Inorganica Chimica Acta, 94 (1984) 189–191

Extraction of Np(IV), Pu(IV) and Am(III) by Bidentate Organophosphorus Extractant

ZHAO HUGEN, YE YUXING, YANG XUEXIAN and LIN ZHANGJI

Institute of Atomic Energy, P.O. Box 275, Beijing, China

Received October 5, 1983

This paper summarizes the extraction of Np(IV), Pu(IV) and Am(III) with dihexyl-N,N–diethyl carbamyl methylene phosphonate (DHDECMP)–diethyl benzene (DEB) in nitric acid.

The distribution ratio of Np(IV), Pu(IV) and Am(III) was studied as a function of a number of parameters such as concentration of nitric acid, salting-out reagent in the aqueous phase, contact time and temperature. Stripping and separation of Np(IV), Pu(IV) and Am(III) from the pregnant organic phase were also studied. The suitable stripping and separation conditions were obtained. The enthalpy changes ΔH_{Np}, ΔH_{Pu}, ΔH_{Am} associated with their extraction process were estimated individually. The composition of extracted complex of Np(IV), Pu(IV) and Am(III) was determined.

Introduction

Since the synthesis of several multifunctional organophosphorus compounds was published by Siddall in the early 1960's [1, 2], many scientists have been using these compounds as new extractants. Some of them can selectively extract actinides and lathanides from acidic wastes. This kind of extractant exhibits great potential in nuclear waste treatment. Up to now, some conceptual flowsheets have been put forward for the removal of actinides from acidic wastes [3–6]. The developments of these processes have reached the pilot plant scale [7, 8].

In order to put forward a conceptual flowsheet for removal and recovery of actinides and lathanides from acidic nuclear wastes we studied the extraction of Am(III), Nd(III) and HNO_3 by bidentate extractant, dihexyl-N,N–diethyl carbamyl methylene phosphonate (DHDECMP) in diethyl benzene (DEB) [9], while we have not found any systematic information published about extraction chemistry of neptunium and plutonium. We have also studied the extraction of Np(IV) and Pu(IV) by DHDECMP–DEB from nitrate medium and separation of Am(III) from Np(IV) and Pu(IV) respectively. The results are summarized in this paper; the data for Am(III) are quoted from reference [9].

Experimental

Materials and Instruments

a) DHDECMP: the source was the same as that described in [9].

b) ^{239}Np and ^{239}Pu tracer: the nuclides, radiochemically pure, were provided by our institute.

c) A well-type NaI(Tl) scintillation gamma counter and ZnS(Ag) α-detector were used.

Experimental and Analytical Procedures

The extraction procedure was the same as that described in [9].

The concentration of ^{239}Np in both phases was determined by a scintillation gamma counter. The concentration of ^{239}Pu was determined by a ZnS(Ag) detector.

All distribution ratios have errors of about ±10%.

Results and Discussion

Effect of Contact Time and Temperature

The experiment shows that equilibrium for all extracted species is reached in approximately 30 seconds of contact. The distribution ratios (D) of Np(IV), Pu(IV) and Am(III) decrease with increasing temperature (Fig. 1), while the effect of temperature on D_{HNO_3} is negligible [9]. Consequently, the extraction process of the metallic ions is considered as an exothermic reaction. From the slope in the log D *vs.* 1/T(K) plots and the Van't Hoff equation:

$$\frac{\Delta \log D}{\Delta(1/T)} = \frac{-\Delta H}{2.303R}$$

the enthalpy change ΔH associated with the extraction process were estimated as follows:

$\Delta H_{Np} = -3.7$ Kcal/Mol

$\Delta H_{Pu} = -7.9$ Kcal/Mol

$\Delta H_{Am} = -7.6$ Kcal/Mol.

0020-1693/1984/$3.00

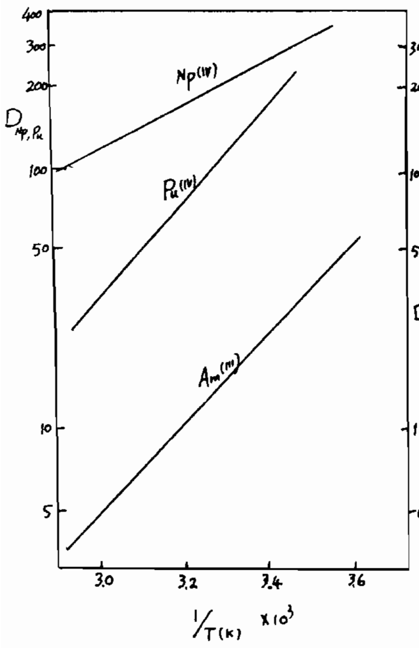

Fig. 1. Effect of temperature on distribution ratio. Condition: Org. phase: 30 vol% DHDECMP–DEB; aq. phase: 3 *M* HNO_3-tracer; phase ratio: O/A = 1; contact time: 5 min.

Effect of Concentration of Nitric Acid

The effect of nitric acid concentration in aqueous phase on D_{Np}, D_{Pu} and D_{Am} is shown in Fig. 2. The distribution ratios of Np(IV), Pu(IV) and Am(III) increase with HNO_3 concentration; it is thus possible to extract these actinides in higher concentrations of nitric acid.

Effect of Concentration of DHDECMP in DEB

The distribution ratios of these elements increase with DHDECMP concentration (Fig. 3).

The logarithmic plots of D_{Np}, D_{Pu} and D_{Am} *vs.* DHDECMP concentration are straight lines with slopes of 2.0, 1.9 and 2.9 respectively. Therefore, extraction reactions for Np(IV), Pu(IV) and Am(III) with DHDECMP can be expressed as

$$M_{aq.}^{4+} + 4NO_{3\,aq.}^{-} + 2DHDECMP_{org.} \rightleftharpoons M(NO_3)_4\cdot 2DHDECMP_{org.}$$

(M = Np, Pu)

$$Am_{aq.}^{3+} + 3NO_{3\,aq.}^{-} + 3DHDECMP_{org.} \rightleftharpoons Am(NO_3)_3\cdot 3DHDECMP_{org.}$$

Effect of Concentration of Salting-out Reagent

The experiment shows that the distribution ratios of Am(III) and Np(IV) increase obviously with concentration of $Al(NO_3)_3$ in aqueous phase (Table I). When the $Al(NO_3)_3$ concentration is equal to 1.5

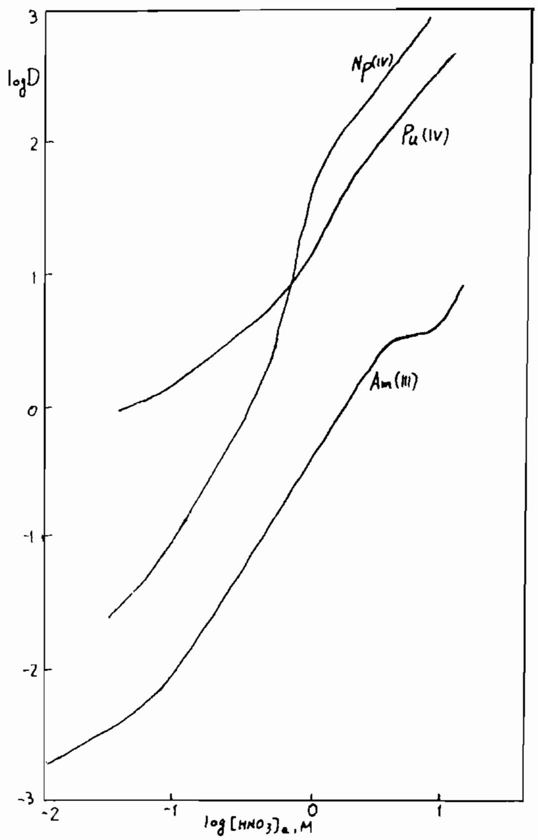

Fig. 2. Acid dependency of Np(IV), Pu(IV) and Am(III) extraction by 30 vol% DHDECMP–DEB. Condition: phase ratio: O/A = 1; contact time: 5 min; temp.: 29 °C.

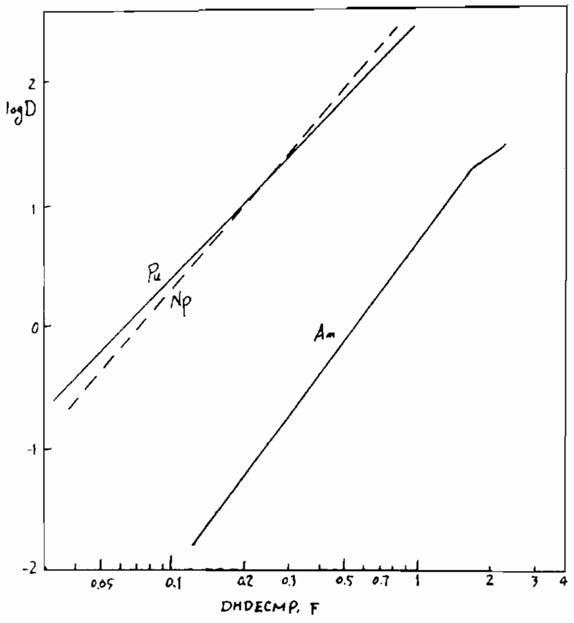

Fig. 3. Log D *vs.* log[DHDECMP]. Condition: aq. phase: 3 *M* HNO_3-tracer; phase ratio: 0/A = 1; contact time: 5 min.; temp. 29 °C.

TABLE I. Effect of Concentration of $Al(NO_3)_3$ on D_{Np} and D_{Am}.

$C_{Al(NO_3)_3}$ (*M*)	Distribution ratio	
	D_{Am}	D_{Np}
0	2.2	2.2×10^2
0.5	3.6	3.2×10^2
1.0	6.9	9.2×10^2
1.5	10	1.1×10^3
2.0	/	1.7×10^3

Org. phase: 30% DHDECMP–DEB; aq. phase: $Al(NO_3)_3$–3 *M* HNO_3-tracer; phase ratio: O/A = 1; contact time: 5 min; temp.: 29 °C.

M in 3 *M* HNO_3 solution, D_{Np} and D_{Am} are 1.1×10^3 and 10 respectively.

Back-Extraction

The stripping conditions of Np, Pu and Am from the organic phase have been investigated: the Am(III) can be recovered quantitatively after stripping twice with 0.01 *M* HNO_3. With (0.05 *M*–0.2 *M*) HNO_3–0.05 *M* $H_2C_2O_4$ for Pu(IV) and Np(IV) to be stripped or with 0.1 *M* HNO_3–0.015 *M* $Fe(NH_2SO_3)_2$ for Pu(IV) to be stripped, the back-extraction is more than 97% after two contacts.

Separation of Americium from Neptunium or Plutonium by Back-Extraction

Experiments show that the Am(III) was quantitatively stripped from the organic phase with 0.05–0.2 *M* HNO_3, while most of the Np(IV) and Pu(IV) remained in the organic phase (Table II). From Table II it can be seen that the separation factor of Am and Np or Am and Pu is more than 50. Consequently, this method may be applied to separating Am from Pu(IV) and Np(IV).

TABLE II. Stripping Data for Am, Np and Pu.

Stripping solution		0.05 *M*. HNO_3	0.2 *M* HNO_3
Back-Extraction Percentage	Am	74	71
	Pu	1.0	1.3
	Np	1.2	1.2
Separation Factor	Am/Pu	74	54
	Am/Np	61	59

Org. phase: 30 vol% DHDECMP–DEB pre-equilibrated with 3 *M* HNO_3 solution containing ^{239}Np, ^{239}Pu and ^{241}Am tracer. Temp.: 30 °C ± 1 °C. Contact time: 5 min.

Conclusion

DHDECMP–DEB solutions can be used to extract Np(IV), Pu(IV) and Am(III) from nitrate media. D_{Np}, D_{Pu} and D_{Am} increase with the concentration of HNO_3 and DHDECMP. The complexes formed in the extraction of metallic ions can be represented as $M(NO_3)_4 \cdot 2DHDECMP$ (M = Np, Pu) and $Am(NO_3)_3 \cdot 3DHDECMP$, respectively.

The enthalpy changes (ΔH) associated with the extraction process were estimated as follows:

$\Delta H_{Np} = -3.7$ Kcal/Mol

$\Delta H_{Pu} = -7.9$ Kcal/Mol

$\Delta H_{Am} = -7.6$ Kcal/Mol.

The separation of Am from Np or Pu can be obtained by back-extraction. The separation factor of Am from Np or Pu is more than 50.

It is possible that DHDECMP–DEB systems can be used directly to recover or remove neptunium, plutonium and americium from acidic nuclear waste solutions containing salts, requiring neither prior denitration nor neutralization.

Acknowledgements

The authors thank Professor Wang Dexi for his advice, and Mr. Zhu Changen for providing DHDECMP.

References

1 T. H. Siddall, *J. Inorg. Nucl. Chem., 25(7)*, 883 (1963).
2 *Ibid., 26(11)*, 1991 (1964).
3 W. W. Schulz and L. D. McIsaac, *USAEC ARH-SA*, 217 (1975).
4 *Ibid., USAEC ARH-SA*, 263 (1977).
5 L. D. McIsaac, J. D. Baker and J. W. Tkachyk, *USAEC ICP-* 1080 (1975).
6 J. D. Navratil, L. L. Martella and G. H. Thompson, *Am. Chem. Soc. Symp. Ser. 117, 'Actinide Separations'*, 445 (1980).
7 H. R. Maxey, D. B. Chamerlain, L. D. McIsaac and G. J. McManus, *ISEC' 80*, 80–193 (1980).
8 J. D. Navratil, L. L. Martella and G. H. Thompson, *ISEC' 80*, 80–106 (1980).
9 Zhao Hugen, Ye Yuxing and Yang Xuexian, *Pro. Int. Symp.: Actinide recovery from waste and low-grade sources*, New York, Aug. 1981, 227–244 (1982).