Separation of Americium(III) from Europium(III) by Dioctylammonium Dioctyldithiocarbamate/Nitrobenzene Extraction

Sunao Miyasita,[1] Makoto Yanaga,[1] Isamu Satoh,[2] and Hideo Suganuma*[1]
[1] *Radiochemistry Research Laboratory, Faculty of Science, Shizuoka University,*
836 Ooya, Suruga-ku, Shizuoka 422-8529
[2] *Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577*

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The extraction of Am(III) and Eu(III) from a nitric medium by dioctylammonium dioctyldithiocarbamate (DOA•DODTC)/nitrobenzene was studied. The separation factor of Am(III)/Eu(III) shows a higher value than the highest one hitherto obtained by a cyanex/kerosene extraction. The high selectivity of a functional group of dithiocarbamate will be contributed to the investigation for the separation of Am(III) from trivalent lanthanoids.

After a recovery of uranium and plutonium in spent nuclear fuel, a high level waste-solution (HLW) contains a variety of radionuclides. If minor actinoids (MA), such as ^{241}Am, ^{243}Am, ^{244}Cm, and so on, can be selectively removed from the HLW, the subject with respect to the HLW processing must be substantially advanced.

The HLW also contains a considerable amount of trivalent rare earth elements (RE). The chemical behavior of the MA(III) is extremely similar to that of trivalent lanthanoids. So, it is very difficult to separate the MA alone from the HLW. In many countries, it is tried to separate the MA from the RE after a collective separation of both groups from HLW.

Typical collective separation methods are a TRUEX process using octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) in U.S.A. and a DIAMEX process using *N*,*N*′-dimethyl-*N*,*N*′-dibutyltetradecylmalonamide (DMDBTDMA) in France. Tachimori et al. found that *N*,*N*,*N*′,*N*′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) is significantly superior to DMDBTDMA.[1] These reagents are able to extract collectively both groups from HLW of about 3 mol/dm^3 HNO_3 aqueous solution and then both the extracted groups are able to be back-extracted into a dilute HNO_3 aqueous solution.

Many investigators have carried out a search for the extractant, which is able to separate selectively MA(III) from RE(III) in the diluted HNO_3 solution. Zhu et al. found that bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) is an appropriate reagent for the separation of both groups (a separation factor of Am(III)/Eu(III) (SF) $= 5.9 \times 10^3$).[2] However, a disadvantage of Cyanex 301 is easy to be oxidized by air. Kolarik et al. obtained 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (DPTP).[3] DPTP also contains defects, a complicating synthesis process of DPTP and an appearance of precipitation in the extraction procedure. Inoue et al. synthesized dithiocarbamate lipophilic chitosan and obtained the SF value of 1.2×10^3 using the extractant.[4]

The object of the present study is to achieve a large SF value in the dilute HNO_3 solution system using a soft extractant synthesized by a simple procedure. From these viewpoints, dioctylammonium dioctyldithiocarbamate (DOA•DODTC) was chosen, though it is generally recognized that dialkyldithiocarbamate ion is unstable in acid solutions.

The DOA•DODTC was synthesized as follows:[5,6] Dioctylamine was dissolved in an ethanol medium and a 25% ammonium solution was added to the solution. Furthermore, carbon disulfide was slowly added into the solution and it was stirred at room temperature for 1 h. The solution was neutralized by a 0.10 mol/dm^3 HCl solution. After the ethanol and the carbon disulfide were removed by evaporation in vacuum, chloroform was added in order to dissolve the synthesized compound. This organic solution was washed with purified water until washing water was neutralized. The organic solution was dried by anhydrous magnesium sulfate and filtered to remove the magnesium sulfate. After the chloroform in the solution was removed by evaporation in vacuum, a yellow viscous liquid was obtained. The liquid was characterized by elemental analysis (Found after 1 week of DOA•DODTC synthesis: C, 70.63; H, 12.85; N, 5.02; S, 10.80%, and Calcd for DOA•DODTC ($C_{33}H_{70}N_2S_2$): C, 70.90; H, 12.62; N, 5.01; S, 11.47%). So, it was treated as the liquid made up of DOA•DODTC.

The solvent extractions of ^{152,154}Eu and ^{241}Am were independently carried out within one week after DOA•DODTC synthesis, based on the following procedures. Aqueous solutions were prepared by mixing a 1.00 mol/dm^3 HNO_3 solution with a 1.00 mol/dm^3 $NaNO_3$ solution. Organic solutions were 0.29 mol/dm^3 DOA•DODTC/nitrobenzene in all extractions. Equal volumes of aqueous and organic solutions were mixed in a vial. After a several μL of trace amounts of ^{152,154}Eu or ^{241}Am dissolved in a 0.10 mol/dm^3 $HClO_4$ solution was added into the vial, it was agitated for 1 h at 298 K. After centrifuged, aliquots from aqueous and organic phases were separated respectively and the radioactivities of the aliquots were measured with a NaI(Tl) scintillation counter.

Figure 1 shows the variation of the distribution ratio (D) of ^{152,154}Eu and ^{241}Am against the hydrogen ion concentration at equilibrium (pH_{eq}) in the aqueous phase. Am(III) is extracted at $pH_{eq} > 5.4$. On the other hand, Eu(III) is extracted at $pH_{eq} > 6.25$. The SF is 2.8×10^4 at $pH = 6.25$. The value is higher than the highest one hitherto obtained by the Cyanex 301 extraction.[2] The value of D of Am(III) and Eu(III) decreases with a decrease of pH_{eq}. In the case of Am(III), the variation of $\log D$ vs pH_{eq} is a convex curve. On the other hand, in the case of Eu(III) appears to be a line of the slope $= +3.5$ or a larger arc convex than the convex curve of Am(III). It is known that an important property of the dithiocarbamate ion is its protonation in acidic solution and the subsequent decomposition into CS_2 and the protonated amine, as a following scheme.[7]

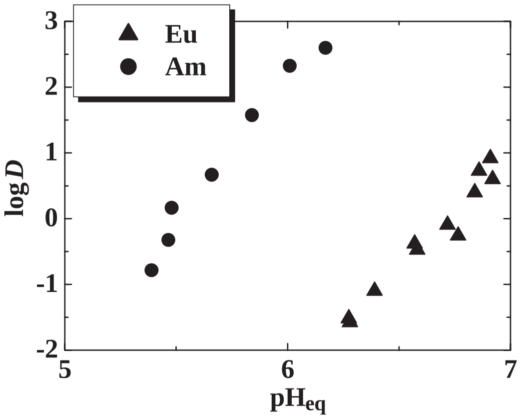


Figure 1. The variation of D of $^{152,154}Eu$ and ^{241}Am against pH_{eq} in aq phase.

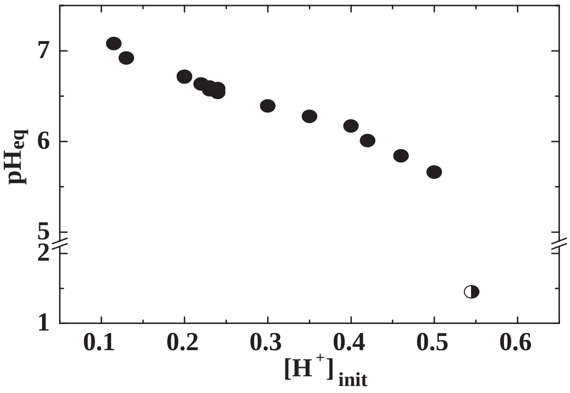
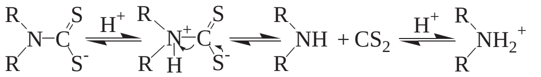


Figure 2. The dependence of pH_{eq} against $[H^+]_{init}$, where the aq phase is 1.00 mol/dm^3 $(H,Na)NO_3$ and the org. phase contains 0.29 mol/dm^3 DOA•DODTC before extraction, when both phases have equal volumes.



$$R_2N{-}C(=S)S^- \underset{}{\overset{H^+}{\rightleftharpoons}} R_2\overset{+}{N}H{-}C(=S)S^- \rightleftharpoons R_2NH + CS_2 \overset{H^+}{\rightleftharpoons} R_2NH_2^+ \quad (1)$$

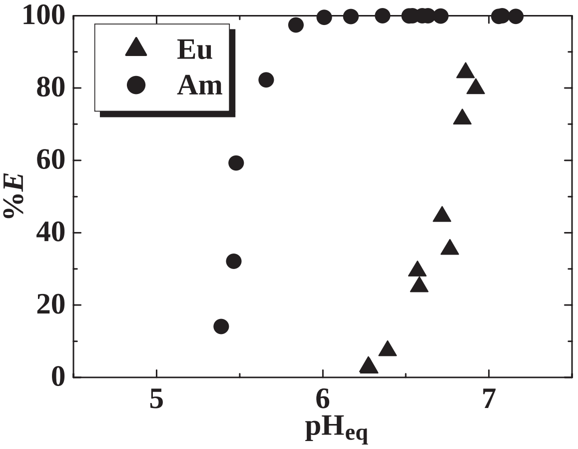


Figure 3. The variation of $\%E$ for $^{152,154}Eu(III)$ and $^{241}Am(III)$ against pH_{eq} in aq phase.

The results in Figure 1 indicate that DODTC ion in aqueous phase is partially destroyed in the region of $pH_{eq} < 7$. In the fact, it was confirmed that the concentration of DOA•DODTC concentration in organic phase, being at equilibrium with the DODTC ion in aqueous phase, is decreased with the decrease of pH_{eq}. So, it is able to conclude that the difference between the variation manner of $\log D$ against pH_{eq} for Am(III) and Eu(III) is also caused by the degree of the change on the DOA•DODTC concentration in the organic phase. The decomposition of DODTC ion significantly affects the pH_{eq}. Figure 2 shows the dependence of pH_{eq} against initial hydrogen-ion concentration ($[H^+]_{init}$) of the aqueous phase, where the aqueous phase is 1.00 mol/dm^3 $(H,Na)NO_3$ and the organic phase contains 0.29 mol/dm^3 DOA•DODTC before extraction, when both phases have equal volumes. The results in Figure 2 imply that the preparation of pH_{eq} is easily controlled by both $[H^+]_{init}$ and the concentration of DOA•DODTC in the organic phase before extraction.

Figure 3 shows the variation of $\%E$ for $^{152,154}Eu(III)$ and $^{241}Am(III)$ against pH_{eq}, derived from the results of Figure 1. The nuclide of $^{241}Am(III)$ is completely separated from $^{152,154}Eu(III)$ in the neighborhood of $pH_{eq} = 6$, in spite of to some extent decomposition of DOA•DODTC and the possibility of hydrolysis effects of Eu(III) and Am(III) in $pH_{eq} > 6$.

In conclusion, we have newly found the extraordinary selectivity of Am(III) over Eu(III) with DOA•DODTC and a simple method for the separation of Am(III) from Ln(III). So, the application of separation of MA(III) by extractants having a functional group of dithiocarbamate is in progress.

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