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Mutual Separation of Actinides from Middle Lanthanides by the Combination of Two Neutral Donors, *N*,*N*,*N*′,*N*′-Tetraoctyl-3,6-dioxaoctanediamide and *N*,*N*,*N*′,*N*′-Tetraethyldiglycolamide

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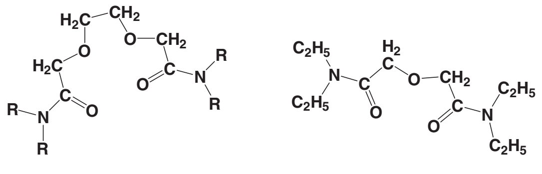
The separation of Am and Cm from Sm, Eu, and Gd was examined by the combination of new extractant, DOODA (*N*,*N*,*N*′,*N*′-tetraoctyl-3,6-dioxaoctanediamide) and masking agent, TEDGA (*N*,*N*,*N*′,*N*′-tetraethyldiglycolamide). DOODA extracts light lanthanides with high *D* values into the organic phase, while TEDGA shows strong complexing ability with middle and heavy lanthanides in the aqueous phase. Americium and Cm behave as light lanthanides in this extraction system, therefore Am and Cm show high separation from middle lanthanides. The separation factors for *D*(Am)/*D*(Sm), *D*(Am)/*D*(Eu), and *D*(Am)/*D*(Gd) are 14.4, 40, and 111, respectively, for 0.3 M DOODA/*n*-dodecane and 10 mM TEDGA/5 M HNO_3. The high separation of Am and Cm from these lanthanides, having high neutron cross section, can be seen in HNO_3–*n*-dodecane in the absence of metal-salt.

In the last few decades, neutral donor extractants for minor actinides (MA) have been developed extensively. Based on the CHON principle, multidentate diamide extractants have been reported from many researchers, not only fundamental but also applicable studies.[1–3] These extractants well extract MA accompanied by lanthanides (Ln). The Ln are troublesome ions, which exist in high concentration in high level radioactive waste (HLW) and show high neutron cross sections. Therefore, the separation of MA from Ln is an important task. Some soft donor extractants show high separation factors, however, the extractants have normally their own complexed structures, and show instability in acid and high radiation field.[4,5] DTPA (Diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid), an aminopolycarboxylic acid, is used in the TALSPEAK (trivalent actinide–lanthanide separations by phosphorus reagent extraction from aqueous complex) and SETFICS (solvent extraction for trivalent-f-elements intragroup separation in CMPO-complexant system) processes as a masking agent of Am and Cm,[6–8] however, DTPA has some disadvantages, namely low solubility in water and the requirement of $NaNO_3$ and pH buffer. We examine the neutral donor for the separation of MA and Ln, which can work in acidic conditions.

N,*N*,*N*′,*N*′-Tetraalkyl-3,6-dioxaoctanediamide (DOODA) is used as the extractant for MA, and *N*,*N*,*N*′,*N*′-tetraethyldiglycolamide (TEDGA) is used as the masking agent of Ln. The structures of DOODA and TEDGA are shown in Figure 1, both reagents are multidentate diamides with podand structures and show high reactivity with MA and Ln. We have focus on the high separation between Ln and MA by using both of extractant and masking agent. DGA has a high complexing ability with middle Ln (m-Ln) and heavy Ln (h-Ln), while DOODA has high *D* values for light Ln (l-Ln), the synergistic effect on mutual separation of all Ln are expected by their combination in a batch experiment. The extraction behavior and separation of Ln and MA in this extraction system is reported in this paper.



DOODA (R: C_8H_{17} or $C_{12}H_{25}$) TEDGA

Figure 1. Structure of DOODA and TEDGA. DOODA(C8): R = C_8H_{17} and DOODA(C12): R = $C_{12}H_{25}$.

The DOODA and TEDGA are synthesized by the following methods.[9,10] DOODA is obtained from the reaction of 3,6-dioxaoctanedioic acid and *N*,*N*-dioctylamine, and TEDGA is synthesized by the condensation of diglycolic anhydride and *N*,*N*-diethylamine. After synthesis, these compounds were purified by silica gel column chromatography twice and purity was confirmed to be over 98% by GC analysis. Solvent extraction was carried out by the following method: 2 cm^3 of the organic phase pre-equilibrated was taken and mixed with the same volume of the aqueous phase, where the radioactive isotopes (Am-241 and Cm-244) or the fourteen Ln elements are dissolved. The mixture of the aqueous and the organic phases was shaken mechanically for 2 h at 25 ± 0.1 °C. After centrifugation, 0.50 cm^3 aliquots taken from both aqueous and organic phases were measured with a liquid scintillation counter (Tri-Carb 1600 TR, Packard Instrument Co.) for α activities in 5 cm^3 of scintillation cocktail. The amounts of Ln ions in the sample solutions prepared from the extraction samples were measured by ICP-MS (SPQ 9000, Seiko-EG&G).

The distribution ratios of all Ln with DOODA(C8) and TODGA (*N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide) plotted against their atomic numbers were shown in Figure 2. Here, the unit of the concentration, mol dm^{-3} is expressed as M in this paper and *D* values are defined as the ratio of metal concentration in the organic phase to that in the aqueous phase ($[metal]_{org}/[metal]_{aq}$). The *D* values of Ln for TODGA are higher than those for DOODA(C8) at the same condition. As shown in Figure 2, the patterns of *D*(Ln) by TODGA and DOODA(C8) with the atomic numbers show a different trend. It is well-known that the charge densities of Ln(III) increase gradually from La to Lu. TODGA has high *D* values for Ln with high charge density, on the other hand, DOODA(C8) has high *D* values for Ln having large ionic radii. The previous paper suggested that the *D* values of Am and Cm are similar to those of l-Ln,[11] so the combination of DOODA and DGA is expected to expand the separation factor between minor actinides and m- and h-Ln.

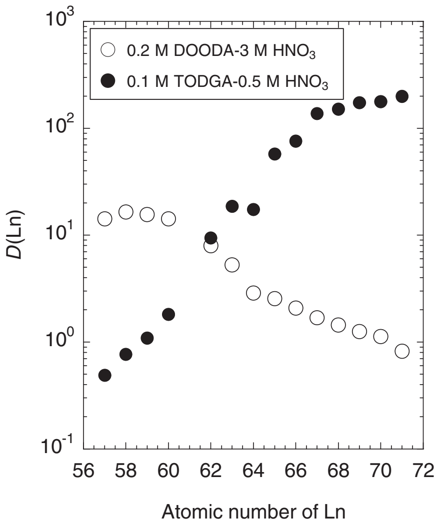


Figure 2. D(Ln) against their atomic number for DOODA and TODGA extraction. Conditions of DOODA(C8) extraction: aqueous phase, 3 M HNO_3; organic phase, 0.2 M/n-dodecane; TODGA extraction: aqueous phase, 0.5 M HNO_3; organic phase, 0.1 M/n-dodecane.

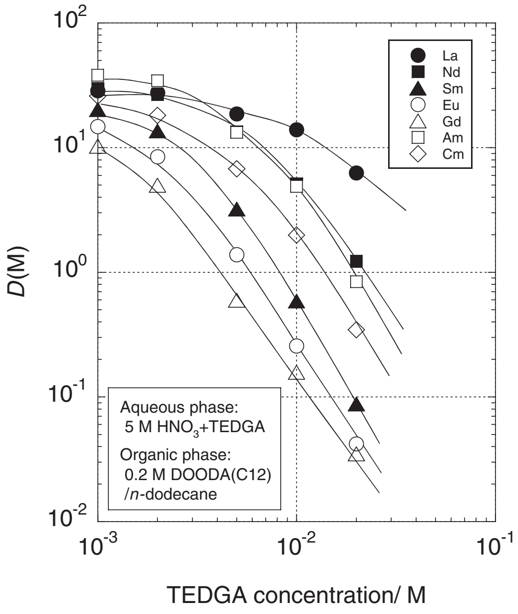


Figure 3. Variation of overall D(Ln) with DOODA extraction in the presence of TEDGA.

Table 1. D values of Ln(III) and An(III) and their separation factors (SF)

	Concentration/M			D(M)	SF	
	DOODA(C12)	HNO_3	TEDGA		Am/Ln	Cm/Ln
Sm	0.2	5	0.01	0.59	8.3	3.39
Eu				0.26	18.8	7.69
Gd				0.16	30.6	12.5
Am				4.9		
Cm				2.0		
Sm	0.3	5	0.01	0.50	14.4	3.8
Eu				0.18	40	10.6
Gd				0.15	111	29.2
Am				8.8		
Cm				3.6		
Sm	0.3	5	—	51.6	0.93	0.653
Eu				39.1	1.23	0.862
Gd				28.5	1.18	1.18
Am				48		
Cm				33.7		

The variation of D(Ln) against TEDGA concentration is shown in Figure 3. Here, we use both of extractants, DOODA(C8) and -(C12), these extractants have the same central frame and are well-soluble in n-dodecane. This figure shows gradual decrease of D(La, Nd) from 2 to 5 mM TEDGA. On the other hand, D(Sm, Eu, Gd) start decreasing clearly from 1 mM TEDGA. Concerning this, the behavior of Am is similar to Nd, which suggests the high separation of Am from Sm, Eu, and Gd. The behavior of D(Cm) is between Nd and Sm, probably most similarly to Pm. These results would be in good correlation with their ionic radius, the ionic radii are 98.3, 97, 95.8, 100, and 98 pm (six coordination) for Nd, Pm, Sm, Am, and Cm, respectively. The D values of these metals under 0.2–0.3 M DOODA/n-dodecane and 5 M HNO_3 are shown in Table 1, accompanied with separation factors, (SF, D(Am)/D(M) and D(Cm)/D(M)). As shown in Table 1, the separation factors by the condition with TEDGA are much higher than that without TEDGA and high separation with over 8 of SF(D(Am)/D(M)) are seen under acidic conditions without any additional salts.

In conclusion, the combination of extractant, DOODA, and masking agent, TEDGA, is examined for the separation of MA/Ln, and D(Ln) and D(MA) are measured under DOODA–TEDGA extraction systems. Extraction behavior of Am and Cm is similar to those for l-Ln, and the results indicate the high separation of MA from m- and h-Ln. The present work suggests the possibility to show high separation between MA and Ln under acidic conditions by the combination of the extractant and the masking agent.

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