-counter (EKCON700, NaI(T1)). The macro concentrations of carrier lanthanides were determined by EDTA titration.

The multistage countercurrent extraction experiments were carried out with glass tube cascades.

2.3. f-f shift absorption spectra measurement

Am or Nd was extracted by saponified 0.3 mol/l HBTMPDTP/methylbenzene from nitrate solution at different pH. The organic phase containing Am-HBTMPDTP or Nd-HBTMPDTP complex was measured using an ultraviolet-visible spectrometer (Unican SP700C) in the range 300–900 nm.

3. Results and discussion

3.1. Extraction of Am and Eu, Nd

The distribution ratio D of Am, Eu, Nd at different pH in the aqueous phase is shown in Fig. 1.

Fig. 2 shows the variation of D with the HBTMPDTP concentration in kerosene.

The slope of the log$D$–pH and log$D$–log[$(HA)_2$] straight lines are close to 3 and 2, respectively. The extraction reaction can thus be written as[1]:

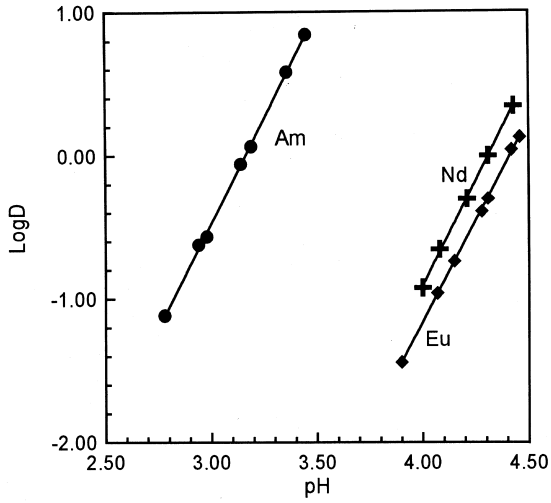

Fig. 1. Logarithmic of distribution ratio D vs. the pH of equilibrated aqueous phase. Organic phase = 0.5 mol/l HBTMPDTP-kerosene. Aqueous phase = tracer ^{241}Am, ^{152,154}Eu and Nd (20 ppm) in 1 mol/l $NaNO_3$ solution; t = 25°C.

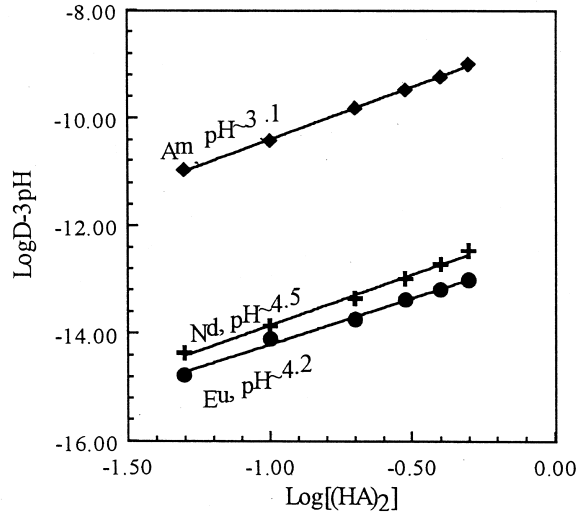

Fig. 2. The relation of log D–3 pH vs. log[$(HA)_2$]*. Organic phase = HBTMPDTP/kerosene. Aqueous phase = tracer ^{241}Am, ^{152,154}Eu and Nd (20 ppm) in 1 mol/l $NaNO_3$ solution; t = 25°C.

$$M^{3+} + 2(HA)_2 = MA_3(HA) + 3H^+ \quad (1)$$

The apparent extraction equilibrium constant K_{ex} can be expressed as:

$$K_{ex} = \frac{[MA_3(HA)]_{(0)} \cdot [H^+]^3_{(a)}}{[M^{3+}]_{(a)} \cdot [(HA)_2]^2_{(0)}} = D \cdot \frac{[H^+]^3_{(a)}}{[(HA)_2]^2_{(0)}} \quad (2)$$

$$\log K_{ex} = \log D - 3pH - 2\log[(HA)_2] \quad (3)$$

The calculated K_{ex} for Am, Eu and Nd from the experimental results shown in Fig. 1 and Fig. 2 are as follows:

$$\log K_{ex}(Am) = -7.78 \pm 0.03 \quad (4)$$

$$\log K_{ex}(Eu) = -11.47 \pm 0.04 \quad (5)$$

$$\log K_{ex}(Nd) = -11.18 \pm 0.02 \quad (6)$$

The above K_{ex} are all apparent equilibrium constants.

3.2. Separation of Am from lanthanides

The separation factor (SF) of Am from Eu and Nd can be expressed as the ratio of K_{ex}(Am) to K_{ex}(Eu) and K_{ex}(Nd):

$$K_{ex}(Am)/K_{ex}(Eu) = 5.9 \times 10^3 \quad (7)$$

$$K_{ex}(Am)/K_{ex}(Nd) = 2.5 \times 10^3 \quad (8)$$

[1]HA denotes HBTMPDTP, it is dimerized in a non polar diluent.

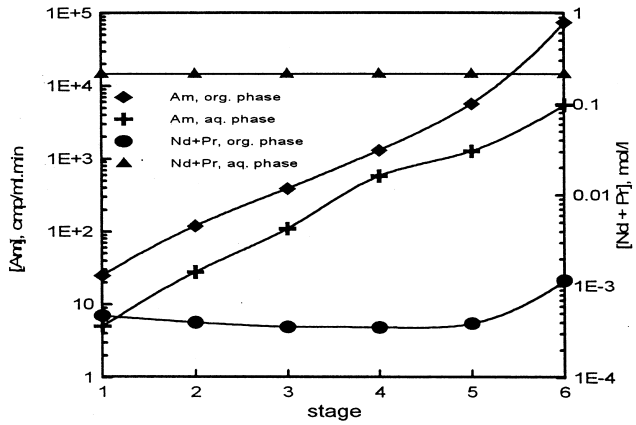

Fig. 3. The distribution of Am, Ln in each stage.

For investigating the possibility of applying HBTMPDTP to the treatment of actual HAW, the separation factors were determined in solutions containing 0.1–0.6 mol/l $Ln(NO_3)_3$ [4]. The SF calculated from the experimental results are:

$$SF(Am/Eu) = 4.5 \times 10^3$$

$$SF(Am/Pr + Nd) = 2.0 \times 10^3$$

The application of HBTMPDTP to separate Am from Ln was proven by the multistage countercurrent extraction experiment (Fig. 3).

The results of the countercurrent extraction experiment indicated that a simple six-stage extraction can separate >99.99% Am from lanthanides and >99% lanthanides from Am.

3.3. Absorption spectra of Am-HBTMPDTP and Nd-HBTMPDTP complexes [5]

The measured absorption spectra of Am-HBTMPDTP and Nd-HBTMPDTP complexes are shown in Fig. 4 and Fig. 5, respectively.

The red shift in the spectra of Am-HBTMPDTP is 11 nm (from 501 nm to 512 nm) and 18 nm (from 575 nm to 593 nm) for Nd-HBTMPDTP. The molecular absorption coefficient increases by 38 l mol^{-1} cm^{-1} for the Nd complex and by more than 100 l mol^{-1} cm^{-1} for the Am complex. The absorption spectra of four kinds of coordination configurations for the Am complex and the Nd complex were calculated by use of the calculation program developed at INET [2]. The calculated results were given in the form of spectra diagrams. By comparing the calculated spectra with the measured ones, it can be deduced that the most probable inner coordination of both extraction complexes are 8-sulfur coordinated cubic symmetries.

4. Conclusion

1. Am^{3+} and Ln^{3+} can be extracted from nitrate solution in the form $AmA_3(HA)$ and $LnA_3(HA)$ by HBTMPDTP/kerosene. The apparent extraction equilibrium constants are $10^{-7.78}$, $10^{-11.47}$ and $10^{-11.18}$ (at 25°C) for Am, Eu and Nd, respectively.
2. Am-HBTMPDTP complex and Nd-HBTMPDTP complex are both 8-sulfur coordinated cubic symmetries.
3. HBTMPDTP is an excellent extractant for separating Am from lanthanides in nitrate solution.

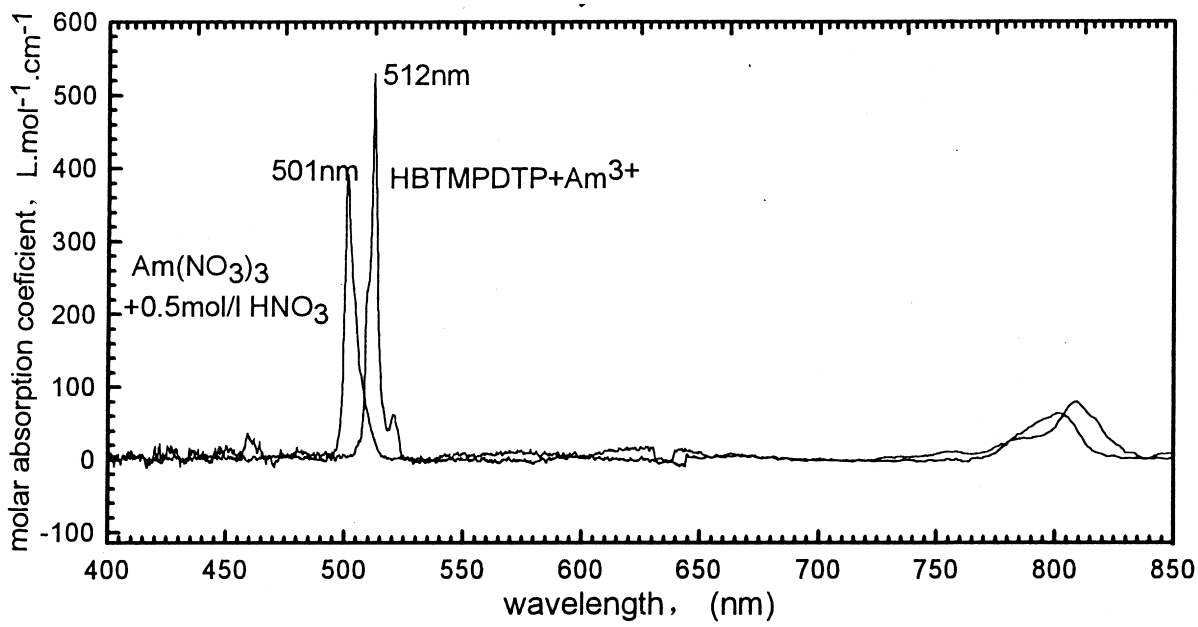

Fig. 4. Absorption spectrum of the Am-HBTMPDTP complex.

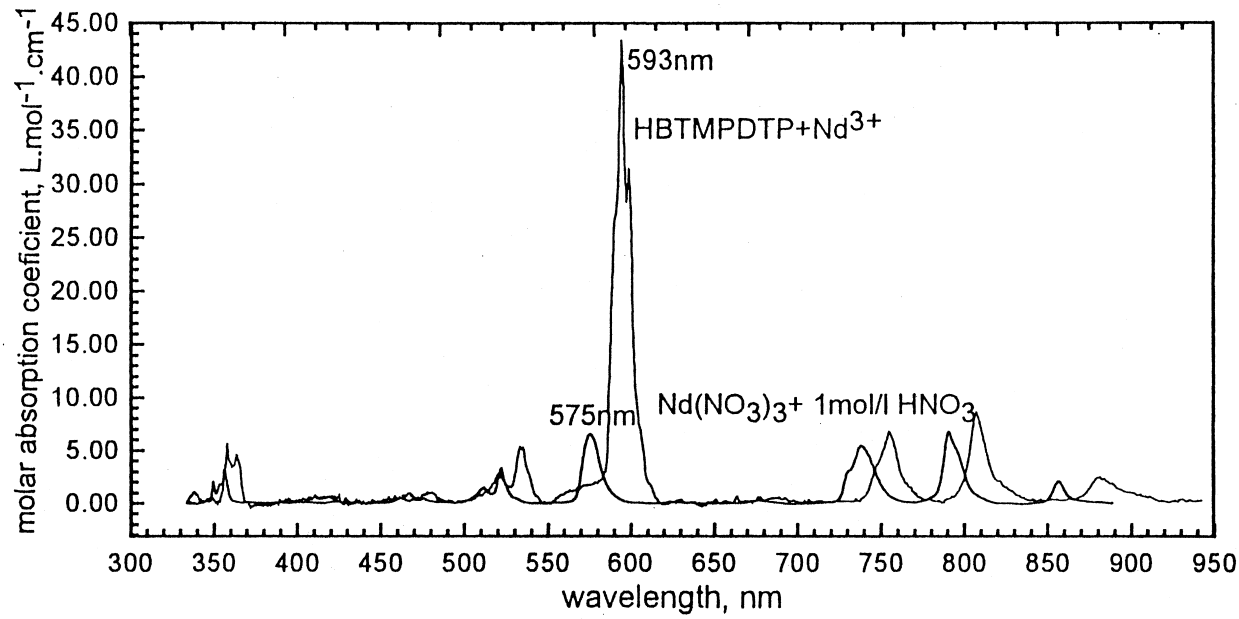

Fig. 5. Absorption spectrum of the Nd-HBTMPDTP complex.

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