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ARTICLE

Extraction, Separation and Isolation of MA from Ln using Two Extractants (TODGA and ADAAM) and a Masking Agent (DTBA)

Yuji SASAKI [1*], Masashi KANEKO [1,2], Yuta KUMAGAI [1] and Yasutoshi BAN [1]

[1] *Japan Atomic Energy Agency, 2-4 Shirakata, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195, Japan*
[2] *Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka, 560-0043, Japan*

Two extractants, TODGA (TetraOctyl-DiGlycolAmide) and ADAAM(EH) (AlkylDiAmideAMine(2-ethylhexyl)), and a masking agent, DTBA (DiethyleneTriamine-*N,N',N''*-triacetic-*N,N''*-BisAmide), were developed in JAEA. TODGA can extract both trivalent actinides (An) and lanthanides (Ln), DTBA may separate An from Ln (separation factor (SF)= 8.3 for *D*(Nd)/*D*(Am)), and ADAAM(EH) has high separation factor (SF= 6) between *D*(Am) and *D*(Cm). The suitable conditions for the extraction, separation and isolations of Am from Ln have been investigated. In this work, we show the basic information of the extraction behavior of An and Ln using TODGA, DTBA and ADAAM(EH). Using the information on these *D*(M) values, the conditions of batchwise multi-stage extraction was set-up and their experiments were performed. The results of the separations for An/Ln and Am/Cm using the suitable conditions were described.

KEYWORDS: TODGA, DTBA, ADAAM, extraction, separation, actinide, lanthanide

I. Introduction

Partitioning and transmutation (PT) technology is a concept to reduce substantially the environmental burdens and the long-time radioactivity generated as far as nuclear energy utilization.[1,2)] In order to fulfill PT technology, minor actinides separation and recovery are essential for minor actinides (MA) fuel production. Some useful extractants and masking agents were developed in JAEA. TODGA can extract both Ln and An from nitric acid,[3,4)] a masking agent, DTBA, shows the SF of 8.3 for Ln and An separation at pH 1~2,[5,6)] and SF of 6 for Am and Cm separation is obtained by ADAAM(EH) from acidic condition.[7-9)] Using the extractants and the masking agent (**Fig. 1**), it is possible to design a separation process for isolating Am from high level radioactive liquid waste (HLW). In this work, some of the fundamental information on extraction and reverse-extraction by TODGA, DTBA and ADAAM(EH) are studied. From the results, the appropriate conditions for the aqueous and the organic phases at each separation process can be determined. Setting-up the conditions of batchwise multi-stage extractions of An/Ln and Am/Cm separations and performing the experiments, the results are shown.

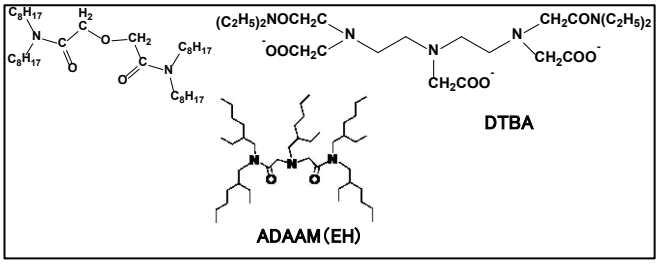

Fig. 1 Structures of TODGA, DTBA and ADAAM(EH)

II. Experimental

The organic phase was prepared by dissolving TODGA or ADAAM(EH) in *n*-dodecane, and the aqueous phase was a solution of pure water from a Milli-Q system (resistivity of 1.82 x 10^7 Ω cm) and HNO_3 with and without DTBA. The purities of three reagents are over 98%. Ethylenediamine (en) was used for pH adjustment and lactic acid is used as pH buffer in pH 1~2. These reagents with the analytical grade obtained commercially are used without further purification. The previous paper reported that en can be used to neutralize the acidity, because two tertiary amino N atoms in en can scavenge protons in the acid.[6)] The organic and aqueous phases were mixed and mechanically shaken at 25°C ± 0.1°C. In this work, no-preequilibrium of the organic phase was taken. After the phase separation, an aliquot of the organic phase including metal ions (1~2 mmol/dm^3(=mM)) was decomposed using $HClO_4$-HNO_3, the residue was dissolved in 0.5 M HNO_3, and the aqueous phase was diluted with 0.5 M HNO_3 prior to the ICP-OES and ICP-MS analysis (SPS3100, Seiko Instruments Inc. and SPQ 9000, Seiko-EG&G). Otherwise, metal concentration in the organic phase is obtained from the subtraction of that of aqueous phase after extraction from the initial value. For the measurements of alpha or beta emitting radioactive nuclides(Tc, Am and Cm), both organic and aqueous phases were mixed in a liquid scintillation cocktail (ULTIMA-gold, 3 ml (=dm^3)), and a liquid scintillation counter (PerkinElmer, Tri-Carb 4910TR) was used to measure their alpha and beta activities. The distribution ratio, *D*, were defined as the metal concentration or radioactivity ratios in the organic ($[M]_{org}$) and aqueous phases ($[M]_{aq}$), $D = [M]_{org} / [M]_{aq}$.

*Corresponding author, E-mail: sasaki.yuji@jaea.go.jp

III. Results and Discussion

1. Metal Extraction by TODGA

It is well-known that TODGA can extract An ions strongly.[3,4] Extraction behavior of fission products (FP) and An by TODGA are shown in **Fig. 2**, the *D* values are plotted against HNO_3 concentration. From this figure, the *D* values for trivalent and tetravalent An are increased with HNO_3 concentration and reached to over 100 or 1000 from acidic condition. In addition, Sr(II), Pd(II), Tc(VII), Y(III) and Zr(IV) as well as Ln(III) show the relatively high *D* values, and the *D* values seem to increase with increasing concentration of acid. The role of TODGA extractant is complete extraction of Ln and An in this separation process, whose concentrations in HLW are approximate 100 mM by ORIGEN-2 calculation,[10] thus higher concentration of more than 0.3 M is requested as the TODGA concentration.

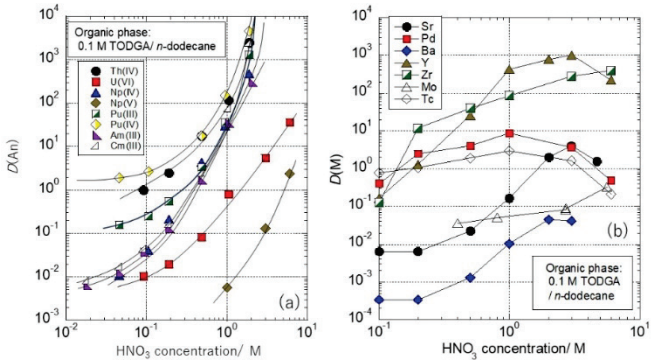

Fig. 2 Extraction behavior of An(a) and FP(b) by TODGA plotted against HNO_3 concentration

2. Separation of Ln/An in TODGA-DTBA System

The masking agent, DTPA (diethylenetriamine-*N,N',N',N'',N''*-pentaacetic acid), is available in TALSPEAK process for An/Ln separation.[11,12]. One of the problems in the use of DTPA for the separation of An/Ln is low solubility in water. Therefore, we improved DTPA and produced DTBA. DTBA has two amide and three carboxylic acid groups in its structure and can be synthesized from the reaction of DTPA anhydride and diethylamine. The advantages of DTBA are the high solubility in water and the strong complexation ability with An at low pH condition.[13] **Figure 3** illustrates Ln-patterns (*D*(Ln) against their atomic numbers) with

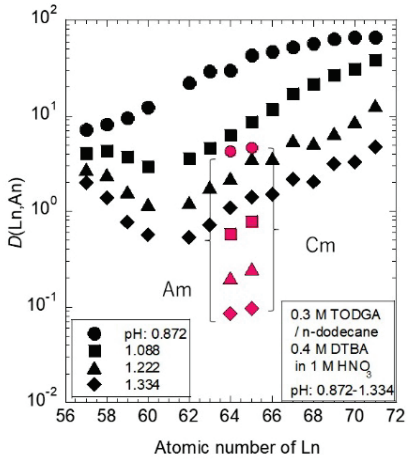

Fig. 3 Ln patterns with Am and Cm data in TOD GA-DTBA extraction system

D(An) in TODGA-DTBA extraction system. These patterns show that in the pH range 1.1~1.3, *D*(Am) and *D*(Cm) were relatively low and less than 1 together with *D*(Nd) and *D*(Sm) over 1, which indicates DTBA affects *D*(Ln) and *D*(An) at these pH conditions. The previous papers suggested the SF value of 8.3 for *D*(Nd)/*D*(Am) in this condition.[5] The reason for the reported high SF(Ln/An) was attributed to higher stability constants of DTPA (and DTBA) for An rather than for Ln.[12] Considering the practical separation by multi-stage extractions, *D* values for all Ln should be over 1 with *D*(An) values under 1, and thus pH condition for An/Ln separation might be better within 1.088~1.222, if the extraction condition in Fig. 3 is taken.

3. Batchwise Multi-Stage Extractions for An/Ln Separation

After co-extraction of Ln and An by TODGA, we examine back-extraction of only An with keeping Ln in the organic phase by batchwise multi-stage extractions using TODGA-DTBA system. The condition of batchwise multi-stage extractions is shown in **Fig. 4**, which includes nine stages of organic phase (0.5 M TODGA) and three stages of feed and six stages of scrub solutions (0.25 M DTBA-0.5 M lactic acid-0.43 M HNO_3-pH 1.15). After all extractions, the Ln yields were determined and the results are listed as follows: La: 0.32, Ce: 0.79, Pr: 2.35, Nd: 3.18, Sm: 2.59, Eu: 1.32, Gd: 0.7% in aqueous phase, and La: 99.7, Ce: 99.2, Pr: 97.7, Nd: 96.8, Sm: 97.4, Eu: 98.7, Gd: 99.3% in organic phase.[6] The experimental result for 98.7% Am is retained in the aqueous phase, so it might be successful separation between Ln and An through this experiment. It is noted that the pH condition should be kept stable during multi-stage extraction, otherwise the recovery ratio in each phase can easily change.[6] After separation of An/Ln, Ln remaining in the organic phase can be stripped easily by the aqueous conditions of the same reagent concentrations as that used in this separation process with higher pH, TEDGA or EDTA solution.[9]

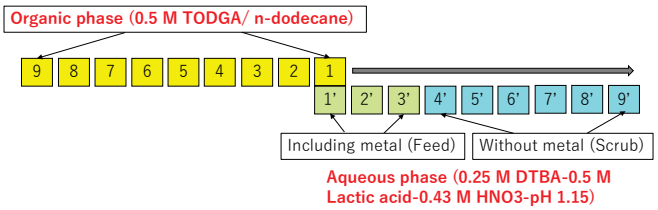

Fig. 4 Conditions of batchwise multi-stage extraction for An/Ln separation

4. Separation of Am/Cm by ADAAM(EH)

The extractant, ADAAM(EH), has the unparallel feature to show the high SF of Am/Cm on acidic condition. The chemical structure of ADAAM(EH) is similar to MIDOA (methylimino-*N,N'*-dioctyl-acetamide)[14], but all of alkyl chains attached with amidic and amino N atoms are 2-ethylhexyl groups. Due to the steric hindrance, not only Am and Cm but also light and middle Ln indicate the high SF. **Figure 5** shows the *D*(Ln) and *D*(An) against HNO_3 concentration, the *D* values increased with increasing HNO_3 concentration until it reached about 1.5 M. After that, further increase in HNO_3 concentration resulted in decrease of *D*

value. As shown in Fig. 5(a)(b), SF for La/Gd, Nd/Sm, and Am/Cm are largely over 1000, over 10, and approximate 6, respectively[9]. It should be noted that ADAAM(EH) having soft N donor atom shows the relatively high *D* and SF for Ln and An, and it can be achieved that the separation of Am and Cm at acidic condition without any masking agents. Based on these results, the conditions of aqueous and organic phases should be determined as 1~1.5 M HNO_3 and 0.1~0.5 M ADAAM(EH) to obtain *D*(Am) >1 with *D*(Cm) < 1 for practical separation by multi-stage extractions.

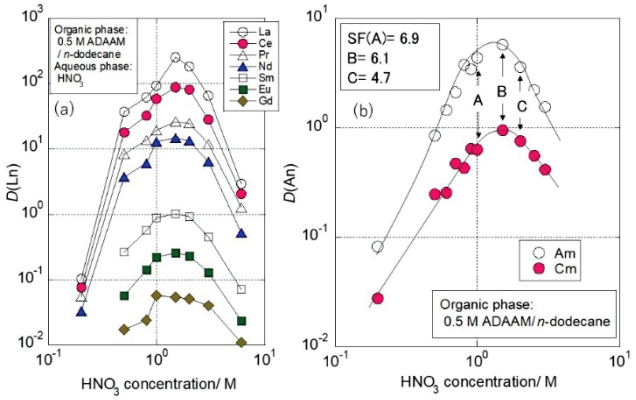

Fig. 5 *D*(Ln)(a) and (An)(b) values by ADAAM(EH) plotted against HNO_3 concentration

5. Batchwise Multi-Stage Extractions for Am/Cm Separation

Considering SF= 6 for Am/Cm, Am/Cm separation requires more stages in the batchwise multi-stage extractions, compared to An/Ln separation. Eleven stages of organic phase (0.2 M ADAAM(EH)/n-dodecane) and three stages of feed and nine stages of scrub solution (1.5 M HNO_3) were set-up (Fig. 6), and it became totally 22 stages of extractions. After all extractions, recoveries of Am and Cm in the organic phase are 96.5 and 1.06 % respectively.[9] The good separation of Am/Cm is achieved. After separation of Am/Cm, Am in the organic phase can be stripped easily by the aqueous conditions of TEDGA or EDTA solution, thus the organic phase can be reused.

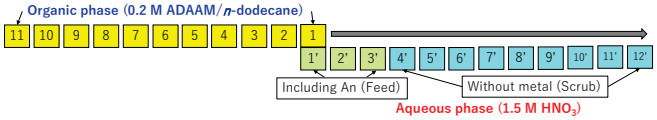

Fig. 6 Conditions of multi-stage extraction for Am/Cm separation

IV. Conclusion

JAEA developed two extractants of TODGA and ADAAM(EH) and one masking agent of DTBA. The specific feature of each TODGA, ADAAM(EH) and DTBA owns the simultaneous extractions of Ln and An, a high SF of Am/Cm from nitric acid, and a high SF of Ln/An at pH 1~2, respectively. By effective combination of these reagents through the separation processes, Am can be isolated from HLW. Low impurities in Am fraction, less separation steps, and less liquid wastes generated at all processes will be the subsequent goals.

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