Selective Separation of Trivalent Europium(III) from Americium(III) using \(N,N^{\prime}\)-Dimethyl-\(N,N^{\prime}\)-di-2-phenylethyl-diglycol Amide (MPEDGA) Extractant in Ionic Liquid

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A diglycolamide based \(N,N^{\prime}\)-Dimethyl-\(N,N^{\prime}\)-di-2-phenylethyl-diglycol amide (MPEDGA) extractant was synthesized and dissolved into 1-butyl-3-methylimidazolium nonafluorobutanesulfonate ([C4mim][NfO]) to prepare the extraction phase. Its separation performance of Am-241 with Eu-152 in nitric acid solution was investigated. The extraction kinetics were fast and could reach equilibrium within 15 min. When [HNO3] = 0.1 M, the maximum \(SF_{\text{Eu-152/Am-241}}\) was obtained as 124. Moreover, with increase in the concentration of HNO3, the extraction ability decreased gradually, and \(SF_{\text{Eu-152/Am-241}}\) decreased as 3 when [HNO3] reached 4 M. Back extraction was successfully completed by using 1 M guanidine carbonate with 0.5 M ethylenediaminetetraacetic acid (EDTA) or 1 M guanidine carbonate with 0.5 M diethylenetriaminepentaacetic acid (DTPA), respectively. Slope analysis revealed a 1:3 complex was formed. Effect of temperature further clarified the extraction process was exothermic.

1. Introduction

The utilization of nuclear power is considered an effective way to produce electricity with a relatively low emission of greenhouse gases [1]. However, large amounts of spent nuclear wastes are generated every year. The minor actinides (MAs), such as americium (Am\(^{3+}\)), curium (Cm\(^{3+}\)) etc. contributes for less than 1 wt% of the spent nuclear wastes issuing from the current light water reactors, but are responsible for much of the long-term radiotoxicity and heat load of high-level liquid waste (HLLW) issued from the PUREX process [2]. The separation and transmutation of MAs can significantly reduce the long-term thermal and radioactive load of the spent nuclear waste intended for disposal in a deep geological repository. However, the bulk of lanthanides (Lns) in HLLW can effectively absorb neutrons and therefore compete the transmutable MAs capturing neutrons. For a good transmutation, it is very necessary to separate MAs from Lns [3]. Selective separation of MAs and Lns represents one of the most challenging tasks due to their similar ionic radii and chemical properties [4]. According to the principle of hard and soft acids and bases, although both MAs and Lns are hard acids, MAs are slightly softer than Lns. Therefore, it has been postulated that ligands containing soft donors such as N or S are promising for the mutual separation of MAs and Lns [5]. In conventional solvent extraction, 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (BTPs) [6], 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPhens) [7] or \(N,N,N^{\prime},N^{\prime}\)-tetrakis(2-pyridylmethyl) ethylenediamine (TPEN) [8] etc. have been widely studied. However, they suffered from poor chemical and irradiation stability, slow extraction kinetics, as well as synthesis difficulties, resulting in their unsuitable utilization in
practical process [9]. Thus, great efforts still needed to explore more efficient extractants or extraction system for MAs/Lns separation.

In recent years, as ionic liquids (ILs) possess many unique properties such as non-flammability, negligible volatility, wide electrochemical window, and high thermal stability, have been attracted much attention as a new class of solvents in many fields of chemistry and industry [10]. The application of ILs to the reprocessing of spent nuclear waste and recovery of MAs from HLLW has been a field of increasing interest and importance in recent years [11]. Mohapatra et al. demonstrated that octyl(phenyl)-N,N'-diisobutyl carbamoylmethylphosphine oxide (CMPO) dissolved in ILs enhanced the extraction ability of MAs and Lns compared with in a traditional organic solvent [12]. Rout et al. studied the separation performance of MAs and Lns by using bis(2-ethylhexyl)phosphoric acid (D2EHPA), bis(2-ethylhexyl)diglycolic acid (HDEHDGA) dissolved in 1-methyl-3-octylimidazolium bis(trifluorosulphonyl)imide (omimNTf2). However, their extraction system can only work well in a relatively high pH area [13]. However, diglycolamide (DGA) derivatives have been identified as the most promising ligands for the extraction of MAs and Lns in HLLW during the past decade, due to their high distribution ratios of MAs and Lns, fulfilling ‘CHON’ principle, and easy synthesis etc. A series of DGA with different side chains have been synthesized, and their extraction properties towards MAs and Lns were studied in the worldwide [14]. Based on their results, it was found that DGA derivatives with a relatively bulky group can decrease the distribution ratio (D) value for MAs, which can be explained as the inducing of steric hindrance during the complexation process with MAs. Though its extraction affinity toward MAs was lower than that of the linear chain DGA homologue, it seemed quite useful for MAs and Lns partitioning studies [15].

In order to develop an extraction system, which can maintain a good separation performance of Am(III) and Ln(III), at the same time can be used in a relatively strong nitric acid solution. In the present work, we selected and synthesized a diglycolamide based novel N,N'-dimethyl-N,N'-di-2-phenylethyl-diglycol amide (MPEDGA) extractant which is a neutral tridentate ligand, and composed of C, H, O, and N atoms (the CHON principle), also considered as a green extractant. Further, the extraction behavior of Am-241 and Eu-152 from nitric acid solution has been investigated using MPEDGA as an extractant in combination with ionic liquid [C₄mim][NfO] as solvent, where [C₄mim]+ is 1-butyl-3-methylimidazolium and [NfO]⁻ is nonafluorobutane-sulfonate. [NfO]⁻ anion was chosen because it was fluorinated anions with relatively satisfactory hydrophobicity, and it was far more stable than the very common tetrafluoroborate and hexafluorophosphate anions. On the other hand, water saturated [C₄mim][NfO] seemed to have more in common with the conventional salt solutions. Thus, in liquid-liquid extraction process, [C₄mim][NfO] could cause the extraction system to form an aqueous biphasic extraction system, which was a benefit for the formation of a unique set of IL phase metal complexes and complex extraction equilibrium [16].

2. Experimental

2.1 Materials

In this study, all chemical reagents such as europium nitrates Eu(NO₃)₃·6H₂O, diglycolic acid, N-methyl-2-phenylethylamine were of analytical grade and were used as received without any further purification. Stock solution of Am-241 (37 MBq/cm³) and Eu-152 (37 MBq/cm³) were provided by Japan Radioisotope Association (JRA) and then diluted into different HNO₃ concentration (0.1 – 4.0 M). The
aqueous solutions were prepared by adding appropriate amounts of nitrate salts in deionized water.

### 2.2 Synthesis of MPEDGA

The ligand used in this study, \( \text{N},\text{N}′-\text{Dimethyl-\text{N},\text{N}′-di-2-phenylethyl-diglycol amide (MPEDGA)} \) was synthesized according to the route shown in Scheme 1, which was mildly modified on the basis of known procedures \[17\]. Firstly, \( \text{N-methyl-2-phenylethylamine (4.6 g, 0.03 mol)} \) and diglycolic acid (2.3 g, 0.02 mol) were dissolved in methanol solution. \( \text{4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) (10.8 g, 0.04 mol)} \) was added slowly into the above mixture and the reaction remained under reflux for 2 h in room temperature. The mixture was filtered. The solvent was removed under reduced pressure. The crude product was purified with silica gel column chromatography (eluent: Hexane/EtOAc = 1:2). The target compound MPEDGA was obtained as a yellow oil (3.2 g, 0.01 mol, 52%).

IR and H-NMR spectra characterized the prepared diamides. IR (deposit from CH2Cl2 solution on a KBr plate: 1730(C=O) cm\(^{-1}\), 1630-1660(C-N) cm\(^{-1}\), \(^1\text{H NMR (CDCl}_3, \text{400 MHz}) \delta 7.31-7.13 \text{ (m, 6H)}, 4.29-4.23 \text{ (m, 2H)}, 4.14-4.07 \text{ (m, 2H)}, 2.82 \text{ (s, 3H)}, \quad \text{\(^{13}\text{C NMR (CDCl}_3, \text{125 MHz}) \delta 170.7 \text{ (C=O)}, 137.5 \text{ (C)}, 128.9-127.6 \text{ (CH)}, 67.7 \text{ (CH}_2\), 50.4 \text{ (CH}_2\), 34.4 \text{ (CH}_3\)\) )

![Scheme 1. Synthesis procedure of MPEDGA.](image)

### 2.3 Extraction studies

All the extraction experiments were conducted using the following method. Firstly, ionic liquid phase was prepared by diluting MPEDGA in 1-butyl-3-methylimidazolium nonafluorobutanesulfonate ([\(\text{C}_4\text{mim}\)][\(\text{NfO}\)], a commonly used room temperature ionic liquid that can provide high solubility for MPEDGA. Then, non-radioactive aqueous phase was prepared by dissolving Eu(NO\(_3\))\(_3\).6H\(_2\)O in deionized water. All radioactive experiments were performed in the glovebox. The aqueous phase used in radioactive experiments was prepared with stock solution of Am-241 (37 MBq/cm\(^3\)) and Eu-152 (37 MBq/cm\(^3\)) in different HNO\(_3\) concentration (0.1 – 4.0 M), each with a radioactivity of 25 kBq/cm\(^3\). Both the aqueous phase and the ionic liquid phase were mixed in a small vial (volume ratio= 1 : 1) and shaken vigorously. After phase separation by centrifugation, the concentrations of non-radioactive metal ions in aqueous phase were determined by inductively coupled plasma optical emission spectrometry (ICP-AES). The activity of Am-241 and Eu-152 were determined by well type NaI(Tl) scintillation spectrometry and liquid scintillation counting, respectively. The extraction percentage (\(E\%\)) and distribution coefficient (\(D\)) were calculated by the following equations, respectively \[18\]:

\[
E\% = 100 \times \frac{([M^{3+}]_{\text{ini}} - [M^{3+}]_{\text{aq}})}{[M^{3+}]_{\text{ini}}} \quad (1)
\]

\[
D = \frac{([M^{3+}]_{\text{ini}} - [M^{3+}]_{\text{aq}})}{[M^{3+}]_{\text{aq}}} \quad (2)
\]
where \([M^{3+}]_\text{in}\) and \([M^{3+}]_\text{aq}\) denote the \(M^{3+}\) concentrations in the aqueous phase before and after extraction.

3. Results and Discussion

3.1 Extraction kinetics of Am-241 and Eu-152

Figure 1 shows the extraction percentage of Am-241 and Eu-152 as a function of contact time at an initial HNO_3 concentration of 2.0 M.

![Figure 1. Variation of the extraction percentage of Am -241 and Eu-152 as a function of equilibration time.](image)

Ionic liquid phase: \([\text{MPEDGA}] = 2 \text{ mM}, V = 0.5 \text{ mL};\) Aqueous phase: \([\text{Am-241}] = 820 \text{ nM, [Eu-152]} = 30 \text{ nM, [HNO}_3\text{]} = 2 \text{ M, } V' = 0.5 \text{ mL};\) Temperature: 298 K; Shaking time: 1 h.

From the results, we can see that the extraction kinetics of Am-241 and Eu-152 were fast and extraction equilibrium was achieved within about 15 min. Hence, all of the other radioactive extraction experiments conducted in this study were performed by shaking vigorously for 1 h, which was long enough to reach a constant state. However, the fast extraction rate by MPEDGA revealed that the use of a phase-transfer agent, which was commonly needed to improve the extraction kinetics was not necessary [19].

3.2 HNO_3 concentration dependence of Am-241 and Eu-152

The effect of HNO_3 concentration on the extraction performance of MPEDGA towards Am-241 and Eu-152 was evaluated in 0.1 – 4 M HNO_3 with the results shown in Figure 2. When \([\text{HNO}_3] = 0.1 \text{ M, a relatively high } D\) value for Eu-152 was observed \((D_{\text{Eu-152}} > 10^5)\), indicating that the extraction of Eu-152 by MPEDGA was very efficient in a weak acidic condition. At the same time, \(D\) value for Am-241 was approximately 2 orders of magnitude lower than \(D_{\text{Eu-152}}\). In addition, the resulting maximum separation factor \(SF_{\text{Eu-152}/\text{Am-241}}\) was calculated as 124. However, with increase in the concentration of HNO_3, the distribution factor of Am-241 and Eu-152 decreased gradually, the \(SF_{\text{Eu-152}/\text{Am-241}}\) decreased to around 3, when \([\text{HNO}_3] = 2 \text{ M. In addition, in the HNO}_3\text{ concentration range, it was found that MPEDGA exhibited preference to Eu-152 compared to Am-241, which encouraged the utilization of MPEDGA as a feasible ligand for the}}\)
separation of Am-241 and Eu-152 from HLLW [20].

Figure 2. Variation of the distribution ratio of Am-241 and Eu-152 as a function of nitric acid concentration. Ionic liquid phase: [MPEDGA] = 2 mM, V = 0.5 mL; Aqueous phase: [Am-241] = 820 nM, [Eu-152] = 30 nM, [HNO₃] = 0.1 – 4 M, V = 0.5 mL; Temperature: 298 K; Shaking time: 1 h.

Figure 3. Slope analysis of Eu³⁺ extraction as a function of MPEDGA concentration in [C₄mim][NfO]. Ionic liquid phase: [MPEDGA] = 90 – 150 mM, V = 0.5 mL; Aqueous phase: [Eu³⁺] = 5 mM, [HNO₃] = 2 M, V = 0.5 mL; Temperature: 298 K; Shaking time: 1 h.
3.3 Extraction stoichiometry of Eu\(^{3+}\)

Slope analysis was carried out as a function of the equilibrium concentration of MPEDGA in the ionic liquid phase to determine the stoichiometry of the formed Eu\(^{3+}\)–MPEDGA complex. As shown in Figure 3, the obtained distribution ratio increased with an increase in the concentration of MPEDGA. A linear regression analysis of the extraction data resulted in a straight line with a slope of around 3. This result suggested that the extracted species was Eu(MPEDGA)\(^{3+}\). For instance, three MPEDGA molecules were required to extract one Eu\(^{3+}\) into ionic liquid, which was consistent with the previous studies of neutral diglycolamide based extractants in an ionic liquid extraction system. In addition, the possible extraction mechanism can also be summarized as shown in equation 3 [21]:

\[
\text{Eu}^{3+\text{aq}} + 3([\text{C}_4\text{mim}])^+\text{IL} + 3\text{MPEDGA}_{\text{IL}} \leftrightarrow \text{[Eu(MPEDGA)\(^{3+}\)]}_{\text{IL}} + 3([\text{C}_4\text{mim}])^{+\text{aq}} \quad (3)
\]

3.4 Temperature dependence of Eu\(^{3+}\)

Extraction experiments towards Eu\(^{3+}\) were further carried out at different temperatures. The distribution ratio of Eu\(^{3+}\) decreased slightly with increasing temperature as shown in Figure 4.

Based on the van’t Hoff equations, the thermodynamic parameters can be calculated by the following equations [22,23]. \(\Delta H\) was provided as the slope from the plot of Log \(D_{\text{Eu}}\) against 1000/T as shown in Figure 4, \(\Delta G\) can be obtained from the intercept in Figure 3, and all the calculated results were summarized as shown in Table 1.

\[
\Delta H = -2.303 \cdot R \cdot \Delta \log D_{\text{Eu}} / \Delta (1000/T) \quad (4)
\]
\[
\Delta G = -2.303 \cdot R \cdot T \cdot \log K_{\text{Eu}'} \quad (5)
\]
\[
\Delta G = \Delta H - T \cdot \Delta S \quad (6)
\]

where, \(D_{\text{Eu}}\) is the distribution ratio of Eu; \(K_{\text{Eu}'}\) is the conditional equilibrium constant; \(\Delta G\) is the change of Gibbs free energy; \(\Delta H\) is the change of enthalpy; \(\Delta S\) is the change of entropy; \(R\) is the gas constant (8.314 J/mol·K).

The value of \(\Delta G\) was determined to be -16.717 kJ/mol at 298 K. It indicated that the extraction was energetically favorable and spontaneous. The value of \(\Delta S\) was determined to be 0.039 J/(K·mol), attributing to the order in the complex formation during extraction. These results also revealed that the extraction reaction was exothermic [24].

| Table 1. Summary of calculated \(\Delta H^o\), \(\Delta S^o\) and \(\Delta G^o\). |
|-----------------|------------------|
| \(\text{Eu}^{3+}\) | \(\Delta H^o\) (kJ/mol) | -4.929 |
|                  | \(\Delta S^o\) (kJ/mol K) | 0.039  |
|                  | \(\Delta G^o\) (kJ/mol)   | -16.717 (298 K) |
Figure 4. Extraction of Eu$^{3+}$ with MPEDGA at different temperatures. Ionic liquid phase: [MPEDGA] = 100 mM, $V = 0.5$ mL; Aqueous phase: [Eu$^{3+}$] = 5 mM, [HNO$_3$] = 2 M, $V = 0.5$ mL; Temperature: 288 – 323 K; Shaking time: 1 h.

3.5 Back-extraction of Am-241 and Eu-152

For the practical utilization of this MPEDGA/[C$_{4}$mim][NfO] extraction system, efficient stripping of the extracted metal ions is an important consideration. As is known, diglycolamide based extractants used in molecular diluents such as n-dodecane, the extraction of the actinide ions is preferably completed at 3–4 M HNO$_3$, while stripping is conducted by just contacting with diluted acid solutions. However, since ionic liquid based extraction systems, show a very high extraction ability of actinide ions at lower acidities areas, stripping of resulting the metal ions from the ionic liquid phase becomes a challenging task. Therefore, complexing agents in buffered medium are highly recommended to be used for the stripping of the actinide ions. Previously, ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) in guanidine carbonate was employed for the quantitative stripping of Am-241 from ionic liquid extraction systems containing diglycolamide based extractants [20]. Therefore, in this study, back-extraction experiments were carried out only once under 1 M guanidine carbonate with 0.5 M EDTA (Type A), 1 M guanidine carbonate with 0.5 M DTPA (Type B) and 1 M citric acid with 0.4 M formic acid, 0.4 M hydrazine hydrate (Type C), respectively. The results of all of the back-extraction experiments were presented as the back-extraction percentage ($BE$, %), which describes the percentage of a particular metal ion that is stripped from the ionic liquid phase into the aqueous phase. Depending on the metal concentration of the specific metal ion, $BE$ was defined as shown in equation 7 [25]:

$$BE\% = 100 \times \frac{[M^{3+}]_{aq}}{[M^{3+}]_{0}}$$  \hspace{1cm} (7)
where $[M^{3+}]_0$ is the concentration of the metal ion in the ionic liquid phase before stripping; $[M^{3+}]_{aq}$ is the concentration of the metal ion in the aqueous phase after stripping.

As the result shown in Table 2, it was observed that almost 100% Am-241 and Eu-152 could be stripped successfully by using 1 M guanidine carbonate with 0.5 M EDTA and 1 M guanidine carbonate with 0.5 M DTPA. However, 1 M citric acid with 0.4 M formic acid, 0.4 M hydrazine hydrate solution showed poor back extraction performance.

| extractant | BE% | Am-241 | Eu-152 |
|------------|-----|--------|--------|
| Type A     | 99.9| 100.0  |        |
| Type B     | 100.0| 100.0  |        |
| Type C     | 0.0 | 0.0    |        |

4. Conclusion

Diglycolamide based MPEDGA extractant was synthesized. Its separation performances towards Am-241 and Eu-152 in ionic liquid [C₄mim][NfO] were investigated. Extraction kinetics were fast and the extraction equilibrium was reached within 15 min. With increasing the concentration of HNO₃, the extraction ability decreased gradually, and maximum $SF_{Eu-152/Am-241}$ could be obtained as 124 at $[HNO₃] = 0.1$ M. $SF_{Eu-152/Am-241}$ could still remain as 3 even though the $[HNO₃]$ reached 4 M. From the results of the slope analysis, it can be confirmed that the formation of a 1:3 complex between Eu³⁺ and MPEDGA occurred in this ionic liquid extraction system. Effects of temperature experiments revealed that the extraction process was found to be exothermic, spontaneous and ordered in nature. All the extracted metal ions could be quantitively stripped into aqueous phase by using 1 M guanidine carbonate with 0.5 M EDTA or 0.5 M DTPA, respectively. Finally, we hope that the MPEDGA/[C₄mim][NfO] extraction system could be used as a potential candidate for the selective separation of Am-241 and Eu-152 from HLLW.

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