Continuous mutual separation of lanthanides by a liquid-liquid countercurrent centrifugal extractor with Taylor vortices

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Abstract

A liquid-liquid countercurrent centrifugal extractor with Taylor vortices which is appropriate for high-performance extraction has been developed. Until now, continuous extraction with more than ten multiple theoretical stages has been demonstrated by a single centrifugal extractor in the case of single specie (zinc extraction with di(2-ethylhexyl)phosphoric acid (D2EHPA)). In the present study, the centrifugal extraction system has been applied to a multispecies case to clarify the separation behavior by countercurrent Taylor mixing. The extraction behaviors of lanthanides (Sm and Eu) with D2EHPA were compared among batch equilibrium measurements, rate measurements by a constant-interfacial-area cell and the continuous experiments by the centrifugal extractor. In the continuous experiment, the separation factor ($SF = D_{\text{Eu}}/D_{\text{Sm}}$) became more than tripled in comparison with the batch equilibrium value due to the multistage extraction effect caused by the countercurrent contact of aqueous/organic phases. The number of theoretical stages of our extractor was evaluated to be 8 to 9 in terms of $D_{\text{Eu}}$ and 4 to 5 in terms of $SF$ at the rotation speed of 1400 rpm. The $SF$ value from the rate measurement data ($SF_{\text{noneq}}$; $SF$ in non-equilibrium state) was slightly lower than the batch extraction data ($SF_{\text{eq}}$; $SF$ in equilibrium state) which resulted in difference between theoretical stages evaluated from $D_{\text{Eu,eq}}$ and $SF_{\text{eq}}$. Although this would slightly decrease the separation efficiency by the continuous extraction, the countercurrent multistage effect was still dominant. By considering this feature, a more effective separation process would be developed by utilizing the countercurrent centrifugal extractor with Taylor vortices.

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1. Introduction

Nuclear fuel cycle produces not only carbon free energy and fissionable metals for new fuels, but also many reusable metals such as lanthanides and precious metals. Some of them are expected to be reused after the cooling period [1,2]. There are many methods to separate chemical species based on liquid-liquid extraction [3]. For advanced chemical reprocessing of nuclear spent fuels, Cs, Sr and actinide/lanthanide separations are important and have been extensively studied [4,5]. In the case of chemical species separation from high level liquid wastes by liquid-liquid extraction, the extraction process needs to be simple, small and fast to mitigate the radiolysis and the production of secondary liquid wastes. Therefore, extractors with high separation performance are needed.

Upon this background, we have developed a liquid-liquid countercurrent centrifugal extractor. Many kinds of extractors have been developed, and most of the annular type extractors for liquid-liquid extraction were developed for fast and massive extraction [6,7]. Our centrifugal extractor can induce Taylor vortices inside the annular fluid region and hold a steady concentration gradient, which allows the extraction with about ten theoretical stages by a single extractor (extraction of zinc with di(2-ethylhexyl)phosphoric acid (D2EHPA)). The features including multistage behavior of this type of extractors were studied [8-12]. Because the previous studies were conducted only under single-specie cases, the separation behavior of multispecies in the extractor was not known. Hence the separation behavior between two species is studied in the present work. To survey the separation performance, we conducted separation experiments of lanthanides (Sm and Eu) with D2EHPA because adjacent lanthanides are comparatively difficult to separate each other due to the chemical similarity. Also, we measured the extraction rates of lanthanides and compared the results with the batch and continuous extraction data using number of theoretical stages evaluated by distribution ratios and separation factors in order to understand the effect of equilibrium and non-equilibrium states on separation behavior. Because mixer-settlers are mainly governed by extraction equilibrium but our extractors should be also governed by non-equilibrium due to the countercurrent contact of organic and aqueous phases.

2. Experiment

The feed aqueous phase was prepared using lanthanide(III) nitrates, where ionic strength was maintained at 0.04 mol/L by sodium nitrate. In the continuous experiment using the centrifugal extractor and the rate measurement, its pH was adjusted to 1.5 by nitric acid. In the batch equilibrium experiment, the pH was adjusted by adding nitric acid or sodium hydroxide. The feed organic phase contained 5 or 10 mmol/L of D2EHPA (Tokyo Chemical Industry Co., LTD) diluted by n-dodecane. In batch equilibrium experiment, 3 mL of the organic and aqueous phases were mixed inside the 13.5-mL vials at 25°C by horizontal shaking for 2 hours. The geometry of the centrifugal extractor shown in Figure 1 was the same as that of the previous study [9]. It consisted of mainly three parts; inner rotor (diameter: 30 mm, height: 400 mm), static outer wall (inner diameter: 40 mm) and settling parts in top (height: 40 mm) and bottom (height: 20 mm). The organic phase was introduced from the bottom injection pipe, and the aqueous phase was introduced from the top injection pipe. Both phases were contacted each other through the annular fluid region (5 mm) so that the dispersed organic droplets ascended based on the difference in the specific gravities. The both phases were then separated in the settling parts at the top and bottom. With increase in the rotation speed, the flow reaches the critical Taylor number and a series of Taylor vortices are induced in the coaxial annular cylinder [13]. The Taylor vortices can effectively agitate the organic and aqueous phases as well as hold the stable concentration gradient, which leads to high extraction performance. When the rotation speed further increases, the flow inside the extractor turns from the spiral flow to dispersion flow, and finally to emulsion flow [10]. The emulsion flow is appropriate for effective mass transfer on aqueous-organic interface, while phase settlement becomes ineffective. In continuous extraction operation, the rotation speed of inner rotor was varied from 800 to 1800 rpm, and the feeding rate of both phases was 10 mL/min.

The extraction rate was measured using a constant-interfacial-area cell as shown in Figure 2, which was the same as that used by Komasawa et al. [14]. The cell consisted of a glass container separated by a Teflon board with a hole in the center (diameter was 30 mm), and two impellers equipped at the upper and lower sides rotated at 100 rpm in the opposite directions without generating droplets; hence, the aqueous-organic interfacial area was constant. This
rotation speed was fast enough to thin the boundary layer without disturbing the aqueous-organic interface. A small portion of the organic phase (1 mL) was periodically sampled, and after back extraction with 0.5 mol/L of nitric acid (1 mL), the metal concentration in the aliquot was measured. The metal concentrations were determined using an inductively coupled plasma atomic emission spectrometer (ICP-E-800, Shimadzu).

The separation performance was evaluated using distribution ratio, $D$, and separation factor, $SF$, defined as follows;

$$D_{\text{Ln,eq}} = \frac{[\text{Ln}^{3+}]_{\text{org,eq}}}{[\text{Ln}^{3+}]_{\text{aq,eq}},}$$

$$SF_{\text{eq}} = D_{\text{Eu,eq}} / D_{\text{Sm,eq}},$$

$$D_{\text{Ln,noneq}} = \frac{[\text{Ln}^{3+}]_{\text{org,noneq}}}{[\text{Ln}^{3+}]_{\text{aq,noneq}}},$$

$$SF_{\text{noneq}} = \frac{(D_{\text{Eu,noneq}}/dt)}{(D_{\text{Sm,noneq}}/dt)},$$

$$D_{\text{Ln,Taylor}} = \frac{[\text{Ln}^{3+}]_{\text{org,Taylor}}}{[\text{Ln}^{3+}]_{\text{aq,Taylor}}},$$

$$SF_{\text{Taylor}} = \frac{D_{\text{Eu,Taylor}}}{D_{\text{Sm,Taylor}}}$$

whereLn denotes lanthanide ions (Eu(III) or Sm(III)). The subscripts of ‘eq’, ‘noneq’ and ‘Taylor’ indicate the data obtained in equilibrium state by batch experiment, non-equilibrium state by rate measurement, and continuous experiment by the centrifugal extractor, respectively.

$$\text{Fig. 1. Geometry of the centrifugal extractor.}$$

$$\text{Fig. 2. The constant-interfacial-area cell.}$$

3. Result and discussions

The stoichiometry of the lanthanide extraction with D2EHPA is known to be expressed by

$$\text{Ln}^{3+} + 3\text{H}_2\text{R}_2(\text{org}) = \text{LnR}_3(\text{HR})_3(\text{org}) + 3\text{H}^+$$

where $\text{H}_2\text{R}_2$ denotes the D2EHPA dimer [15]. The apparent extraction equilibrium constant, $K_{\text{ex,ln}}$, is defined as

$$K_{\text{ex,ln}} = \frac{[\text{LnR}_3(\text{HR})_3(\text{org})][\text{H}^+]^3}{[\text{Ln}^{3+}]^3[\text{H}_2\text{R}_2]^3(\text{org})}$$

Here $[\text{H}_2\text{R}_2]^*$ denotes the effective molar concentration of $\text{H}_2\text{R}_2$ calculated by the Alstad’s empirical equation using the coefficient, $A$, of 0.83 (mol/L)-1/2 obtained for D2EHPA dissolved in n-dodecane [15, 16]. From this equation, the following relationship is derived:

$$\log D_{\text{Ln,eq}} - 3\text{pH} = 3\log [\text{H}_2\text{R}_2]^*_{\text{org}} + \log K_{\text{ex,ln}}$$

The results of the batch equilibrium experiment for Eu and Sm extraction from the respective single lanthanide solutions (0.5 mmol/L Ln(III)) are shown in Figure 3 on the basis of Eq. (6), where the straight lines with the slope
of 3 were fitted to the experimental data. From the intercepts of these straight lines, the $K_{ex,Eu}$ and $K_{ex,Sm}$ values were obtained as 1640 and 841, respectively. Thus, the $SF_{eq}$ ($= K_{ex,Eu} / K_{ex,Sm} = D_{Eu, eq} / D_{Sm, eq}$) was calculated to be 1.95.

Figure 4 shows the time course of $D_{Ln,noneq}$ of Eu and Sm measured by the constant-interfacial-area cell. The $D_{Ln, noneq}$ of each lanthanide ion linearly increased with time after the initial 10 minutes. The ratio of the slopes of the straight lines is 1.76 which is defined as $SF_{noneq}$.

Continuous extraction experiment using the mixed solution containing 0.5 mmol/L each of Eu(III) and Sm(III) was then conducted, and the $D$ and $SF$ values are compared as well as the results of multistage calculation in Figure 5. With increase in the rotation speed, the $D_{Eu,Taylor}$ and $SF_{Taylor}$ were elevated and maximized at 1400 rpm. Higher rotation than 1600 rpm generated a considerable amount of entrainment of the organic phase into the outlet aqueous phase and vice versa, which hindered the stable concentration gradients of the lanthanide ions and extractant in the annular fluid region. Also, smooth movement of the feed aqueous and organic phases was severely hindered due to the strong vortices (flooding) and resulted in worsened extraction performance. With increase in the rotation speed, the size of the vortices does not change greatly due to the stable turbulent vortices coming from high aspect ratio of fluid region, while the dispersion behavior becomes more significant. When the rotating speed was 1400rpm, $D_{Eu, Taylor}$, $D_{Sm, Taylor}$ and $SF_{Taylor}$ were 10.7, 1.71 and 6.21, respectively. By using the $K_{ex}$ values obtained above, the countercurrent multistage calculation assuming each theoretical stage was done at the same solution and flow rate conditions as those in the continuous experiment [17-19]. The calculated $D_{Eu, eq}$, $D_{Sm, eq}$ and $SF_{eq}$ were, respectively, 5.49, 1.09 and 5.06 for four stages and 6.62, 1.05 and 6.31 for five stages as shown in Figure 5. Hence, the number of theoretical stages corresponding to the extraction at 1400 rpm can be evaluated to be 8 to 9 in terms of $D_{Eu, eq}$ and 4 to 5 in terms of $SF_{eq}$. If the separation is governed by equilibrium, theoretical stages evaluated from $D_{Eu, eq}$ and $SF_{eq}$ should be the same. This difference in the theoretical stages is caused by the fact that $SF_{noneq}$ is lower than $SF_{eq}$. This characteristics is needed to be considered in separation process. Consequently, we have quantitatively confirmed that our centrifugal extractor has the separation ability with multiple theoretical stages.
1. Conclusions

The liquid-liquid countercurrent centrifugal extractor with Taylor vortices has been applied to the separation between Eu(III) and Sm(III) using D2EHPA to clarify the multispecies separation behavior. The results were compared with the equilibrium and rate data and are summarized as follows:

- By the liquid-liquid countercurrent centrifugal extractor, the $D$ and $SF$ values were elevated and maximized when the rotation speed of inner rotor was 1400 rpm; the $SF_{Taylor}$ became more than tripled in comparison with the batch equilibrium value ($SF_{eq}$).
- The difference in $SF$ values in the batch and continuous extraction comes from the multistage extraction effect due to the countercurrent contact of aqueous/organic phases.
- In the case of Eu/Sm separation, the performance in terms of $D_{Eu, eq}$ and $SF_{eq}$ (equilibrium state) were evaluated to be equivalent to 8 to 9 and 4 to 5 theoretical stages, respectively.
- The $SF_{noneq}$ was slightly lower than the $SF_{eq}$ which led the difference in the number of theoretical stages in terms of $D_{Eu, eq}$ and $SF_{eq}$. Although this would slightly decrease the separation efficiency by the continuous extraction, the countercurrent multistage effect of our extractor is still dominant.

On the basis of these results, it is concluded that there is a possibility to develop a compact and efficient separation process using the centrifugal extractor with Taylor vortices by considering the separation behavior above and optimizing the operation and solution conditions.

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