High-Performance Alkyl Diamide Amine and Water-soluble Diamide Ligand for Separating of Am(III) from Cm(III)

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Alkyl diamide amine (ADAAM), a new high-performance reagent with a simple structure, was examined for the mutual separation of Am(III) and Cm(III). The combination of ADAAM and N,N,N′,N′-tetraethyldiglycolamide (TEDGA) as a masking agent shows selectivity for Am(III) over Cm(III) in highly acidic media with separation factors of up to 41.

Keywords Minor actinide, Am(III), Cm(III), soft N-donor, hard O-donor, masking agent

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Introduction

High-level liquid radioactive waste contains minor actinides (MAs; Np, Am, and Cm) that account for its major long-term radiotoxicity. Japan Atomic Energy Agency (JAEA) has been developing partitioning and transmutation systems since the 1970s. The partitioning and transmutation strategy aims to minimize the long-term radiotoxicity by separating these elements (partitioning) and fissioning them to short-lived or eventually stable nuclides (transmutation). Such transmutation would greatly reduce the mass of MAs in a geological repository and increase the effective capacity of each repository. JAEA has been developing the technique of transmutation using an accelerator driven system (ADS). In an ADS, the separation of trivalent Am (Am(III)) and trivalent Cm (Cm(III)) from the chemically similar trivalent lanthanides (Ln(III)) is the key step. If possible, after Am(III) and Cm(III) are separated from Ln(III), additional refinement, including the separation of Am(III) and Cm(III) (Am(III)/Cm(III) separation), should be conducted. In an ADS, removing the pyrogenic nuclide Cm(III) would reduce the difficulties in MA fuel fabrication. However, Am(III)/Cm(III) separation is one of the most difficult because of the very similar chemical properties of the atoms, which possess the same charge and ionic radius. The separation of these two closely related MAs is even more challenging than that of MA(III) and Ln(III). Although various ligands and separation methods have been studied for the Am(III)/Cm(III) separation, an effective approach for practical use has not yet been developed.

A highly practical reagent, called alkyl diamide amine (ADAAM), was developed. ADAAMs can function as mixed tridentate ligands by using the central soft N-donor atom and the two hard O-donor atoms on the central frame. In the present study, four types of ADAAMs were examined for the solvent extraction of Am(III), whose structures are shown in Fig. 1. Among the four ADAAMs, the one with the largest distribution ratio of Am(III) (D Am) was further examined for the mutual separation of Am(III) and Cm(III). In addition, by employing either as water-soluble masking agents, improved separation of Am(III) from Cm(III) can be expected.

Experimental

Reagents and chemicals

ADAAMs and N,N,N′,N′-tetraethyldiglycolamide (TEDGA) used as the extractants were synthesized by Chemicrea Inc. (Tokyo, Japan). The radioactive isotopes Am(III) and Cm(III)
were purchased from Japan Radioisotope Association (Tokyo, Japan). Nitric acid (HNO₃) was purchased from Wako Pure Chemical Industries. Special-grade n-dodecane (Tokyo Chemical Industry Co., Ltd.) was used as the organic diluent.

**Extraction procedure**

All solvent-extraction experiments were carried out at 298 K. An organic phase was prepared by dissolving the relevant ADAAM in n-dodecane after pre-equilibrating it with the same concentration of HNO₃ used in the following extraction experiments. A certain volume (2 mL) of the organic phase was taken in a stoppered glass tube together with an equal volume of an aqueous nitric acid solution spiked with a radioactive MA(III) solution. The concentrations of metal ions used in the extraction experiment were sub ppb-level for MA(III). The extraction tube, filled with the two phases, was shaken mechanically for 10 min in a shaking device to attain equilibrium. After centrifugation and separation of the phases, the concentrations of Am(III) and Cm(III) in the aqueous and organic phases were measured using an α-silicon semiconductor detector (Alpha Ensemble SEIKO EG&G Co., Ltd.). The distribution ratio of Am(III) (D₃m) and D₃m were calculated as the ratios of the rate of α-activity in the organic phase to that in the aqueous phase for the two radionuclide metal ions. The selectivity of Am(III) over Cm(III) was expressed by a separation factor (SF₃m/Cm = D₃m/D₃m). Solvent extraction experiments in which the aqueous phase contained TEDGA were conducted using the same method.

**Results and Discussion**

The four ADAAMs shown in Fig. 1 were used to extract Am(III) from nitric acid to n-dodecane. The effect of the ADAAM concentration on the extraction of Am(III) from HNO₃ is shown in Fig. 2. The extraction conditions were fixed at 1.5 M HNO₃ and 0.02 - 0.3 M ADAAMs in n-dodecane. Among the four ADAAMs, ADAAM(2EH, N(2EH)) (Fig. 1a) provided the largest D₃m, and was chosen for further examination; this is hereafter referred to as ADAAM(EH). The increase in D₃m was caused by bulky 2-ethylhexyl alkyl chains with amide N atoms; furthermore, the 2-ethylhexyl chain bound to the central N atom increased D₃m more effectively than the n-octyl chain. Details of the effects of alkyl chains will be provided in a forthcoming paper.

The separation of Am(III) from Cm(III) using ADAAM(EH) was investigated; Fig. 3 shows the dependences of D₃m and D₃m on [ADAAM(EH)]_org at 1.5 M HNO₃ solution. The D₃m and D₃m values increased linearly with increasing [ADAAM(EH)]_org, and the value of the slopes of the lines was approximately one for both D₃m and D₃m. In addition, the D₃m values were higher than those of D₃m, and the maximum SF₃m/Cm value obtained was approximately 5.5. Thus, one ADAAM(EH) molecule coordinated with one MA(III). ADAAM(EH) is a molecular organic ligand that can be used for extracting metal ions, similar to diglycolamide. A logarithmic plot showing a slope of one indicates the extraction of metal ions as follows:

$$\text{MA}^{n+} + \text{ADAAM(EH)} + 3\text{NO}_3^{-} \rightleftharpoons \text{MA}^{(\text{ADAAM(EH)})\text{(NO}_3^3\text{)}_{\text{org}}}}.$$  (1)

The dependence of the D₃m and D₃m values on the concentration of [HNO₃]_aq at [ADAAM(EH)]_org = 0.2 M in n-dodecane is shown in Fig. 4. The SF₃m/Cm values are high, up to a maximum of 5.5. The values of D₃m and D₃m increase as [HNO₃] increases from 0.1 to 1 M, peaking at this value; upon further increasing the [HNO₃] to 5 M, the D₃m and D₃m values decrease drastically. The nitrogen donor atoms are likely protonated at high H⁺ concentrations, causing a decrease in the D₃m and D₃m values. The decrease in D₃m through N-donor protonation can be indicated by the following equilibrium (2):

$$\text{MA}^{(\text{ADAAM(EH)})\text{(NO}_3^3\text{)}_{\text{org}}} + \text{H}^{+} \rightleftharpoons \text{H}^{+}\text{(\text{ADAAM(EH)})\text{(NO}_3^3\text{)}_{\text{org}}} + \text{MA}^{n+} + 2\text{NO}_3^{-}.$$  (2)

This unusual graph can be explained by the increase and decrease in D₃m resulting from extraction (1) and protonation (2), respectively. ADAAM(EH) showed an unparalleled extraction ability and selectivity for the separation of Am(III) from Cm(III) in highly acidic media. The variations in the distribution ratios of Ln (D₃m) for

![Fig. 2 Dependence of the distribution ratios of Am(III) as functions of [ADAAM]_aq, for four different ADAAMs at [HNO₃]_aq = 1.5 M.](image)

![Fig. 3 Dependence of the distribution ratio of Am(III) and Cm(III) on [ADAAM(EH)]_org at [HNO₃]_aq = 1.5 M.](image)
ADAAM(EH) and $N,N',N',N'$-tetradoceyldiglycolamide (TDdDGA) (Fig. 5) are illustrated in Fig. 6. ADAAM(EH) shows a gradual decrease in $D$ when moving from light to heavy lanthanides, which is the reverse of the trend observed for TDdDGA. ADAAM(EH) extracts more Am(III) than Cm(III), whereas TDdDGA extracts more Cm(III) than Am(III). Therefore, by employing either as a water-soluble masking agent, improved separation of Am(III) from Cm(III) can be expected, giving a better SF$_{Am/Cm}$ value. TEDGA (Fig. 5) was selected as an effective masking agent for Am(III) and Cm(III), and the distribution ratios of ADAAM(EH) and TEDGA to $D_{MA}$ were investigated. The relationship between SF$_{Am/Cm}$ and the TEDGA concentration at 1.5 M HNO$_3$ and at 0.75 M ADAAM(EH) was shown in Fig. 7. The SF$_{Am/Cm}$ value increases with the increase in the TEDGA concentration, presumably because of the slight preference of TEDGA for Cm(III) in the aqueous phase. The highest SF$_{Am/Cm}$ value, as observed from this figure, is 41, which is one of the highest values reported to date. This result confirms that ADAAM(EH) can preferentially extract Am(III) over Cm(III) from a 1.5 M HNO$_3$ solution with an SF$_{Am/Cm}$ value of 5.5, and TEDGA better masks the harder Cm(III) better than Am(III). Therefore, the SF$_{Am/Cm}$ value is substantially improved, reaching a maximum value of 41, when this masking agent is used. In contrast, water-soluble ADAAMs (e.g., ADAAM(Me, N(Me)) bind strongly to Am(III) as compared to Cm(III)), whereas TDdDGA extracts Cm(III) from Am(III) into the organic phase; therefore, a high SF$_{Cm/Am}$ value can be expected with this combination.

Conclusions

In summary, ADAAM(EH), a new extractant with soft N-donor and hard O-donor atoms, was tested for the extraction of Am(III) from Cm(III) in HNO$_3$ into $n$-dodecane. Am(III) and Cm(III) were separated with high SF$_{Am/Cm}$ values (up to 5.5) from highly acidic solutions (up to 1.5 M HNO$_3$). ADAAM(EH) is a highly practical extractant, which has been reported previously (it is a

![Image](https://example.com/image1.png)

Fig. 4 Dependence of the distribution ratio of Am(III) and Cm(III) on [HNO$_3$]$_{aq}$ at [ADAAM(EH)]$_{org}$ = 0.2 M.

![Image](https://example.com/image2.png)

Fig. 5 Molecular structures of TEDGA as a masking agent and TDdDGA as an extractant.

![Image](https://example.com/image3.png)

Fig. 6 Selectivity for lanthanides using ADAAM(EH) or TDdDGA. [ADAAM(EH)] = 0.5 M; [TDdDGA] = 0.1 M; aqueous phase, [HNO$_3$]$_{aq}$ = 1.5 M or 0.5 M when using ADAAM(EH) or TDdDGA.

![Image](https://example.com/image4.png)

Fig. 7 Distribution ratios of Am(III) and Cm(III) as functions of [TEDGA]$_{aq}$ at [HNO$_3$]$_{aq}$ = 1.5 M in 0.75 M ADAAM(EH).
simple reagent that exhibits good solubility in diluents, clear and fast phase separation, fast extraction and back-extraction kinetics, easy synthesis, and low cost).12

Furthermore, the combination of ADAAM(EH) as the extractant and TEDGA as the masking agent resulted in a marvelous selectivity for Am(III) over Cm(III) with separation factors of up to 41.

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