Study on Selective Separation of Uranium by N,N-dialkylamide in ARTIST Process

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Abstract-An innovative chemical separation process (ARTIST: Amide-based Radio-resources Treatment with Interim Storage of Transuranics) was proposed for the treatment of spent nuclear fuel. The main concept of ARTIST process is to recover and stock all actinides (An) and to dispose the fission products (FP). One of the main purposes of this process is selective isolation of uranium. Since the brached alkyl type N,N-dialkyl-monoamides (BAMA) have the steric hindrance on the complexation with metal cations, BAMA can be used to separate An(VI) from An(IV). N,N-di-(2-ethyl)hexyl-2,2-dimethylpropanamide (D2EHDMPA) can recover U(VI) selectively without accumulating Pu(IV) in uranium isolation process. From extraction behavior of Np, D2EHDMPA can extract and separate U(VI) from Np(VI) without reduction from Np(VI) to Np(V) or Np(IV).

INTRODUCTION

N,N-dialkylamides are noted as one of the alternative extractants of tri-butylphosphate (TBP) in the field of nuclear fuel reprocessing (1-8). Extraction behavior of U(VI) and Pu(IV) with N,N-dialkylamides is almost similar to those with TBP. N,N-dialkylamides have some advantages, namely, their complete incinerability (CHON principle) and high stability for hydrolysis and radiolysis. Their main degradation products are carboxylic acids and secondary amines which hardly affect the separation of U(VI) and Pu(IV) from fission products(FP). Further, the synthesis of N,N-dialkylamides is relatively easy. The development of the novel separation method of transuranium elements (TRU) and FP elements is very important task for the management and disposal of radioactive nuclides in the spent nuclear fuel (SF). In our laboratory, the innovative chemical separation process (ARTIST: Amide-based Radio-resources Treatment with Interim Storage of Transuranics) has been proposed, which the process is organized by the solvent extraction techniques(9-13). The mutual separation of U, TRU and FP is included into the schematic diagram of ARTIST process, and our goal is to establish the simple process for the treatment of SF. One of the main steps of ARTIST is the isolation of uranium from SF by BAMA (branched alkyl monoamide). Uranium is the principal ingredient of SF, and isolation of U can simplify the following process for the recovery of TRU. The BAMA extractants have steric hindrance on the coordination with actinide 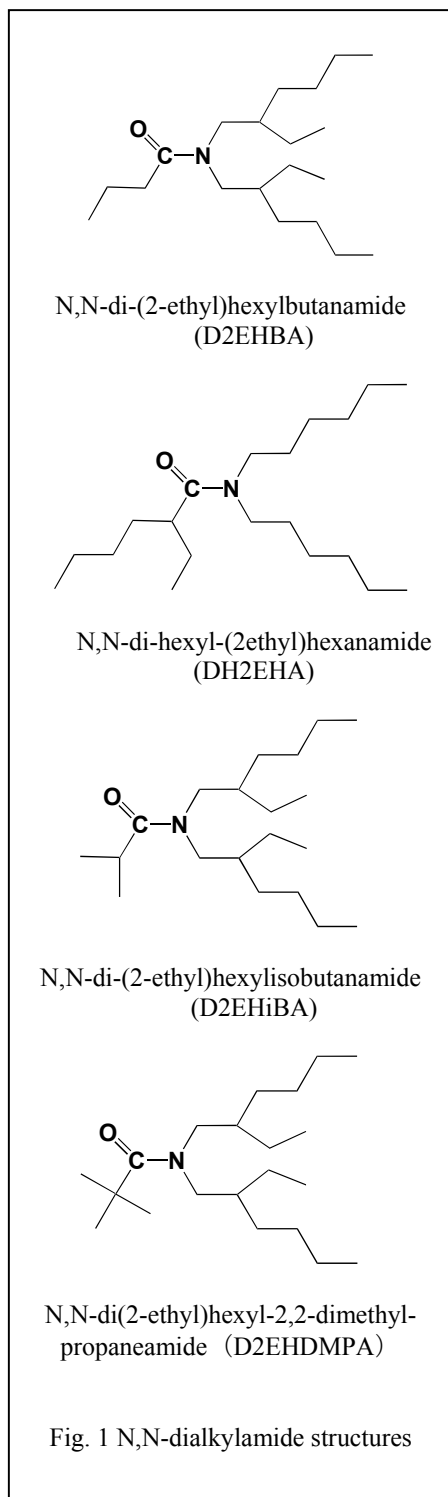ions, which gives higher distribution coefficient of U(VI) than that of Pu(IV). In this paper, the extraction behavior of U(VI), Pu(IV), Np(IV) and Np(VI) by several kinds of BAMA is reported.

EXPERIMENTAL

Chemicals

Four kinds of branched N,N-dialkylamides: N,N-di-(2-ethyl)hexylbutanamide(D2EHBA), N,N-di-hexyl(2-ethyl)hexanamide(DH2EHA), N,N-di-(2-ethyl)hexylisobutanamide(D2EHiBA) and N,N-di-(2-ethyl)hexyl-2,2-dimethylpropane-amide (D2EHDMPA) were synthesized, and the synthetic method in the literature was used to all runs(8). The carboxylic chloride reacted with the secondary amine dissolved in chloroform under $0\ ^{o}C$, and tri-ethylamine as a scavenger of chloride was also added in the glass reactor. The mixture was stirred for several hours, and then the sample was washed with water, $1.0\ mol/dm^3$ HCl and $1.0\ mol/dm^3$ NaOH in order to remove mainly the quaternary ammonium salt and the initial materials. The organic samples obtained were purified by distillation under vacuum. All amide compounds were identified by NMR (UNITY plus 400, Varian), FT-IR (FTS-135, BIO-RAD), Liquid Chromatography (LC-7100, HITACHI) and Gas Chromatography (GC-14A, SHIMADZU). The high degree of purity of these N,N-dialkylamides was confirmed by the gas chromatography: D2EHBA, 100%; DH2EHA, 99.7%; D2EHiBA, 97.0%; D2EHDMPA, 99.7%, respectively. The structures of used BAMA are shown in Fig. 1. Other chemicals were in analytical grade and used as received. The radioactive tracers of ^{233}U, ^{238}Pu and ^{237}Np were obtained from Sceti

Company Ltd. Np(IV) and Np(VI) were prepared using 0.05 mol/dm³ ferrous and 0.01 mol/dm³ ceric solution in 3.0 mol/dm³ HNO₃, respectively.

N,N-di-(2-ethyl)hexylbutanamide
(D2EHBA)

N,N-di-hexyl-(2ethyl)hexanamide
(DH2EHA)

N,N-di-(2-ethyl)hexylisobutanamide
(D2EHiBA)

N,N-di(2-ethyl)hexyl-2,2-dimethyl-propaneamide（D2EHDMPA）

Fig. 1 N,N-dialkylamide structures

Distribution measurement

Equal volumes of aqueous and pre-equilibrated organic phases containing U(VI) and Pu(IV) were shaken for 10 minutes in a thermostatic atmosphere at 25 ℃ within ±0.1℃. After the equilibration, the system was centrifuged for 5 minutes. The concentrations of metal ions used in the extraction were 8.4×10^{-7} mol/dm³ for U(VI) and 4.2×10^{-12} mol/dm³ for Pu(IV), Np(IV) and Np(VI), respectively. Distribution coefficients ($D_{U(VI)}$, $D_{Pu(IV)}$, $D_{Np(VI)}$ and $D_{Np(IV)}$) of U(VI), Pu(IV), Np(VI) and Np(IV) between N,N-dialkylamide in dodecane and nitric acid solution were determined by measurements of their activities in both phases. Their α-activities were measured by using liquid scintillation counter (Packard, 2700TR/AB) with 5 ml of scintisol EX-H cocktail.

For extraction with macro amounts U(VI), aqueous phase of 0.5 mol/dm³ and 1.0 mol/dm³ U(VI) and 3.0 mol/dm³ HNO₃, and organic phase of 1.0 mol/dm³ and 1.5 mol/dm³ N,N-dialkylamide in dodecane were treated in a similar manner as above.

RESULTS AND DISCUSSION

The distribution coefficients of U(VI) and Pu(IV), $D_{U(VI)}$ and $D_{Pu(IV)}$, between 1.0 mol/dm³ BAMA in n-dodecane and various nitric acid solution are shown in Fig. 2. D_U and D_{Pu} by D2EHBA branching nitrogen alkyl chain are larger than those by DH2EHA branching carbonyl alkyl chain, respectively. This difference is attributed to alkyl chain branching position of R_1 or R_2 in N,N-dialkylamide molecule, $R_1C(O)N(R_2)_2$. U(VI) and Pu(IV) coordinate to D2EHBA or DH2EHA on the position of carbonyl oxygen atom. Branching position of DH2EHA is closer to carbonyl oxygen than D2EHBA branching one in nitrogen alkyl chain. In the previous work on extraction of U(VI) and Pu(IV) by linear alkyl type N,N-dialkyl amide, the D_U value was as same as the $D_{Pu(IV)}$ value(9). However, for the extraction by D2EHBA and DH2EHA, the $D_{Pu(IV)}$ value is smaller than the $D_{U(VI)}$ value. Such behavior as Pu(IV) can be explained on the basis of increased steric hindrance caused by BAMA molecules around Pu(IV) that is already coordinated with nitrate anions. Owing to this steric hindrance, separation factor of $D_{U(VI)}/D_{Pu(IV)}$ with DH2EHA is larger than that
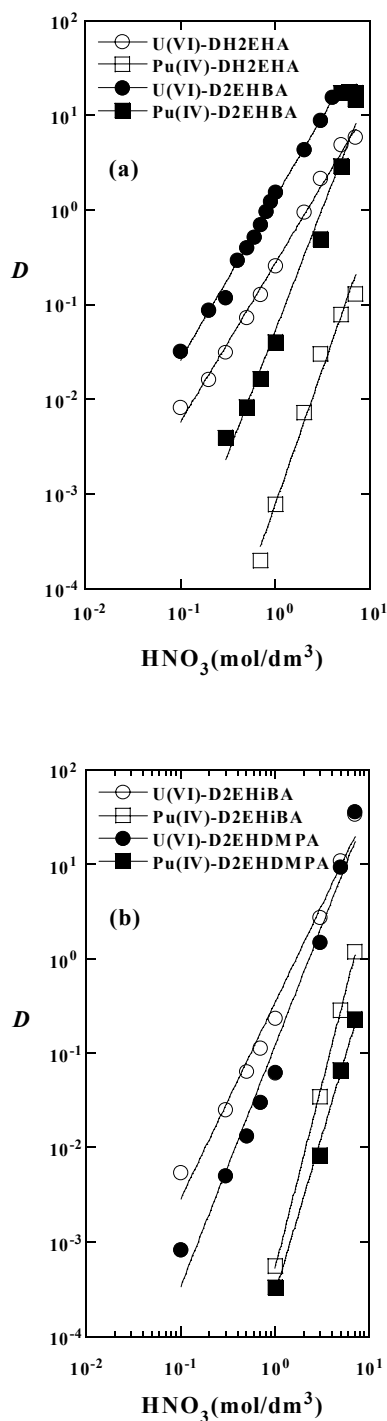
Fig. 2 Nitric acid concentration dependency of D_M on the extraction of U(VI) and Pu(IV) by BAMA in n-dodecane, (a); D_M by D2EHBA and DH2EHA, (b); D_M by D2EHiBA and D2EHDMPA

with D2EHBA, suggesting that for U-Pu separation DH2EHA is more efficient than D2EHBA.

In order to improve separation factor of $D_{U(VI)}/D_{Pu(IV)}$, both carbonyl alkyl chain and nitrogen alkyl chain branched BAMA, D2EHiBA and D2EHDMPA, were used for U(VI) and Pu(IV) extraction. Both $D_{U(VI)}$ and $D_{Pu(IV)}$ values by D2EHDMPA are smaller than those by D2EHiBA. Separation factor of $D_{U(VI)}/D_{Pu(IV)}$ for D2EHDMPA is larger than that for D2EHiBA. These results are also attributed to steric hindrance of the extractant around the metal ion. The magnitude of $D_{U(VI)}$ and $D_{Pu(IV)}$ by each BAMA can be explained from the viewpoint of steric hindrance around carbonyl oxygen atom. From the results of U(VI) and Pu(IV) extraction by several kinds of BAMA, branching of carbonyl alkyl group has an important role of U(VI) separation from Pu(IV). D2EHDMPA is the most appropriate extractant to separate U(VI) from Pu(IV) without chemical reduction from Pu(IV) to Pu(III) like Purex process.

Table1 summarizes $D_{U(VI)}$, $D_{Pu(IV)}$, $D_{Np(VI)}$ and $D_{Np(IV)}$ values by four kinds of BAMA. The magnitude of $D_U(VI)$ is the order of D2EHBA > D2EHiBA > DH2EHA > D2EHDMPA. On the other hand, the magnitude of $D_{Pu}(IV)$ is the order of D2EHBA > DH2EHA > D2EHiBA > D2EHDMPA. Furthermore, the value of $D_{Np(VI)}$ by D2EHDMPA is smaller than 1. This result demonstrates that Np(VI) can be separated from U(VI) by D2EHDMPA without reduction from Np(VI) to Np(V) or Np(IV).

Table1 Comparison of D_{An} by four kinds of 1.0 mol/dm^3 BAMA in n-dodecane. (C_{HNO3}= 3.0 mol/dm^3)

	$D_{U(VI)}$	$D_{Np(VI)}$	$D_{Pu(IV)}$	$D_{Np(IV)}$
D2EHBA	8.85	5.62	1.93	0.26
DH2EHA	1.82	4.19	0.27	<0.01
D2EHiBA	2.73	1.23	0.034	<0.01
D2EHDMPA	1.50	0.79	<0.01	<0.01

The extraction of 0.5 mol/dm^3 and 1.0 mol/dm^3 U(VI) from 3.0 mol/dm^3 HNO$_3$ acid solution by four kinds of BAMA was investigated. Table 2 shows the extracted uranium concentrations in organic phase. D2EHBA, D2EHiBA and D2EHDMPA do not form the third phase except for DH2EHA. Uranium concentrations in organic phase with each 1.0 mol/dm^3 BAMA at 3.0 mol/dm^3 HNO$_3$ were evaluated as 0.50 mol/dm^3 for D2EHBA, 0.35 mol/dm^3 for D2EHiBA and 0.28 mol/dm^3 for D2EHTMAA, respectively.

From the results of U(VI) extraction, bulky BAMA, D2EHiBA and D2EHDMPA, gave good separation factor of U(VI)/Pu(IV) and poor extractability for macro amount of U(VI). To introduce D2EHDMPA to ARTIST process, the extraction condition of 0.5 mol/dm^3 U(VI)-1.5 mol/dm^3 D2EHDMPA is optimum for U(VI) selective separation.

Table2   Extracted U(VI) concentration in organic phases under various extraction conditions. (C$_{HNO3}$= 3.0 mol/dm^3)

(unit:mol/dm^3)

	1.0 mol/dm^3 BAMA		1.5 mol/dm^3 BAMA	
	0.5 mol/dm^3 U(VI)	**1.0 mol/dm^3 U(VI)**	**0.5 mol/dm^3 U(VI)**	**1.0 mol/dm^3 U(VI)**
D2EHBA	0.32	0.50	0.40	0.64
DH2EHA	0.31	Third phase	0.39	Third phase
D2EH iBA	0.24	0.35	0.32	0.50
D2EH DMPA	0.20	0.28	0.30	0.46

CONCLUSION
Solvent extraction study of U(VI), Pu(IV), Np(VI) and Np(IV) by four kinds of BAMA was carried out and the following results were obtained.
Four kinds of BAMA show good separation factors for U/Pu. D2EHDMPA can extract and separate U(VI) from Np(VI) without reduction from Np(VI) to Np(V) or Np(IV). From the

results of 1.0 mol/dm^3 U(VI) extraction, D2EHBA, D2EHiBA and D2EHDMPA do not form the third phase, however, D2EHiBA and D2EHDMPA have poor extractability for macro amount of U(VI). To introduce D2EHDMPA to ARTIST process, the extraction condition of 0.5 mol/dm^3 U(VI) - 1.5 mol/dm^3 D2EHDMPA is optimum for U(VI) selective separation.

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