Extraction Capacity of Diglycolamide Derivatives for Ca(II), Nd(III) and Zr(IV) from Nitric Acid to *n*-Dodecane Containing a Solvent Modifier

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In order to evaluate the extraction property of new extractants, diglycolamide (DGA) compounds, we investigated the maximum extraction of di-, tri-, and tetravalent metal ions using nitric acid and *n*-dodecane. The limits of metal concentration (LOC) for Ca(II), Nd(III) and Zr(IV) in the organic phase are strongly influenced by HNO₃ and the extractant concentration. For the purpose of enhancing the LOC value, we employed a modifier of the solvent, *N,N*-dihexyl-octanamide (DHOA) and DGA with a long alkyl chain, and examined the results. It was evident that LOC increased with the DHOA concentration and the length of the alkyl chain attached to the N atom of DGA. The stoichiometric values of LOC(Zr) estimated from the extraction reaction were confirmed by using the extraction condition: tetraoctyl-DGA/1 M DHOA + *n*-dodecane and 3 M HNO₃.

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Introduction

For reprocessing spent nuclear fuel (SF) and partitioning high-level radioactive liquid waste (HLW), many extractants have been synthesized and tested concerning application to the process. In our laboratory, *N,N,N',N'*-tetraoctyl-diglycolamide (TODGA) was developed for the recovery of long-lived alpha emitters, such as Pu(IV), Np(IV), Am(III) and Cm(III).¹⁻⁵ Since TODGA gives a high distribution ratio (*D*) of actinide (An) ions between HNO₃ and *n*-dodecane phases, this is a promising extractant for an innovative chemical-separation process. From a detailed investigation, TODGA shows high *D* values of di-, tri-, tetravalent metal ions.⁶ Because of the variety of metal concentrations in SF and HLW, it is important to know the extraction capacity of metals with the different oxidation states using TODGA. For neodymium, an example of trivalent lanthanides and actinides, it was already reported that the stoichiometric extraction of Nd(III) to DGA concentration can be attained by mixing with the modifier of monoamide and using DGA with a long alkyl chain, *i.e.*, *N,N,N',N'*-tetradodecyl-diglycolamide (TDdDGA).⁷

We developed an analytical method for a precise determination of the extraction capacity,⁷ and utilized it to evaluate the extraction capacities of calcium, neodymium and zirconium by TODGA, TDDGA(*N,N,N',N'*-tetradecyl-diglycolamide) and TDdDGA with and without a modifier. It had already been confirmed that *D* of Ca(II) and Zr(IV) by TODGA are higher than any other metal ions with the same oxidation state,⁶ and that the analytical method is effective on metals with high *D* values. The results of the extraction capacity obtained under different experimental conditions are summarized and discussed in this paper.

Experimental

Chemicals

Three DGA extractants (TODGA, TDDGA and TDdDGA) and *N,N*-dihexyl-octanamide (DHOA) as a modifier of diluent were employed. Their molecular formulas are O-(CH₂-CO-N(C₈H₁₇)₂)₂, O-(CH₂-CO-N(C₁₀H₂₁)₂)₂, O-(CH₂-CO-N(C₁₂H₂₅)₂)₂, C₇H₁₅-CO-N(C₆H₁₃)₂ for TODGA, TDDGA, TDdDGA and DHOA, respectively. TODGA, TDDGA and TDdDGA were purchased from Kanto Chemical Co. Inc. and DHOA was obtained from Wako Pure Chemical Industries Ltd. These reagents have the purity of more than 98%, and are ready to use without further purification. Calcium (Ca²⁺), Nd, and Zr solutions were prepared by dissolution of CaO (purity >99.9%), Nd₂O₃ (purity >99.9%) and ZrO(NO₃)₂·(H₂O)₂ (purity >97%) (Wako Pure Chemical Industries Ltd.) using nitric acid, and were used after dilution to a suitable concentration. Other reagents, *e.g.*, *n*-dodecane and nitric acid, were of the analytical grade.

Extraction procedure

A certain concentration (1.0–4.0 M (mol/dm³)) of nitric acid containing an appropriate concentration of Ca(II), Nd(III) or Zr(IV) as an aqueous phase and a certain concentration (0.05–0.3 M) of DGA/*n*-dodecane with and without DHOA as an organic phase were prepared. The same volumes (0.5–1.0 ml) of both phases were mixed and shaken mechanically at 1500 rpm for 30 min at 25°C.

After extraction, Ca(II), Nd(III) or Zr(IV) in the aqueous phase was diluted by using nitric acid and distilled water until reaching a suitable concentration for ICP-AES spectrometry. Ten-times as much volume of water, or 0.2 M oxalic acid–2 M HNO₃, as that for the organic phase was used for the backward-extraction of Ca(II) or Zr(IV). The aqueous solution after

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Fig. 1 Relationship between the Ca(II) concentration in the aqueous phase before extraction and the Ca(II) concentration in the organic phase after extraction. Condition: organic phase, 1 ml of 0.1 M TODGA, 0.1 M TODGA-0.2 M DHOA, 0.1 M TODGA-0.5 M DHOA, 0.1 M TODGA-1 M DHOA, 0.1 M TDDGA, 0.1 M TdDGA in *n*-dodecane; aqueous phase, 1 ml of 3 M HNO₃. 1, LOC for 0.1 M TODGA; 2, LOC for 0.1 M TODGA-0.2 M DHOA; 3, LOC for 0.1 M TODGA-0.5 M DHOA; 4, LOC for 0.1 M TODGA-1 M DHOA; 5, LOC for 0.1 M TDDGA; 6, LOC for 0.1 M TdDGA.

Fig. 2 Relationship between the Zr(IV) concentration in the aqueous phase before extraction and the Zr(IV) concentration in the organic phase after extraction. Condition: organic phase, 1 ml of 0.1 M TODGA, 0.1 M TODGA-0.2 M DHOA, 0.1 M TODGA-0.5 M DHOA, 0.1 M TODGA-1 M DHOA, 0.1 M TDDGA, 0.1 M TdDGA in *n*-dodecane; aqueous phase; 1 ml of 3 M HNO₃. 1, 0.1 M TODGA; 2, 0.1 M TODGA-0.2 M DHOA; 3, 0.1 M TODGA-0.5 M DHOA; 4, 0.1 M TODGA-1 M DHOA; 5, 0.1 M TDDGA; 6, 0.1 M TdDGA.

backward-extraction was diluted by 0.5 M HNO₃. Here, the temperature at the backward-extraction was controlled to 35°C in order to accelerate the stripping. The organic phase including Nd(III) was completely decomposed by HNO₃-HClO₄, and the residue was dissolved by 0.5 M HNO₃. The concentrations of these metal ions in the sample solutions were measured by ICP-AES (SPS 3100, Seiko Instruments Inc.).

Results and Discussion

Determination of LOC for Ca(II) and Zr(IV)

The previous results supported that the main extraction reaction of Ca(II), Nd(III) and Zr(IV) by TODGA from HNO₃ into *n*-dodecane can be described as follows:

Here, the n , n' , and n'' values corresponding to the number of HNO₃ molecule depend on the HNO₃ concentration,⁸ and the associated number of TODGA to the reaction (1)–(3) is 2 for Ca(II) and 3 (or 4) for Nd(III) and Zr(IV). It is noted that Zr(IV) can form a zirconyl complex, ZrO²⁺, and that reaction (3)

does not take this cation into consideration. Assuming no third phase and no free TODGA in the organic phase, the extraction solvent containing 0.1 M TODGA gives the maximum concentrations of Ca(II), Nd(III) and Zr(IV) in the organic phase to be $100/2 = 50$, $100/3 = 33.3$, and 33.3 mM, respectively. These metal concentrations are considered to be the stoichiometric values.

The determination method of the maximum concentrations of Ca(II) and Zr(IV) in the organic phase was the same as that of Nd(III), which was reported elsewhere.⁷ One to one hundred mM of Ca(II) or Zr(IV) in nitric acid and a definite concentration of DGA in *n*-dodecane was prepared. After extraction, the metal concentration in the organic phase was measured and plotted against the initial metal concentration in the aqueous phase. Because of the high D values, Ca(II) and Zr(IV) in the aqueous phase were well-extracted; the results are plotted as a 1:1 relation in Figs. 1 and 2. A comparatively high metal concentration was used at a batch experiment. Due to an inadequate extractant concentration, the plots gradually deviated from the 1:1 relation, as shown in Fig. 1. If the metal concentration in the organic phase was over the extraction capacity, the third phase was formed. The composition of the third phase was the extractant, HNO₃, *n*-dodecane and metal. After the metal ion was accumulated in the third phase, the metal concentration in the organic phase decreased. In this case, a specific point was observed. It can be pointed out that the specific point suggests the existence of the third phase. The experimental conditions to suppress the third phase formation are considered to be: TODGA + (0.5–1) M DHOA/*n*-dodecane

Fig. 3 Relationship between the TODGA concentration and LOC (Ca, Nd, Zr). Condition: organic phase, 1 ml of 0.1–0.5 M TODGA/*n*-dodecane; aqueous phase, 1 ml of 3 M HNO₃.

Fig. 4 Relationship between the HNO₃ concentration and LOC (Ca, Nd, Zr). Condition: organic phase, 1 ml of 0.1 M TODGA/*n*-dodecane; aqueous phase, 1 ml of 1–4 M HNO₃.

and TD, TDdDGA for Ca and TODGA + 1 M DHOA for Zr. The highest Ca(II) and Zr(IV) concentration in the organic phase under each condition is regarded as the extraction capacity, and is called the limit of the metal concentration (LOC).

Dependence of the HNO₃ and TODGA concentration on LOC

Figure 3 shows the relationship between the TODGA concentration and LOC (Ca, Nd, Zr). Here, the aqueous phase was fixed to 3 M HNO₃. LOC for Ca(II), Nd(III) and Zr(IV) increased with the TODGA concentration, which resulted in an increase of the molar ratio of metal/TODGA in the organic phase. For instance, the molar ratios of Nd/TODGA were 0.064, 0.105, and 0.12 for 0.1, 0.3 and 0.5 M TODGA/*n*-dodecane, and other metals exhibited a similar behavior as Nd(III). When TODGA was dissolved in *n*-dodecane, TODGA/*n*-dodecane had a higher polarity than that of *n*-dodecane without TODGA. In general, the metal-complex is stable under a solvent with high polarity; the stability of the Nd-TODGA complex might increase with the TODGA concentration. The stoichiometric Nd/TODGA ratio is 0.33; the maximal LOC, 0.12, described above, is smaller than the stoichiometry. The extraction condition can be improved.

The dependence of the HNO₃ concentration on LOC (Ca, Nd, Zr) is shown in Fig. 4. Ca(II) and Nd(III) have analogous behavior: LOC decreases with an increase of the HNO₃ concentration. Because of complexation with HNO₃ the activity of TODGA is low^{9,10} and the third phase is easy to form at a high concentration of HNO₃,⁷ the LOC value is lowered at a high HNO₃ concentration. The behavior of LOC (Zr) has a peculiar relation with HNO₃. LOC (Zr) increases with HNO₃ from 1 to 3 M, showing the maximal 7.8 mM, and then decreases with the HNO₃ concentration. Because of hydroxide complexation, Zr(IV) is easy to form the third phase at low acidity, which leads to a low LOC. The decrease of LOC from

Fig. 5 Relationship between the DHOA concentration and LOC (Ca, Nd, Zr). Condition: organic phase, 1 ml of 0.1 M TODGA–0.1 M DHOA/*n*-dodecane; aqueous phase, 1 ml of 3 M HNO₃.

3 M HNO₃ is due to the same reason as that of Ca(II) and Zr(IV).

Dependence of DHOA concentration on LOC

In order to suppress the third phase and to increase LOC, the modifier was introduced into *n*-dodecane. DHOA is one of the

Fig. 6 Relationship between the number of carbon atoms in the alkyl chain attached to the N atom in DGA and LOC (Ca, Nd, Zr). Condition: organic phase, 1 ml of 0.1 M DGA/*n*-dodecane; aqueous phase, 1 ml of 3 M HNO₃.

Fig. 7 Relationship between the DGA concentration and LOC (Ca). Condition: Organic phase, 1 ml of 0.1 – 0.3 M TODGA, 0.1 M TODGA-0.2 M DHOA, 0.1 M TODGA-0.5 M DHOA, 0.1 – 0.3 M TODGA-1 M DHOA, 0.1 M TDDGA, 0.1 – 0.3 M TDdDGA in *n*-dodecane; aqueous phase, 1 ml of 3 M HNO₃.

suitable modifiers; this compound has the same components (C, H, N and O) as DGA and high solubility in *n*-dodecane. Figure 5 shows the relationship between the DHOA concentration and LOC (Ca, Nd, Zr). It is apparent that LOC increases with the DHOA concentration. Because the addition of a modifier changes the nature of *n*-dodecane to a polar solvent, the metal complex is more stable than that in pure *n*-dodecane. DHOA suppress the third phase formation and enhances LOC for these metals. As described above, LOC of Ca(II), Nd(III) and Zr(IV) under these conditions were 50, 33.3, and 33.3 mM, respectively. It is noted that LOC (Zr) by 0.1 M TODGA-1 M DHOA (37 mM) exceeds the stoichiometry (33 mM). Concerning this, LOC (Nd) by 0.1 M TODGA-(0.5 – 1) M DHOA reaches to the stoichiometric values.⁷ The reason for the above stoichiometry is that DHOA as well as TODGA can extract Zr(IV). It was confirmed that *D* (Ca, Nd) by DHOA is negligibly small; however, *D* (Zr) is 0.22 under 3 M HNO₃ and 1 M DHOA/*n*-dodecane. From this point, LOC (Zr) using DHOA, itself, was measured; the result was 0.15 mM for 3 M HNO₃ and 1 M DHOA. The sum of the respective LOC (Zr) of 0.1 M TODGA and 1 M DHOA is 33.15 mM, which is still lower than 37 mM. It appears that one of the synergistic effects is present in maximal Zr(IV) extraction by TODGA-DHOA. We obtained a lower LOC (Ca) than those for Nd(III) and Zr(IV) under the same condition, although there was no third phase formation. It is considered that effect of the DHOA concentration on the increase of LOC (Ca) is weak.

Influence of DGA with a different alkyl chain attached to the N atom on LOC

It has already been reported that the length of the alkyl chain combined to DGA influences LOC (Nd), and DGA with more than 17 and monoamide with more than 13 of C/O ratio have no

third phase.^{7,11} Here, the C/O ratio is defined as the ratio of carbon against oxygen atoms in the extractant. In the present work, we determined LOC (Ca, Zr) using TODGA, TDDGA and TDdDGA. The dependence of LOC values on the number of carbon atoms in the alkyl chain attached to N atoms is shown in Fig. 6. It is evident that DGA containing the long alkyl chain gave a high LOC. Because of the third phase formation, LOC (Zr) was much lower than the stoichiometric value (33 mM). For Ca, LOC in Fig. 6 is still lower than the stoichiometric value (50 mM). As shown in Fig. 1, there is no specific point in the relation for TODGA, TDDGA and TDdDGA; these conditions hardly form the third phase. In the absence of a third phase, Ca(II) is present in both the aqueous and organic phases. Taking the results of no third phase and a lower LOC than stoichiometry into consideration, 50 mM Ca(II) in a non-polar solvent is extremely high, which leads to a distribution of metal into both phases.

We summarize the data of this work in Figs. 7 and 8. These figures show the relation between the LOC (Ca, Zr) and DGA concentrations by using a TODGA-DHOA mixture and the different DGA compounds. From Fig. 7, the order of LOC (Ca) is TDdDGA > TDDGA > TODGA + 0.5 M DHOA > TODGA + 1 M DHOA > TODGA + 0.2 M DHOA > TODGA. The order of LOC (Zr) in Fig. 8 is TODGA + 1 M DHOA > TODGA + 0.5 M DHOA > TODGA + 0.2 M DHOA > TDdDGA > TDDGA > TODGA. Due to the different chemical characteristics, the hydrolytic property of Ca(II) and Zr(IV) and chemical forms in the organic phase, the experimental condition for high LOC is different for each metal. The recommended condition to have a high LOC (Ca) is to use TDdDGA/*n*-dodecane; that for Zr(IV) is TODGA + 1 M DHOA/*n*-dodecane.

Fig. 8 Relationship between the DGA concentration and LOC (Zr). Condition: organic phase, 1 ml of 0.1–0.2 M TODGA, 0.1 M TODGA–0.2 M DHOA, 0.1 M TODGA–0.5 M DHOA, 0.05–0.2 M TODGA–1 M DHOA, 0.1 M TDDGA, 0.1 M TDdDGA in *n*-dodecane; aqueous phase, 1 ml of 3 M HNO₃.

Conclusion

We measured and compared LOC (Ca, Nd, Zr) under different conditions. Each metal has a different chemical behavior, which exhibits the individual features on the extraction capacity. It was confirmed that the highest LOC (Ca) and LOC (Zr) can be obtained by the following condition: TDdDGA and

TODGA + 1 M DHOA, respectively. The stoichiometric value of Zr(IV) can be reached using the condition, TODGA + 1 M DHOA, which is the same condition as that for Nd extraction. However, LOC (Ca) hardly reaches the stoichiometric value by any conditions, even without third-phase formation.

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