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Mutual separation of trivalent lanthanide and actinides by hydrophilic and lipophilic multidentate diamides

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Not only the separation of actinide (An) from lanthanide (Ln) but also the separation of Am and Cm are required. Although there includes difficulty of the mutual separation of these metals, we take the solvent extraction method using lipophilic and hydrophilic diamides and aminopolyacetic acid dissolved in both aqueous and organic phases, in order to get high separation factors. It is clear that combination of two ligands (TODGA as an extractant and DTPA or DTPABisamide as a masking agent) give around and higher 10 of SF for Nd/Am and Nd/Cm, and combination of two ligands (DGA and DOODA ligands) give around 2 of SF for Am/Cm in column separation.

Keywords: actinides; lanthanides; separation; solvent extraction; extraction chromatography

1. Introduction

Actinide (An) separation from lanthanide (Ln) is required for the purpose of removal of matrix lanthanides, reduction of neutron scavenging nuclides, and reduction of strong radioactivities and heats. In addition, it is also important to separate Am from Cm, the reasons why are the decrease of the heat source from MA fuel and reduction of the radioactive exposure by the neutrons that Cm-244 emit owing to the spontaneous fission. However, it is well-known that the mutual separation of these metals is quite difficult because these metal ions show the same oxidation state, similar ionic radii, and adjacent in the periodic table. Recently, the extractants, DGA and DOODA, well-extract An and Ln, are developed and used to see the many properties[1-4]. In this work, we take the solvent extraction and extraction chromatography using lipophilic and hydrophilic diamides and aminopolyacetic acid dissolved in both aqueous and organic phases, in order to get high mutual separation factors.

2. Experimental

Two mL of the organic phase of extractants (TODGA (*N,N,N',N'*-tetraoctyl-diglycolamide) or DOODA(C8) (*N,N,N',N'*-tetraoctyl-dioxaoctanediamide)) /*n*-dodecane [1,2] is mixed and shaken with the same volume of the aqueous phase, which contains metal ion with and without masking agent (water-soluble DGA, DOODA, EDTA (ethylenediamine-*N,N,N',N'*-tetraacetic acid), EDTABisamide (ethylenediamine-*N,N'*-diacetic

bisamicacid), DTPA (Diethylenetriamine-*N,N,N',N',N'*-pentaacetic acid) and DTPABisamide (Diethylenetriamine-*N,N,N',N',N'*-triacetic bisamicacid)) [5-7] in HNO₃ or NaNO₃, at 25 °C for 30min. After centrifugation, the radioactivity of the aqueous and the organic phases is measured by a liquid scintillation counter. The non-radioactive metal concentrations in the aqueous phases were measured by ICP-AES or ICP-MS, and the concentrations of the organic phase are obtained by subtraction of aqueous phase concentration from initial one. Here, the concentration of Ln and An are 10-100 ppm and sub-ppb level for solvent extraction and the experimental errors are considered to be within 5%. The *D*(M) values are defined as the ratio of [M] in the organic phase versus [M] in the aqueous phase. [M] means the metal concentration in each phase.

The chromatographic experiments are performed as follows: the extractants were impregnated in SiO₂-P. The solid absorbent is packed in the column size of 6 mmφ x 150 mm H. The dead volume is evaluated to 3 mL. The desired solution is poured in this column as the flow rate of 2.5-3.3 mL/min. After elution, each metal in eluent is measured by the suitable instruments.

3. Results and discussion

3.1. Separation of An/Ln by EDTA and EDTABisamide

We use the extraction of TODGA in the organic phase and EDTA or EDTABisamide in the aqueous phase. One of the advantages to use EDTABisamide is to have high solubility in water. In **Figure 1**, Ln patterns (*D*(Ln) vs. Atomic number of Ln) obtained are shown at

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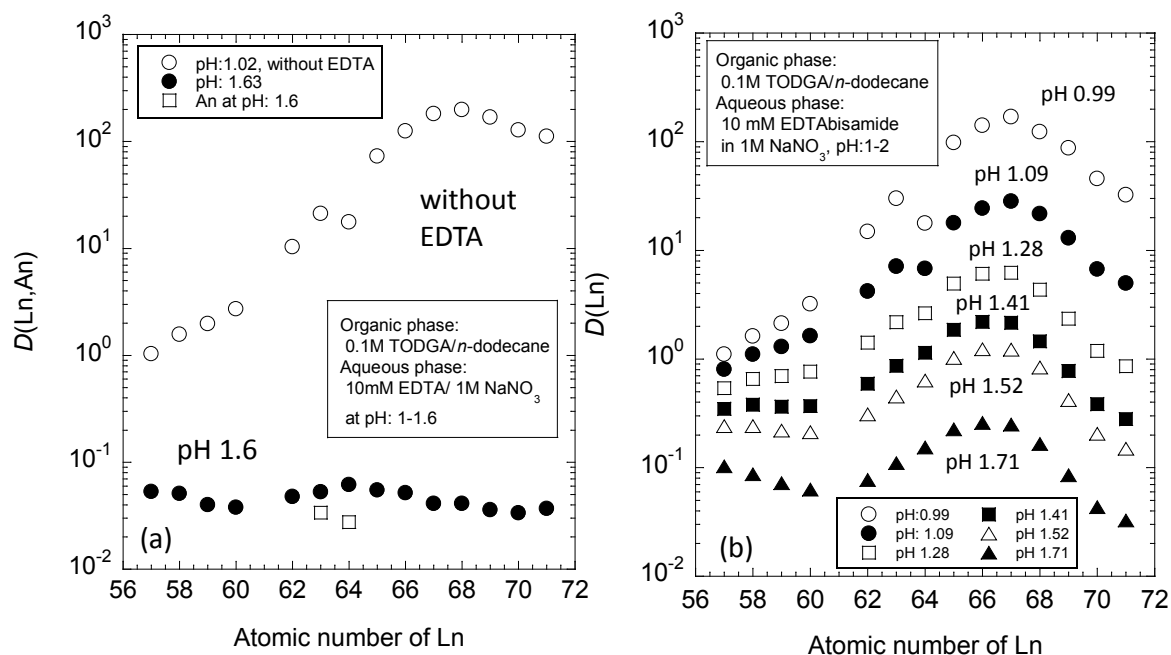


Figure 1. Ln pattern using 0.1M TODGA/*n*-dodecane and EDTA or EDTA bisamide/ 1M NaNO₃ with the different pH, (a): EDTA, (b): EDTA bisamide.

different pH condition. Figure 1(a) indicates the result of EDTA and Figure 1(b) is for EDTA bisamide. These compounds have carboxylic acid groups and are dissociated in solutions, the carboxylic acid groups may react with Ln and An at high pH conditions. As shown in Figures 1(a) and (b), the gradual decrease of D against pH suggest the complexation of Ln with EDTA and EDTA bisamide in the aqueous phase. It seems that the decrease of D for heavy Ln is more remarkable than light Ln, indicating that the complexation with heavy Ln is greater than light Ln. At high pH, Ln pattern show the almost flat shapes and less deviation among 14 Ln metal ions, which indicates that mutual separation of Ln is quite difficult at such condition. The separation of An and Ln can be evaluated using the results in Figure 1(a) for EDTA and Figure 1(b) for EDTA bisamide. From Figure 1(a), small difference between $D(\text{Ln})$ and $D(\text{An})$ is observed, which suggests EDTA works hardly mutual separation of Ln and An.

Figure 2 shows the results of SF (separation factor) of Ln/An against pH using EDTA bisamide. From Figure 2, SF of Ln/An by EDTA bisamide is changeable at different pH, SF seems high at high pH condition. Probably, the different chemical reaction of La from those of Am and Cm occurs.

3.2. Separation of An/Ln by DTPA and DTPA bisamide

We use the extraction system of TODGA in the organic phase and DTPA or DTPA bisamide in the aqueous phase. One of the advantages to use DTPA bisamide is to have high solubility in water. In **Figure 3**, Ln patterns are shown at different pH condition. Figure 3(a) indicates the result of DTPA and Figure 3(b) is for DTPA bisamide, all data in Figure 3(a)

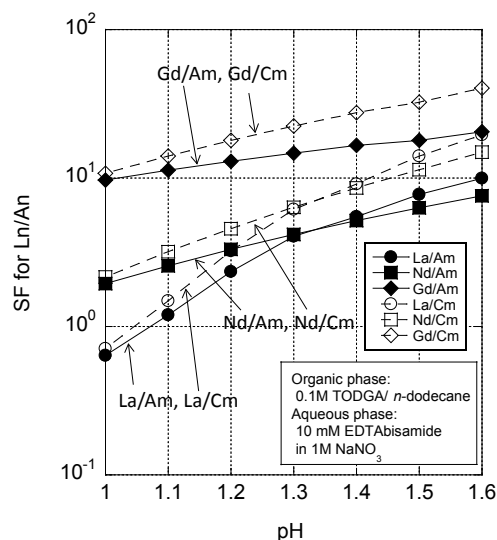


Figure 2. Separation factors obtained from the results in Figure 1(b).

are referred from reference [7]. Both figures indicate that D values of middle and heavy Ln change widely compared to light Ln when pH increases from 1 to 2, which means these water-soluble reagents react strongly to middle and heavy Ln. At the same pH condition, $D(\text{Ln})$ using DTPA bisamide is 10 times lower than that using DTPA. Compared to EDTA and EDTA bisamide, it is clear that DTPA and DTPA bisamide indicate the strong complexation with middle and heavy Ln.

Using these D values, SF for Ln/An is studied. **Figure 4** show SF against pH values, Figure 4(a) is for DTPA and Figure 4(b) is for DTPA bisamide. From Figure 4, almost constant or gradual decrease of SF for

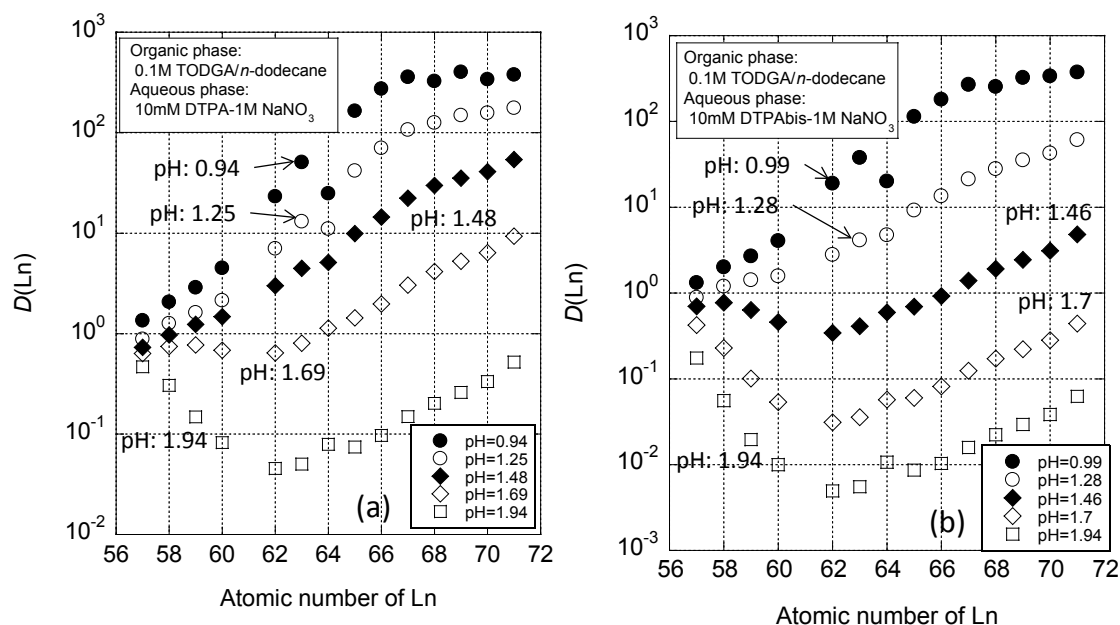


Figure 3. Ln pattern using 0.1M TODGA/*n*-dodecane and DTPA* or DTPAbisamide/ 1M NaNO₃ with the different pH, (a): DTPA, (b): DTPAbisamide.

*: Data is referred by the Ref. [7].

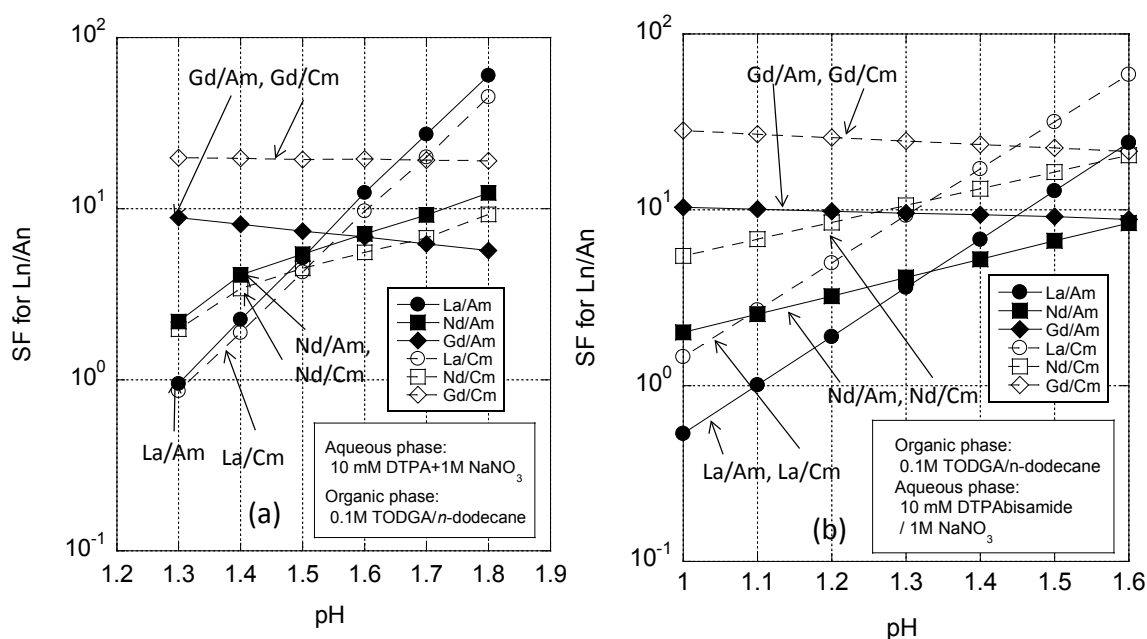


Figure 4. Separation factors obtained from the results in Figure 3, (a): DTPA*, (b): DTPAbisamide

*: Data is referred by the reference [7].

Gd/An with pH is observed, which indicates that Gd and Am or Cm show the same chemical reaction at the pH conditions. However, SF for La/An and Nd/An increase clearly with pH, which suggests different chemical reaction between these metal ions. This behavior can be seen in solvent extraction with EDTAbisamide (Figure 2). La and Nd have the different reactions with dissociated DTPA or DTPAbisamide from those of Am and Cm, then changeable SF values are observed. At

pH 1.6-1.8, it appears that SF for Nd/Am and Nd/Cm are approximate 10 or over.

3.3. Separation of Am/Cm

In order to obtain high separation factor of Am and Cm, both of extractant and masking agent are used in an extraction system. In this work, we take Ln pattern as criterion how to decide two reagents. For example, Ln

patterns for extractants of DGA and DOODA are shown in **Figure 5**. As shown in Figure 5, DGA shows preference of heavy Ln and DOODA shows in reverse. Trivalent An is similar chemical behavior as Ln, then the combination of extractant of DGA in organic phase and masking agent of water-soluble DOODA or extractant of DOODA and water-soluble DGA may show the effective separation.

We take the preliminary test of extraction chromatography in order to see the mutual separation of Ln and An. The results are shown in **Figures 6 and 7**, and summary of column separation are shown in **Table 1**. Figure 6 indicates the results of elution of Ln using eluent of water-soluble DOODA through TODGA column (Figure 6(a)) and that using water-soluble DGA through DOODA column (Figure 6(b)). Figure 6(a) shows the elution trend from light to heavy Ln, because TODGA in absorbent shows the strong affinity with heavy Ln. On the other hand, Figure 6(b) indicates the elution trend from heavy to light ones, which corresponds to the affinity trend of DOODA in absorbent. In these figures, easy separation between Nd and Sm is found.

Am and Cm show the most similar behavior to these metals in Ln series. The results of Am and Cm are shown in Figure 7. From this figure, Am and Cm can be separated by these extraction columns. Table 1 shows the results of these column separation, namely K_d values, peak position, half width, recovery and D values by solvent extraction as a reference. Using these values, SF for column separation of Am/Cm are 2.25 (DGA column) and 1.95 (DOODA column). These results are satisfied for mutual separation of MA.

4. Conclusion

The separation of not only Ln and An but also Am

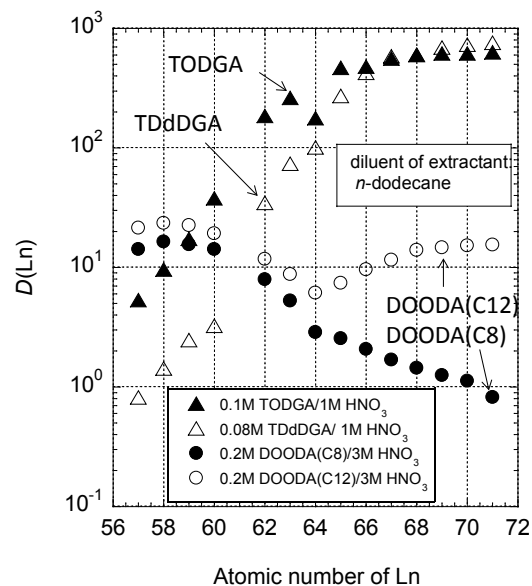


Figure 5. Ln patterns for extractants of TODGA, TDdDGA, DOODA(C8) and DOODA(C12)

and Cm using solvent extraction and extraction chromatography are studied. Utility of two ligands (one is extractant, another is masking agent) is very important to get high separation factors between these metal ions, in this work we employ Ln pattern as criterion in order to decide the available ligands for this purpose. It is clear that combination of two ligands (TODGA as an extractant and DTPA or DTPABisamide as a masking agent) give around and higher 10 of SF for Nd/Am and Nd/Cm, and combination of two ligands (DGA and DOODA ligands) give around 2 of SF for Am/Cm in column separation.

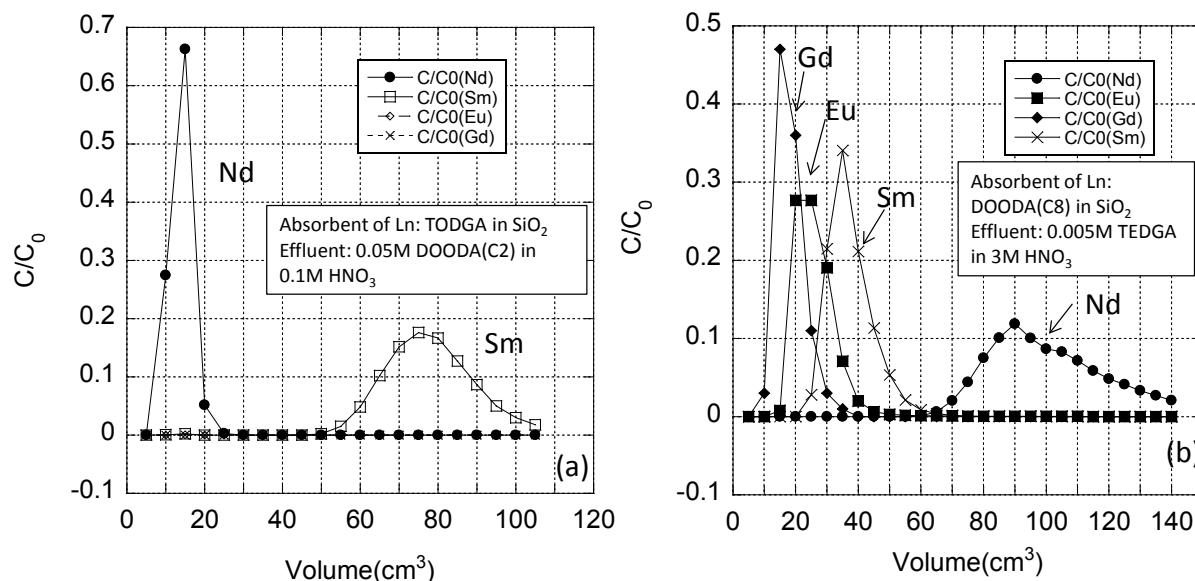


Figure 6. Column separation of Ln using DGA and DOODA column, (a): DGA column, (b): DOODA column.

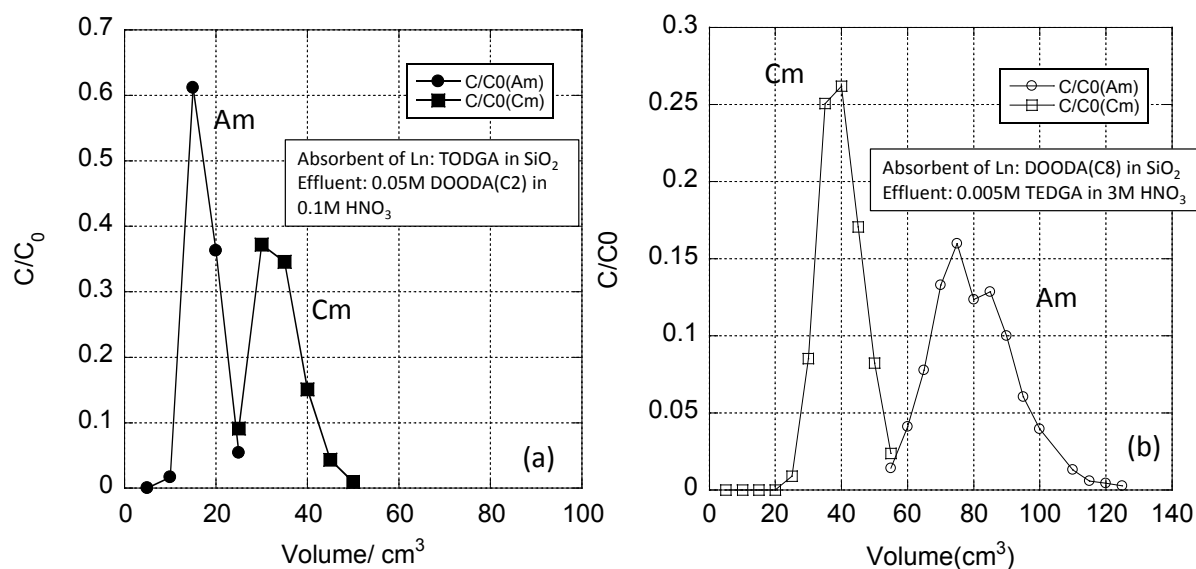


Figure 7. Column separation of Am and Cm using DGA and DOODA column, (a): DGA column, (b): DOODA column

Table 1. Results of column separation of An and Ln.

1. TODGA column (effluent: 0.05M DOODA(C2)/0.1M HNO_3)

	Kd	Peak position	Half width	recovery	D by solvent extraction (0.1M TODGA/ 0.1M HNO_3)
Nd	1.61	15 ml	8 ml	99 %	0.012
Sm	24.1	75	25	98	
Eu	71.9	-	-	0	0.0363
Gd	163	-	-	0	
Am	1.51	15	10	105	0.015
Cm	3.33	30	15	101	0.0365

2. DOODA column (effluent: 0.005M TEDGA/3M HNO_3)

	Kd	Peak position	Half width	Recovery	D by solvent extraction (0.3M DOODA/ 3M HNO_3)
Nd	70.45	90 ml	35 ml	94 %	21
Sm	25.57	35	15	100	12.05
Eu	14.26	22.5	15	86	8.97
Gd	8.45	15	10	104	6.15
Am	47.0	75	30	90	13.3
Cm	17.7	40	20	88	8.5

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