

# CO-SEPARATION OF Am AND RARE EARTH ELEMENTS FROM A HIGHLY ACIDIC RADWASTE SOLUTION BY A SOLVENT EXTRACTION WITH (DIMETHYLDIBUTYL TETRADECYLMALONAMIDE-DIHEXYLOCTANAMIDE)/N-DODECANE

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This study was carried out to investigate the high-acidity co-separation of Am and RE from a simulated radwaste solution by a solvent extraction using a mixture of Dimethyldibutyltetradecylmalonamide (DMDBTDMA, as an extractant) and dihexyl octanamide (DHOA, as a phase modifier) diluted with n-dodecane (NDD). All the experiments were conducted as a batch type. First, the environmentally friendly DMDBTDMA and DHOA composed of only CHON atoms were self-synthesized. Then, the conditions for the prevention of a third phase, generated in the organic phase were examined. In addition, the effects of the concentration of nitric acid, DHOA, oxalic acid and H<sub>2</sub>O<sub>2</sub> on the co-extraction of Am and RE were elucidated. Consequently, the optimum condition of (0.5M DMDBTDMA+0.5M DHOA)/NDD-0.3M C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>-4.5M HNO<sub>3</sub> and O/A=2 was obtained through experimental work. Under this condition, the extraction yields were found to be about 80% for Am, more than 70% for RE such as La, Eu, Nd, Ce, etc., 3% for Cs and Sr, 69% for Fe and less than 11% for Mo and Ru. For the co-extraction of Am and RE, Fe should be removed in advance or prevented from a co-extraction with Am by controlling the different extraction rates of Am and Fe. About 95% of the Am and RE in the organic phase were stripped using a 0.5M HNO<sub>3</sub>.

**KEYWORDS** : Americium, Rare Earth Elements, Extraction/Stripping, DMDBTDMA, DHOA

## 1. INTRODUCTION

The potential harmfulness of high-level radioactive waste (HLW) generated by the reprocessing of spent fuel is primarily due to the presence of radiotoxic minor actinides (MA: Np, Am, Cm etc.). For the diminution of long-term radiotoxicity and the volume reduction of HLW, the removal of MA from HLW is therefore important. Among the MA, trivalent actinides (An(III)) such as americium (Am) and curium (Cm) have similar chemical properties to those of Rare Earth elements (RE: La, Nd, Ce, Eu, Y etc.). For this reason, it is not easy to separate An(III) from RE. Several methods such as a solvent extraction, precipitation, adsorption and ion exchange have been suggested for the separation of An(III), and solvent extraction methods with various new extractants have recently being developed in a few countries [1-5]. One line of study is focusing on the development of an extractant composed of CHON atoms that can be incinerated

as a waste without causing significant air pollution. Dimethyldibutyltetradecylmalonamide (DMDBTDMA), developed in France, is a CHON type extractant of di-amide compounds. Although its synthesizing yield is very low, it offers several advantages: it is easily synthesized, low cost, has high resistance against radiation and hydrolysis, and its degradation products have a negligible impact on the extraction process [6-8]. However, a third phase generated in the organic phase tends to lower the separation efficiency and also hinders the normal operation of an extraction system. In order to avoid a mal-operation, the operation of a system in a safe region where the third phase is never generated is proposed. It would be possible to maintain normal operation by controlling variables such as the extractant concentration, temperature, and acidity etc., or by introducing an aromatic compound as a diluent, or through using a phase modifier [9]. However, it is known that all the measures above, except for a control of the extractant concentration, result in a remarkable

**Table 1.** Chemical Compositions and Concentrations of the Simulated HLW

| Element | Compound   | Concentration, (M)      |
|---------|--|-------------------------|
| Am      | Am-241   | Tracer                  |
| La      | La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O                               | 1.13 x 10 <sup>-3</sup> |
| Ce      | Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O                               | 1.46 x 10 <sup>-3</sup> |
| Nd      | Nd(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O                               | 1.98 x 10 <sup>-3</sup> |
| Eu      | Eu-152   | Tracer                  |
|         | Eu(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O                               | 1.71 x 10 <sup>-4</sup> |
| Y       | Y(NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O                                | 8.09 x 10 <sup>-4</sup> |
| Cs      | Cs(NO <sub>3</sub> )   | 1.86 x 10 <sup>-3</sup> |
| Sr      | Sr(NO <sub>3</sub> ) <sub>2</sub>  | 8.33 x 10 <sup>-4</sup> |
| Mo      | (NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O | 1.74 x 10 <sup>-3</sup> |
| Fe      | Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O                               | 1.90 x 10 <sup>-3</sup> |
| Ru      | Ru(NO)(NO <sub>3</sub> )(OH)   | 8.11 x 10 <sup>-4</sup> |
| U       | UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O                 | 1.05 x 10 <sup>-3</sup> |

reduction in the distribution ratio of An(III), and thus decrease the overall separation efficiency. Therefore, the development of a new extractant that can prevent the generation of a third phase and have higher distribution ratios while being compatible with aliphatic compounds as a diluent is desirable. With this background, the addition of an octanol or mono-amide type solvent [9] as a phase modifier is suggested, as well as the use of tetrapropene hydrogenate (TPH), which is a kind of aliphatic compound [10,11], as a diluent. TPH is used in France as the only diluent of DMDBTDMA for preventing the third phase formation; however, it is a non-commercial product as yet. Therefore, it was intended in this work to utilize a conventional diluent such as kerosene or n-dodecane (NDD), both of which are commercial products and thus easy to obtain, and also to find a methodology to prevent a third phase formation.

Continuing the above trend of process development, this work elucidates the co-extraction behavior of Am and RE by introducing a new extraction system of (DMDBTDMA-DHOA)/NDD, where aliphatic NDD was chosen as a diluent and dihexyloctan amide (DHOA) of a CHON type was employed as a modifier to prevent formation of a third phase. The DMDBTDMA and DHOA were self-synthesized and introduced to experimental work in order to evaluate their applicability for the co-separation of Am and RE. The variables of temperature and acidity were controlled in order that the developed system remains in a safe region without a third phase generation. The extraction behaviors of iron (Fe) and molybdenum were also examined because they have similar behaviors to that of Am. The effect of ruthenium (Ru) on the extraction of Am was also investigated, and then the co-

extraction characteristics of Am and RE were evaluated in terms of their technical feasibility for an extraction.

## 2. EXPERIMENTAL

### 2.1 Preparation of a Simulated HLW Solution

A simulated HLW solution was prepared to contain various elements which tend to affect an extraction of An(III). It contained the objective elements of Am and RE (La, Ce, Nd, Eu and Y) as well as other components such as cesium (Cs), strontium (Sr), Mo, Fe, Ru and uranium (U). All of the elements except for Mo were a nitrate form of Junsei products. Oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and nitric acid (HNO<sub>3</sub>) were Aldrich products of a high purity and thus they were used without any further purification. C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> were used to inhibit the extraction of Mo, Fe and Ru. The radioisotopes Am-241 and Eu-152 dissolved in 2M HNO<sub>3</sub> were purchased from the Isotope Product Laboratory (IPL) in the USA. Table 1 shows the chemical compositions and concentrations of the simulated HLW solution.

### 2.2 Preparation of Extractant

DMDBTDMA (purity 99.5%) as an extractant and DHOA (purity 99%) as a phase modifier were synthesized using the procedure described by Kim et. al [12]. The organic phase was prepared by mixing the DMDBTDMA and DHOA with NDD as a diluent. The mixture was then stirred so that it was pre-equilibrated with a HNO<sub>3</sub> solution. Finally, only the organic phase was taken by using a filter paper (Whatman, IPS).

**Table 2.** Conditions of the Third Phase Formation in the Organic Phase(X=no 3<sup>rd</sup> phase, O =3<sup>rd</sup> phase)

| System   | Temp.(°C)              | DHOA [M] | HNO <sub>3</sub> |      |    |      |    |   |
|--|------------------------|----------|------------------|------|----|------|----|---|
|  |                        |          | 1~3M             | 3.5M | 4M | 4.5M | 5M |   |
| (DMDBTDMA-xM DHOA)/NDD<br>[DMDBTDMA]= 0.4~0.6M | 40                     | 0        | X                | X    | X  | X    | O  |   |
|  |                        | 0.1~1    | X                | X    | X  | X    | X  |   |
|  | 30                     | 0        | X                | X    | X  | O    | O  |   |
|  |                        | 0.1~1    | X                | X    | X  | X    | X  |   |
|  | 25                     | 0        | X                | X    | O  | O    | O  |   |
|  |                        | < 0.3    | X                | X    | X  | X    | O  |   |
|  |                        | 0.5~1    | X                | X    | X  | X    | X  |   |
|  | 20                     | 0        | X                | O    | O  | O    | O  |   |
|  |                        | < 0.3    | X                | X    | X  | X    | O  |   |
|  |                        | 0.5~1    | X                | X    | X  | X    | X  |   |
|  | 0.5M DMDBTDMA/decaline | 20~40    | -                | X    | X  | X    | X  | X |

### 2.3 Experimental Procedure

All the experiments were conducted as a batch type at room temperature (25°C). The experimental procedures were as follows: ① For the co-extraction of Am and RE, the extractants of DMDBTDMA/NDD and (DMDBTDMA-DHOA)/NDD were contacted with the simulated radwaste solution in a 20 mL vial; ② For the stripping of Am and RE, the loaded organic phase extracted by the system of (0.5M DMDBTDMA-0.5M DHOA)/NDD-0.3M C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>-4.5M HNO<sub>3</sub> at O/A (the volume ratio of organic phase to aqueous phase)=2 was contacted with a diluted HNO<sub>3</sub> solution. Firstly, a certain amount of the organic phase and the aqueous phase of each experimental condition was taken and put into contact with each other for about 60 minutes in a dry air bath shaker (International Science Co. 36-sin-100) equipped with a timer and temperature controller. After both phases were separated, an aqueous phase sample was taken for chemical analysis. The concentrations of the metal components and hydrogen ions in the aqueous phase were measured. Finally, the concentrations of the metal components and hydrogen ions in the organic phase were calculated by material balances.

### 2.4 Chemical Analyses

The concentrations of Am-241 and Eu-152 were measured by a multichannel analyzer (Oxford TC702, HPG detector), and Cs concentration was measured using an atomic absorption spectrophotometer (Perkin Elmer, 3100), while the concentrations of other elements were measured by an inductive coupled plasma spectrophotometer (ISA Jobin-Yvon JY 50P and JY 38 plus). The concentration of HNO<sub>3</sub> in the aqueous phase was analyzed by a titration with a 0.1N NaOH standard solution using an automatic titrator (Metrohm 716 DMS Titrino). Meanwhile, the

distribution ratio (*D*), extraction yields (*E*), and stripping yields (*S*) were calculated by the following equations using the measured aqueous phase concentrations.

$$D = C_{Org.}/C_{Aq.}, \quad E(\%) = 100 \times RD/(1 + RD), \quad S(\%) = 100 - E \quad (1)$$

where *C*<sub>Org.</sub> and *C*<sub>Aq.</sub> denote the concentration (mole/L) of a certain element in the organic and aqueous phases, respectively, and R represents the volume ratio of organic phase to aqueous phase (O/A).

## 3. RESULTS AND DISCUSSION

### 3.1 The Third Phase Formation

Table 2 shows the conditions of the third phase formation in the organic phase; these conditions were monitored by visual observation with changes of the concentrations of DMDBTDMA, DHOA and HNO<sub>3</sub>, and with the reaction temperature and diluent at O/A=1. The signs of O and X in Table 2 indicate the formation or non-formation of the third phase, respectively. In order to avoid the third phase formation, it would be helpful to use a phase modifier such as DHOA or to use an aromatic diluent like decaline. Furthermore, it would also be helpful to decrease the concentration of HNO<sub>3</sub> or to elevate the reaction temperature. Also, an increase of the DMDBTDMA concentration would provide a favorable condition to inhibit the third phase formation because it is a general trend that a higher concentration of extractant tends to reduce the third phase formation, though it is not noticeable in Table 2, probably due to the fact that the DMDBTDMA

concentration is in a very low range. In this work, however, high temperature, low concentration of HNO<sub>3</sub> and the addition of a phase modifier (DHOA) rather reduced the extraction ratio of An(III). The increase of the DMDBTDMA concentration also brought about unfavorable results by elevating the distribution ratios of not only An(III) and RE but also the impurity components such as Ru, Zr, Mo, and Fe, etc. [6-8]. Consequently, it would be hard to find the optimum condition for the recovery of An(III) by controlling only one factor among others and therefore it will be necessary to investigate all the factors influencing an extraction.

### 3.2 Extraction of Nitric Acid

It has been reported that nitric acid is extracted in the form of L<sub>2</sub>(HNO<sub>3</sub>), L(HNO<sub>3</sub>), L(HNO<sub>3</sub>)<sub>2</sub> and L(HNO<sub>3</sub>)<sub>3</sub> at a DMDBTDMA/TPH-HNO<sub>3</sub> system [13,14], and in the form of DHOA(HNO<sub>3</sub>) at a DHOA/NDD-HNO<sub>3</sub> system [15], where underscoring indicates the organic phase.

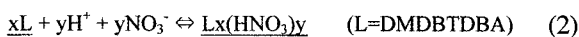


Figure 1 shows the extraction of nitric acid into the organic phase with its concentration of the aqueous phase in the systems of 0.5M DMDBTDMA/NDD, (0.5M DMDBTDMA+0.5M DHOA)/NDD and 0.5M DHOA/NDD. The extractions of nitric acid were found to increase with the HNO<sub>3</sub> concentration in all the systems. In the case of 0.5M DMDBTDMA/NDD, about 0.44M HNO<sub>3</sub> was

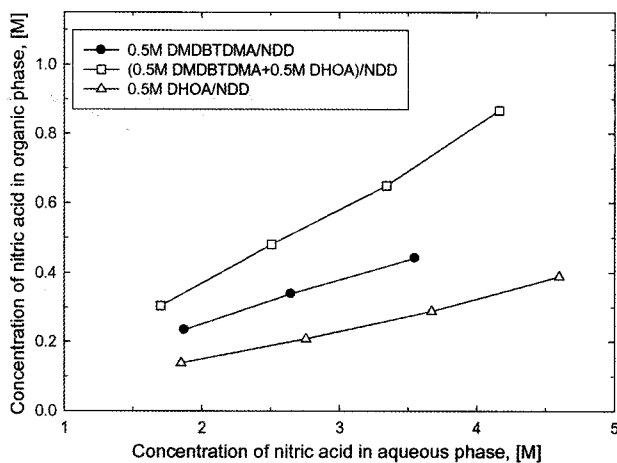


Fig. 1. Nitric Acid Extraction Isotherms in Various Extractant Systems

extracted at 3.5M HNO<sub>3</sub>, and the third phase was formed above 3.5M HNO<sub>3</sub>, thus interrupting the measurement. When (0.5M DMDBTDMA+0.5M DHOA)/NDD was used, 0.87M of nitric acid was extracted at 4.2M HNO<sub>3</sub>. About 0.3M of nitric acid was extracted by 0.5M DHOA/NDD. Accordingly, the amount of nitric acid extracted by 0.5M DMDBTDMA/NDD can be estimated to be 0.57 M, which is similar to the amount of DMDBTDMA used. Therefore, most of the HNO<sub>3</sub> forms extracted by DMDBTDMA are conjectured to be L(HNO<sub>3</sub>), which is a 1:1 reaction of DMDBTDMA and HNO<sub>3</sub>. It is also conjectured that the concentration of free-DMDBTDMA available to co-extract the An(III) and RE would be quite low. It has been reported that the free-DMDBTDMA concentration was about 20% of the initial DMDBTDMA concentration in the DMDBTDMA/TPH-3M HNO<sub>3</sub> system and 10% when 4M HNO<sub>3</sub> was used [13]. Meanwhile, DMDBTDMA and DHOA extract a considerable amount of HNO<sub>3</sub>; thus, it will be necessary to make the organic phase become pre-equilibrated with the HNO<sub>3</sub> solution prior to the An(III) extraction in order to maintain a constant concentration of HNO<sub>3</sub> in the aqueous phase during the extraction.

### 3.3 Co-extraction of Am/RE

#### 3.3.1 Effect of the DHOA Concentration

Figure 2 shows the distribution ratios of each element with the DHOA concentration in the (0.5M DMDBTDMA-xM DHOA)-5M HNO<sub>3</sub> system. A third phase is formed when the concentration of DHOA is less than 0.3M, whereas it was never found when the DHOA concentration was above 0.5M. When 0.5M DMDBTDMA/NDD was put into contact with more than 3.5M HNO<sub>3</sub> at 25°C, a third phase was formed by a slight decrease of the

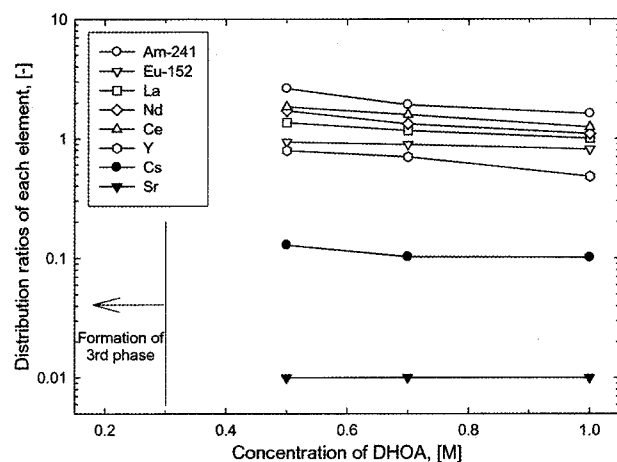


Fig. 2. Distribution Ratios of each Element with the Concentration of DHOA in the (0.5M DMDBTDMA-xM DHOA)/NDD-5M HNO<sub>3</sub> System

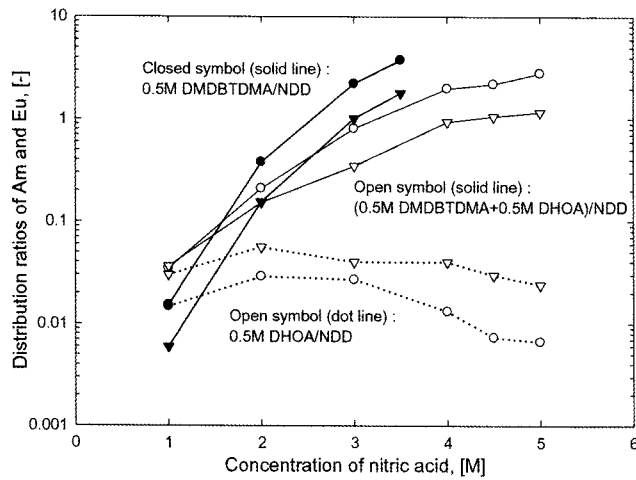


Fig. 3. Distribution Ratios of Am and Eu with the Concentration of HNO<sub>3</sub> in Various Extractant Systems

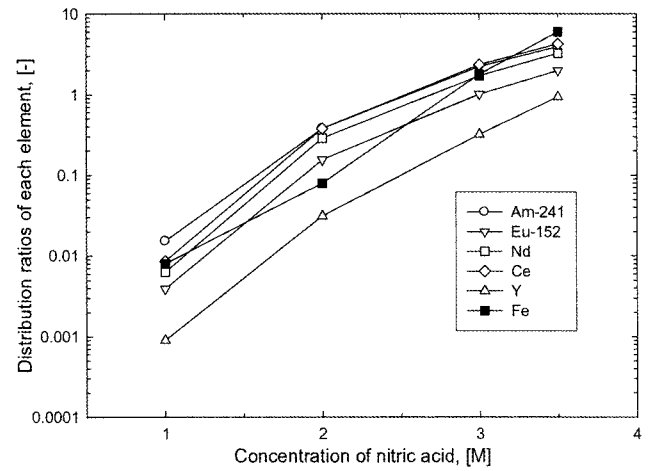


Fig. 4(a). Distribution Ratios of each Element with the Concentration of HNO<sub>3</sub> in the 0.5M DMDBTDMA/NDD-xM HNO<sub>3</sub> System

temperature (1~2°C), disordering the extraction system. However, the introduction of DHOA provided a favorable condition without generating a third phase. On the other hand, the distribution ratios of each element decrease with increasing DHOA concentrations. Though the cause is not examined in this study, this result is similar to Tachimori et al.'s [16] finding that the distribution ratios of Am and Nd are slightly decreased with increasing DHOA concentrations in a Tetraoctyl-3-oxapentanediamide-DHOA/NDD-1M HNO<sub>3</sub> system. Therefore, when a phase modifier is added to prevent the third phase formation in the organic phase, its content should be properly controlled by considering the decrease in the distribution ratio of An(III). The extraction of Cs and Sr was limited because their distribution ratios were very low, as reported in the literature [17].

Figure 3 shows the distribution ratios of Am and Eu with the HNO<sub>3</sub> concentration in various extraction systems. Though DHOA also extracts Am and RE, the yields are less than 3% regardless of the HNO<sub>3</sub> concentration, and thus its effect on the extraction of Am and RE is negligible. DHOA serves only as a favorable phase modifier. In the case of 0.5M DMDBTDMA/NDD, the system is disturbed above 3.5M HNO<sub>3</sub>. However, if DHOA is added to the system, it provides a favorable condition until 5M HNO<sub>3</sub> without the third phase formation. The only disadvantage in this case (0.5M DMDBTDMA-0.5M DHOA/NDD) lies in the decrease in the distribution ratios.

### 3.3.2 Effect of the HNO<sub>3</sub> Concentration

Figures 4-(a) and (b) show the distribution ratios of each element with the HNO<sub>3</sub> concentration of the aqueous phase in the systems of 0.5M DMDBTDMA/NDD-xM HNO<sub>3</sub> and (0.5M DMDBTDMA+0.5M DHOA)/NDD-xM HNO<sub>3</sub>, respectively. The distribution ratios of Am

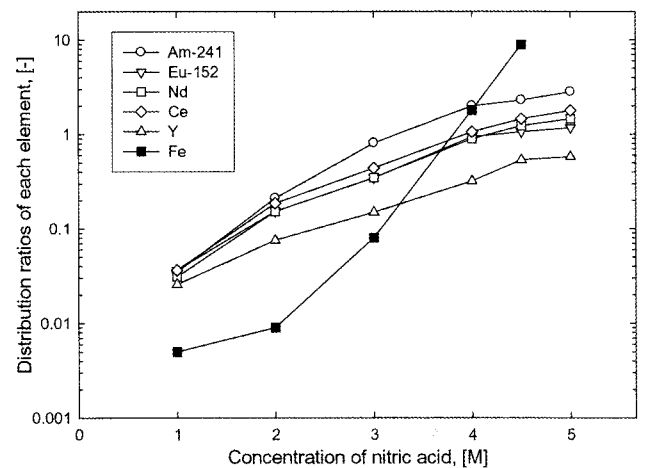


Fig. 4(b). Distribution Ratios of each Element with the Concentration of HNO<sub>3</sub> in the (0.5M DMDBTDMA+0.5M DHOA)/NDD-xM HNO<sub>3</sub> System

and RE increase with the HNO<sub>3</sub> concentration in both systems in the order of Am > Ce > Nd > Eu >> Y. The case of lanthanides, especially, is similar to the results of [1,8], where the distribution ratios tend to decrease with an increase of the atomic number. As for the (0.5M DMDBTDMA+0.5M DHOA)/NDD system, the distribution ratios were rather reduced when compared with the case when DHOA was not added (see Figure 4-(a)), despite the HNO<sub>3</sub> concentration increase from 3.5M to 5M. The distribution ratio of Am is insufficient at 5M HNO<sub>3</sub>, because DHOA suppresses the extraction of An(III) and RE. Therefore, the enhancement of the distribution ratio of Am by means of increasing the O/A ratio is considered necessary.

### 3.3.3 Effect of the Phase-contact Time and Temperature

Figures 5 and 6 show the distribution ratios of Am and Eu with the phase-contact time and temperature in the systems of 0.5M DMDBTDMA/NDD-3.5M HNO<sub>3</sub> and (0.5M DMDBTDMA+0.5M DHOA)/NDD-4.5M HNO<sub>3</sub>, respectively. The extraction seems to be completed within 5 minutes in both systems. However, the temperature has such an influence on the extraction that the distribution ratios tend to decrease with an increase of the temperature in both systems. This is due to the fact that the extraction of Am and RE with DMDBTDMA/TPH is an exothermic reaction ( $\Delta H < 0$ ) [14], and thus the distribution ratio decreases with an increase of the temperature as presented

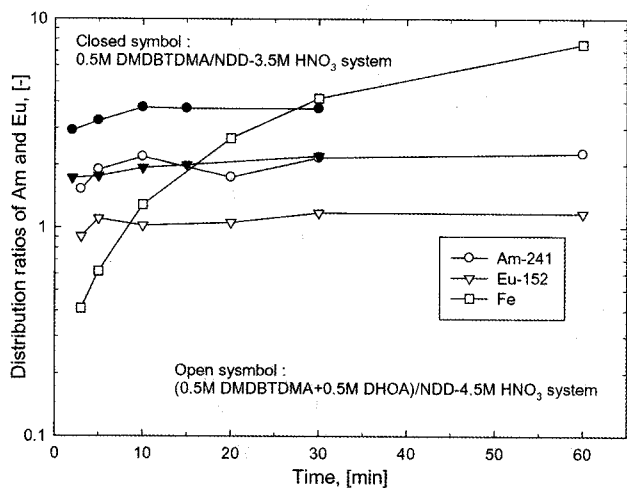


Fig. 5. Distribution Ratios of Am and Eu with Contact Time in Different Extractant Systems

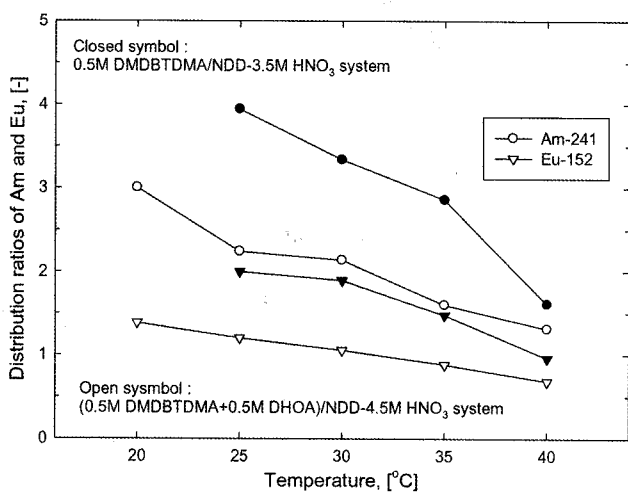


Fig. 6. Distribution Ratios of Am and Eu with Reaction Temperature in Different Extractant Systems

in the literature [14]. In the latter system above, about 76% of Am ( $D_{Am}=3.17$ ) was extracted at 20°C and 56% ( $D_{Am}=1.27$ ) at 40°C. Though a higher temperature provides a favorable condition to prevent a third phase, it brings about unfavorable results in terms of the overall separation efficiency. Therefore, the temperature should be properly controlled in a system so that it does not disturb the extraction process. In the former system, however, a third phase forms at 20°C, and thus the operation ranges were rather narrow when compared with the system where DHOA was added.

### 3.3.4 Effect of Oxalic Acid and H<sub>2</sub>O<sub>2</sub>

Figure 7 illustrates the distribution ratios of Mo, Ru, Fe and Am with the concentrations of oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) and H<sub>2</sub>O<sub>2</sub> in the (0.5M DMDBTDMA+0.5M DHOA)/NDD-4.5M HNO<sub>3</sub> system. It shows that C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> is more effective than H<sub>2</sub>O<sub>2</sub> for hydrophilic complex formation, which is attributed to its relatively higher stability constant. At 0.3M C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, only 5% of Mo ( $D_{Mo}=0.05$ ) and 6% of Ru ( $D_{Ru}=0.06$ ) were extracted, showing that this condition is applicable for avoiding their co-extraction with Am and RE. In the case of Fe, it also creates a non-extractable complex with C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, and its extraction yield decreases significantly with the concentration of C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>. However, about 38% of Fe ( $D_{Fe}=0.61$ ) is still extracted at 0.5M C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>. Cuillerdier et al. [6] also revealed a similar result for an Fe extraction with a C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> concentration in various di-amide extraction systems. However, in the case of H<sub>2</sub>O<sub>2</sub>, 90±1% of Fe ( $D_{Fe}=8.09\sim 10.11$ ) was extracted regardless of the H<sub>2</sub>O<sub>2</sub> concentration. This shows that a complex is not formed between H<sub>2</sub>O<sub>2</sub> and Fe, which agrees with Madic's result [17] that H<sub>2</sub>O<sub>2</sub> inhibits an extraction of Mo, but has no effect on the extraction of Fe. Finally, Am shows a constant extraction yield of 66±2% ( $D_{Am}=1.78\sim 2.13$ )

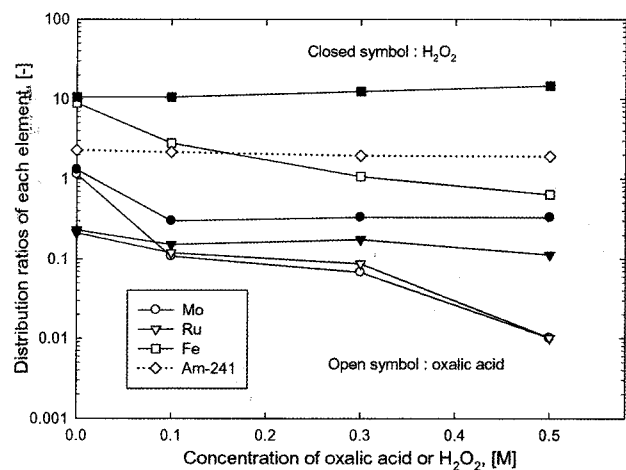


Fig. 7. Distribution Ratios of each Element with the Concentrations of C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> in the (0.5M DMDBTDMA+0.5M DHOA)/NDD-4.5M HNO<sub>3</sub> System

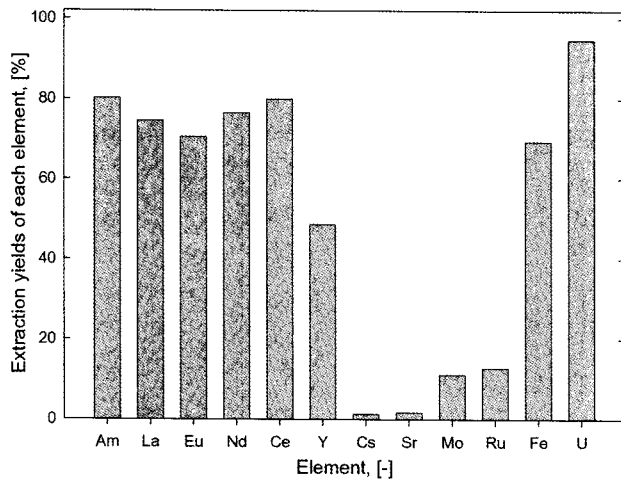


Fig. 8. Extraction Yield (%) of each Element in the (0.5M DMDBTDMA+0.5M DHOA)/NDD -0.3M C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>-4.5M HNO<sub>3</sub> and O/A=2 System

without regard to the addition of C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> or H<sub>2</sub>O<sub>2</sub>. All the results show that the extractions of Mo and Ru can be inhibited by using C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> because hydrophilic complexes are created between them. However, it will still be hard to prevent a co-extraction of Fe with Am. In this work, however, a methodology to prevent a co-extraction of Fe with Am was suggested by utilizing a difference in the extraction rates of Am and Fe by DMDBTDMA. Therefore, if the contact time between the aqueous and organic phases (residence time in the reactor) is properly controlled with the addition of C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, then a considerable amount of Fe accompanied by Am can be avoided. The extraction of Am is completed within 5 minutes, as shown in Figure 5, but Fe demands 50~60 minutes for its complete extraction. Nigond et al.[18] and Weigl et al.[19] also revealed that the extraction rate of Am was much higher than that of Fe in the DMDBTDMA/TPH system.

Figure 8 is a histogram that shows the extraction yield (%) of each element in the system of (0.5M DMDBTDMA+0.5M DHOA)/NDD-0.3M C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>-4.5M HNO<sub>3</sub> at O/A=2. It shows a favorable result in view of the Am extraction yield because over 80% of the Am was extracted while over 70% of the RE (except Y) was extracted, and less than 11% of Mo and Ru were extracted. As for Fe, about 69% was extracted, which could be solved by controlling the different extraction rates of Am and Fe, or regulating the residence time (/contacting time) properly when a continuous multistage extraction system such as a centrifugal contactor (having a short residence time) is employed. In the case of U, since its distribution ratio on DMDBTDMA is so high, it should be separated in advance before a co-extraction of Am and RE.

### 3.4 Stripping of Am and RE

Figure 9 shows the distribution ratios of each element

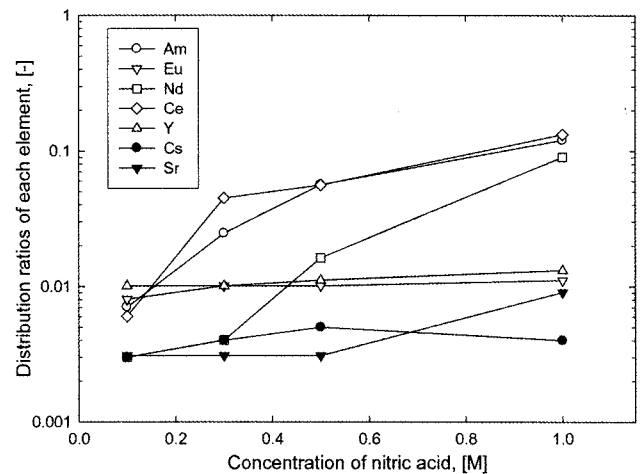


Fig. 9. Distribution Ratios of each Element with a Low Concentration of Nitric Acid in the Loaded Organic System Extracted by (0.5M DMDBTDMA+0.5M DHOA)/NDD-0.3M C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>-4.5M HNO<sub>3</sub> at O/A=2

with a low concentration of HNO<sub>3</sub> from the organic phase of Figure 8, which resulted in a reduced stripping with an increase of the HNO<sub>3</sub> concentration. This phenomenon has already been predicted by Figure 4-(b), where the distribution ratio increases with the HNO<sub>3</sub> concentration. The order of the stripping yield, Cs ≈ Sr > Y ≈ Eu > Nd > Ce ≈ Am, is almost the reverse of that of the extraction yield. Since over 95% of Am and RE ( $D_{Am,RE} < 0.05$ ) is stripped from the organic phase at 0.5M HNO<sub>3</sub>, it seems to be a suitable condition for stripping the Am and RE.

## 4. CONCLUSIONS

A new extraction system based on the use of a DMDBTDMA extractant diluted with n-dodecane for the separation of Am and RE was suggested in this work. The merits of DMDBTDMA are retained or augmented in the new system, in that the extractant is an environmentally friendly CHON type and can be used in a range of a relatively higher HNO<sub>3</sub> concentration by the phase modifier DHOA. In the extraction system, the DHOA served only as a phase modifier without having any extractive function. When 0.5M DHOA was added to the system, no third phase was generated up to 5M HNO<sub>3</sub> and/or 20°C. The extraction yield of Am was about 80% in the system of (0.5M DMDBTDMA+0.5M DHOA)/NDD-0.3M C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>-4.5M HNO<sub>3</sub> and O/A=2 and about 95% of Am and RE was stripped from the organic phase by 0.5M HNO<sub>3</sub>. Meanwhile, Mo, Fe and Ru created hydrophilic complexes with oxalic acid, thus inhibiting their co-extraction with Am. In the above system, less than 11% of the Mo and Ru were extracted. Though a considerable amount of Fe (about 69%) was extracted with the Am, this could be

solved by exploiting the different extraction rates of Am and Fe.

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