ABSTRACT

The tridentate neutral ligands, having two amidic carbonyl donors and an etheric oxygen, were synthesized in our laboratory and examined the extraction of actinides and fission products. Among the synthesized diglycolamides (DGA) with varying length of alkyl chains attached to two N atoms, N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) and N,N,N',N'-tetradeacyl-3-oxapentanediamide (TDDGA), showed a sufficient solubility in n-dodecane. The extractability of both TODGA and TDDGA for actinides (An), i.e., U(VI), Pu(IV), Am(III), and Cm(III), in nitric acid solution was satisfactorily high and its order was in a succession of An(III), An(IV) > An(VI) > An(V). The extraction of fission products (FPs), except Zr(IV) and lanthanides (Lns), are relatively small, indicating the sufficient separation of actinides, Zr(IV) and Lns(III) from other FPs. The extraction kinetics, maximum loading in the organic phase, back-extraction behavior, and radiolytic stability of TODGA showed that TODGA is applicable to the treatment of the high level waste.

INTRODUCTION

As the transuranium elements, i.e., neptunium, plutonium, americium and curium contained considerably in the high level waste solution (HLW) are long lived alpha emitters and considered as hazardous metal ions, the complete recovery of them from HLW has been the major task of the partitioning in the OMEGA program. Due to their relatively low charge densities, Am(III) and Cm(III) usually show a weak complexing ability with the most chelating agents in the nitric acid solution. Some bidentate neutral ligands have been developed as a useful extractant for Am and Cm. For example, the derivatives from phosphine oxide and diamide (1-2) has been synthesized and studied on actinides (An) extraction. The distribution ratios of Am(III) by 0.2 mole/dm$^3$ (denote as M hereafter) octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (O($\phi$D(iB)CMPO) + 1.2M TBP employed in the TRUEX process and 0.5M dimethyldi-nbutyltetradecylmalonamide (DMDBT DMA) in the DIAMEX process, as representatives of Am extraction, are 22.5 (from 3M HN0$_3$ to n-dodecane) and 4.3 (from 4M HN0$_3$ to TPH), respectively (3,4). During the course of the investigation of a new type of CHON-type extractants for the recovery of Am and Cm in HLW, we introduced the diglycolamide (DGA) to be the most effective extractant for Am and Cm (5). The diglycolamide has a favorable character to bind the metal cations by tridentate mode forming very stable complexes (6). In the present paper, the extraction behavior of N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) not only for actinides but also for fission products and HNO$_3$ is described. In addition, other properties of TODGA, i.e., extraction rate, maximum loading in the organic phase, back-extraction efficiency, and the radiation stability are reported.

EXPERIMENTAL

Chemicals

The standard solutions of all metals for the usage in atomic absorption spectrometry (Wako Pure Chemical Industries, Ltd) were employed in all extraction experiments. The radioactive tracers of $^{233}$U, $^{237}$Np, and $^{238}$Pu were obtained from Scetico company, LTD, and $^{239}$Th, $^{241}$Am, $^{244}$Cm, and $^{252}$Cf were from Isotope Products Laboratories. The nitric acid and n-dodecane of the analytical grade were used. The Np(V) and Pu(IV) cations prepared by the methods in the references (5) were used. Six kinds of diglycolamides with alkyl chains of different length attached to amidic N atoms, N,N,N',N'-tetrapropyl-3-oxapentanediamide (TPDGA), N,N,N',N'-tetrabutyl-3-oxapentanediamide (TBDGA), N,N,N',N'-tetracetyl-3-oxapentanediamide (TADGA), N,N,N',N'-tetrahexyl-3-oxapentanediamide (THDGA), and N,N,N',N'-tetradeacyl-3-oxapentanediamide (TODGA) were synthesized through the condensation reaction (7).

Irradiation of Gamma Ray

Sample solution taken in a glass tube with a cap was irradiated by $^{60}$Co gamma rays at a dose rate of 4.25 kGy/h at room temperature. Three types of samples, i.e., TODGA alone, TODGA in n-dodecane and TODGA in n-dodecane saturated with HNO$_3$, were irradiated and subjected to americium extraction.

Extraction Procedure

After pre-equilibration, a certain volume (0.5-2 ml) of the organic extractant phase was taken in an extraction tube with an
equal volume of an aqueous nitric acid solution spiked with 10 μl of radioactive tracer solution or the metal standard solution. The concentrations of metal ions used in the extraction experiment were, in ppm, 500 for Sr, Zr, Mo, Ru, Pd, Ba, Nd and 1x10⁵ for Eu, 5x10⁵ for Th, 0.1 for U, 1 for Ta and Np, 6x10⁵ for Pu, 3x10⁴ for Am, 1x10⁵ for Cm and 2x10⁴ for Cf. The extraction tube filled with two phases was shaken mechanically for 2 hours at 25 ± 0.1 °C. After centrifugating and separating both phases, the duplicate 0.50 ml aliquots were taken and measured by NaI scintillation counter (COBRA, Packard Instrument Company) for the gamma activities of ¹⁵²Eu and ²⁴ⁱAm, liquid scintillation counter (Tri-Carb 1600 TR, Packard Instrument Company) for the alpha activities of ²³⁰Th, ²³³U, ²³⁷Np, ²³⁸Pu, ²⁴⁴Cm and ²⁵²Cf in 5 ml of PICO-AQUA cocktail. The amounts of non-radioactive metal ion in the sample solutions prepared from both phases were measured by ICP (SPS 1200AR, Seiko-EG & G).

RESULTS AND DISCUSSION

Selection of DGA

The solubilities of diglycolamides, TPDGA, TBDGA, TADGA, THDGA, TODGA and TDDGA, in water or n-dodecane, and the distribution ratios of Am(III) (Dₘₐₜ) in the extraction system of 0.1 M DGA/ chloroform or 0.1 M DGA/ n-dodecane and 1 M HNO₃ were summarized in Table 1. It is obvious that the long alkyl chain, longer than hexyl radicals, attached to N atoms gives enough lipophilicity of DGA molecule to dissolve in n-dodecane at any ratio, but contrarily minute in water. The complete dissolution of extractant in non-polar aliphatic solvent, e.g., n-dodecane and TPH, is necessary to an industrial use, thereby TODGA and TDDGA satisfy one of the conditions for the application to partitioning of the HLW.

From the point of extractability, Table 1 reveals that DGA with a shorter carbon chain provides higher Dₘₐₜ with chloroform as a diluent and seems superior to TODGA and TDDGA. It should be pointed out, however, that such a DGA is easy to form the third phase when the non-polar solvent is used. Another evidence that Dₘₜ by TODGA is a little higher than that by TDDGA made us to use TODGA as a candidate extractant for the partitioning of HLW in the following study.

Table 1 Solubility of DGAs in water and n-dodecane, and distribution ratios of Am(III); Dₘₜ for different DGAs

<table>
<thead>
<tr>
<th>DGA</th>
<th>Solubility in water</th>
<th>Dissolution in n-dodecane</th>
<th>Dₘₜ* Chloroform</th>
<th>Dₘₜ* N-dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPDGA</td>
<td>57 (mM)</td>
<td>poor</td>
<td>0.41</td>
<td>-</td>
</tr>
<tr>
<td>TBDGA</td>
<td>2.3</td>
<td>poor</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>TADGA</td>
<td>0.25</td>
<td>poor</td>
<td>0.11</td>
<td>-</td>
</tr>
<tr>
<td>THDGA</td>
<td>0.11</td>
<td>soluble</td>
<td>0.089</td>
<td>40</td>
</tr>
<tr>
<td>TODGA</td>
<td>0.042</td>
<td>non-limited</td>
<td>0.071</td>
<td>30</td>
</tr>
<tr>
<td>TDDGA</td>
<td>0.042</td>
<td>non-limited</td>
<td>0.042</td>
<td>18</td>
</tr>
</tbody>
</table>

*: Determined by using 0.1 M DGA/solvent and 1 M HNO₃.

Extraction of Actinides

The distribution ratios of actinides(Dₘₜ) by TODGA in Fig. 1(a) and Fig. 1(b) indicate the dependence of Dₘₜ on the concentration of HNO₃ and TODGA, respectively. Here, the concentrations of HNO₃ and TODGA were expressed to as [HNO₃] and [TODGA] in the following sentences. The peculiar feature of Dₘₜ with TODGA is its dependency on nitric acid concentration, as seen in Fig. 1(a), Dₘₜ for most actinides increases drastically over the acidity of 0.3 M, and the slope exceeds three for Am(III), Cm(III) and Th(IV). Thus it seems that the extraction of actinides is enhanced by an increasing nitric acid, rather than being suppressed by the competitive extraction of HNO₃. With HNO₃ concentration fixed at 1 M in Fig. 1(b), all plots seems on the respective straight lines. Assuming the activity coefficient of TODGA being constant in these conditions, the slopes of these lines signify the number of TODGA molecules involved in the extraction reactions. From the linear regression analysis, the equations obtained of Dₘₜ(y) vs. [TODGA](x) were y = 3.4x+5.6 for Th(IV), y = 3.1x+2.9 for U(VI), y = 2.8x+4.0 for Pu(VI), y = 3.7x+5.3 for Am(III) and y = 4.2x+6.0 for Cm(III). From these, three and four TODGA molecules are involved in the extraction of Th(IV), U(VI), Pu(VI) and Am(III), Cm(III), respectively.
Fig. 1 Distribution ratios of Ans with TODGA
(a): [HNO$_3$] dependence; (b): [TODGA] dependence

Fig. 2 Distribution ratios of various FPs with TODGA
(a): [HNO$_3$] dependence; (b): [TODGA] dependence
Extraction of Fission Products

The extraction of 14 elements contained in the HLW, fission products, Cr, Fe and Ni, were investigated by using TODGA. Fig. 2(a) and Fig. 2(b) show the dependencies of $D_M$ ($M =$ Sr, Zr, Mo, Tc, Ru, Pd, Ba, Eu) on the concentrations of HNO$_3$ and TODGA. Other elements, Cr, Fe, Ni, Rh, Te and Cs were also examined, and their D values were lower than 0.1, under the condition of 1M TODGA/ n-dodecane and 3M HNO$_3$. In Fig. 2(a), the distribution ratios of all elements, except anionic TeO$_4^-$, increase gradually from low acid region to ~3M HNO$_3$ in the aqueous phase, after which $D_M$ for Sr, Tc, Ru, Pd, Ba decrease. The extraction of Eu(III) is similar to that of An(III), but the former is overwhelming the latter at the high HNO$_3$ concentration. The extraction of Zr(IV) is exhaustive in all HNO$_3$ concentration region over 0.5M.

Fig 2(b) shows that the separation factors between Eu(III) and FPs ($D_{Sp} = D_{Eu}/D_{FP}$) are higher than 10$^5$. This value increases with an increase in TODGA concentration. From Figs. 1(a) and 2(a), the separation of Zr(IV) from actinide fraction seems a major subject in case of applying TODGA to the HLW-partitioning. We examined the effect of oxalic acid on holding Zr(IV) back in the aqueous solution. The effect was successful by adding the oxalic acid of more than 0.2M (Table 2).

Extraction of HNO$_3$

It is important to know the extraction behavior of HNO$_3$, because the acid in the organic phase sometimes suppresses or enhances the extraction of the objective metal cations and/or influences the back-extraction of the metal ion in case of low acid stripping. Figure 3 indicates the dependence of $D_{H}$ on the initial concentrations of HNO$_3$ in the aqueous phase(a) and concentration of TODGA(b). The extraction of HNO$_3$ by TODGA is similar to that by malonamide (0.5M malonamide/ TPH; max. $D_{H}$: approximately 0.2)(8) and lower than that by CMPO (0.2M CMPO+1.2M TBP/ CONOCO: max. $D_{H}$: approximately 1)(9). The slope values in Figs. 3(a) and (b), respectively, are 0.82 and 1.1, which suggest the stoichiometry of the extracted molecule being HNO$_3$:TODGA= 1:1.

<table>
<thead>
<tr>
<th>Oxalic acid concentration (M)</th>
<th>$D_{H_{Eu}}$</th>
<th>$D_{H_{Sr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.84</td>
<td>&gt;300</td>
</tr>
<tr>
<td>0.2</td>
<td>0.258</td>
<td>&gt;300</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0618</td>
<td>&gt;300</td>
</tr>
<tr>
<td>0.4</td>
<td>&lt;0.01</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

Table 2 Distribution ratios of Zr(IV) and Eu(III) in the system 0.1M TODGA and 3M HNO$_3$, with varying concentration of oxalic acid.
Other Extractive Characteristics of TODGA

The extraction equilibrium was quickly attained by shaking the extraction vessel violently for less than 3 min. The maximum loading of Nd(III) in the organic phase as a function of TODGA concentration from 3M HNO₃ solution without third phase formation, and the efficiency of back extraction were investigated, and the results are summarized in Tables 3 and 4.

As described above, Am(III) or Cm(III) are accompanied by 3 to 4 molecules of TODGA. Table 3 indicates that about 2 to 3 times as much as extractant concentration calculated by the stoichiometry is needed to avoid the third phase formation in the n-dodecane solvent. The max. loading obtained here is little lower than that reported in CMPO and TBP system (10).

Table 4 shows the back-extraction of Nd(III) by distilled water from the organic phase of 0.1M TODGA or 0.5M TODGA in n-dodecane by stripping twice, whereas complete back-extraction of Nd(III) in 0.5M TODGA/n-dodecane was attained by the washing more than 5 times. The difference of the efficiency may be due to the concentration of HNO₃ extracted simultaneously with Nd(III) in the organic phase. The Dₘ values in the system of 0.1M and 0.5M TODGA/n-dodecane and 3M HNO₃ are 0.034 and 0.173, respectively, see Fig. 3(b). Thus, many washings of the 0.5M TODGA solvent phase with H₂O are required in decreasing the acidity of the aqueous phase to reach the condition of both low Dₘ and low Dₜₜ.

Radiolytic Effect on Am(III) Extraction

Three kinds of samples were irradiated by Co-60 gamma rays (1.84 eV/atom) in the presence of n-dodecane, and (c) 0.1M TODGA/n-dodecane pre-equilibrated with 3M HNO₃. The extent of radiolysis of TODGA was in the order of (b) > (c) > (a), demonstrating an enhancing effect of n-dodecane, that is, fraction of the radiolytic decomposition of TODGA in the system (b) was 3 to 4 times larger than that in the undiluted TODGA. Generally speaking, the extraction of Am(III) was depressed by the gamma ray irradiation. Dₐₐm however, did not change remarkably by using the solvent with an absorbed dose less than 2 x 10⁵ Gy. Thereby the radiolytic effect to the extraction of Am and Cm will be negligibly small in the partitioning process of the HLW.

CONCLUSION

The extraction of actinides and FPs by TODGA was studied. TODGA revealed its excellent nature for extraction of actinides in the high acid aqueous solution. The distribution ratios of lanthanides(III) and Zr(IV) are also high but those of other FPs are low. The extraction rate, maximum loading of Nd(III) without third phase formation, back-extraction efficiency, and the radiolytic stability of TODGA suggest the favorable capability of TODGA for application to the partitioning of HLW.

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REFERENCES