Article

Solvent Extraction of Rare Earth Metals by Microchannel Extractor

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Abstract

In order to apply a microchannel extractor to solvent extraction, the extraction of three rare earth metals (yttrium, europium and lanthanum) with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) dissolved in toluene was performed on the microchannel extractor, which has two inlets and two outlets. A parallel two-phase flow without mutual mixing was observed in the microchannel, and each phase successfully flowed out from each outlet. The extraction and back-extraction rates were measured, and the metal transfer between the two phases accompanied with an interfacial chemical reaction was proved to proceed satisfactorily in a short phase contacting time. The productivity of metals was confirmed to increase by using an extractor having a long channel and a large specific interfacial area.

1 Introduction

In recent years, much attention has been denoted to the application of microfluidic devices, which are composed of microchannels fabricated on a microchip platform, to a chemical processing. Microchannel has some advantages such as a creation of a large specific surface area and a short diffusion length for the chemical species in a microspace, and so forth. Making the most of these advantages, many applications of such devices have been attempted in the fields of organic synthesis, catalytic and analytical chemistry.[1-5] An efficient extraction without phase separation may be feasible when a microfluidic device can be utilized as the extractor because two different layers flow in a narrow space to readily form a liquid-liquid interface.[6]

The aim of this study is to apply the microchannel extractor to solvent extraction. Rare earth metals, which play an important role in developing a high technology, are very difficult of mutual separation and purification owing to the similarity of their chemical and physical properties. A cost-effective separation technique, therefore, is desired. In the present study, we focussed on the extraction and separation of three different rare earth metals, yttrium(Y), europium(Eu) and lanthanum(La). Extraction and back-extraction rates of metals with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (commercial name, PC-88A) as an extractant were measured by using the microchannel extractor fabricated on a silicon (Si) or a glass chip. We discuss the possibility of applying the microfluidic device to solvent extraction based on the extraction behavior obtained with the microchannel extractors.

2 Experimental

2.1 Microchannel extractor

Fig.1 Schematic illustration of microchannel extractor (a) Extractor 1
(b) Sectional view of channel (c) Extraction reaction at liquid-liquid interface

The microchannel extractor mainly used in this work (Extractor 1) was fabricated on a silicon chip (20 mm x 40 mm) by photolithography and wet etching methods as reported in a previous paper.[5] The extractor having two inlets and two outlets is schematically illustrated in Fig. 1 (a). The channel size was measured by a laser microscope (Keyence Japan Co., VK-8500). Another extractor (Extractor 2), which was fabricated on a glass substrate, having a long channel for the phase contacting section was kindly provided by Tosoh Co., Japan. The specifications of these microchannels are summarized in Table 1.

Table 1 Specification of microchannels

Extractor	1	2
Length of phase contacting section [mm]	23	200
Width [μm]	400	100
Depth [μm]	100	25

2.2 Reagents

Extractant, PC-88A, was kindly supplied by Daihachi Chemical Industry Co. Ltd., Japan and used without further purification. For the forward extraction, an organic solution was prepared by dissolving PC-88A in toluene. An aqueous solution containing three rare earth metals (La, Eu and Y) of each 0.1 mol/m^3 was prepared by dissolving their nitrate salt hexahydrates in a nitric acid solution. The pH in the aqueous solution was adjusted with 100 mol/m^3 -nitric acid and 100 mol/m^3 -4-aminobutyric acid solutions. An organic solution containing PC-88A and the metal complexes was prepared by the extraction of metals. A solution made up with 100 mol/m^3 -nitric acid and 100 mol/m^3 -4-aminobutyric acid was used as a back-extraction solution.

2.3 Procedure

The aqueous and the organic solutions were fed separately into the microchannel extractor with a microsyringe pump (KD Scientific Model 210) as shown in Fig. 1(a), where the volumetric flow rates of both solutions are equal. A concentration of each metal in the aqueous effluent continuously led to its own outlet was measured by an ICP-atomic emission spectrometer (Perkin Elmer Co., Optima 3100 RL).

3 Results and Discussion

3.1 Extraction and back-extraction rates

Lanthanide ion, M^{3+} , is known to be extracted as the complex, MR_33HR , formed with the dimeric

extractant PC-88A, $(HR)_2$, in toluene as follows [7]:

After joining the aqueous and the organic solutions, the parallel two-phase flow without mutual mixing was observed in the microchannel as schematically shown in Fig.1 (b). During the phase contacting, metal ions in the aqueous feed phase are extracted as the metal complex according to the reaction expressed as Eq. (1) at the aqueous-organic interface, as schematically illustrated in Fig.1 (C). For the back-extraction, the metals in the organic phase are back-extracted to the aqueous phase by the reverse reaction of Eq. (1)

The apparent extraction and back-extraction rates of metals, J_M and J'_M ($\text{mol}/\text{m}^2\text{s}$), were defined respectively based on the change in the metal concentration of the aqueous phase as follows:

$$J_M = v_{aq} (C_{M0} - C_M) / A \quad (2)$$

$$J'_M = v_{aq} C_M / A \quad (3)$$

where v_{aq} (m^3/s) is the volumetric flow rate of the aqueous phase and A is the aqueous-organic interfacial area (m^2) in the microchannel calculated by using the actual size listed in Table 1. The subscript 0 denotes the initial concentration of chemical species.

Figure 2 shows the relationship between J_M and pH in the aqueous phase at v_{aq} $5.6 \times 10^{-10} \text{ m}^3/\text{s}$. The rate was proportional to the three times of pH in a low pH range and converged in the constant value (about $4 \times 10^{-6} \text{ (mol}/\text{m}^2\text{s})$) in a high pH range. The relationship between J'_M and the initial hydrogen ion concentration in the aqueous solution, C_{H0} , is shown in Fig. 3. In the low C_{H0} range, it was found that J'_M was proportional almost C_{H0} cubed and also approached a constant value at a high C_{H0} . The extraction behavior resembled that obtained by a hollow fiber membrane extractor, which is a continuous two-phase contacting type extractor like the microchannel

Fig. 2 Effect of pH on J_M

Fig. 3 Effect of C_{H0} on J'_M

extractor used in this study. In the previous study by using the membrane extractor,[8] we elucidated the extraction mechanism of metal ions as follows: The metal extraction is completed through a sequence of three steps, that is, the diffusion of metal ions in the aqueous phase to the aqueous-organic interface, the formation of the metal complex with extractant at the interface and the diffusion of the complex to the organic phase. The extraction rate is controlled by one or more steps of the three. In a low pH range, J_M is controlled by the interfacial chemical reaction and/or the diffusion rate of the metal complex in the organic phase. It is obvious that the mutual separation of metals is possible based on the difference in the interfacial complexation rate or the stability of the

resultant metal complex among the metals, as shown in Fig.2. While, in a high pH range, where J_M is independent on the concentration of chemical species, the extraction rate is controlled by the rate of metal diffusion in the aqueous phase. The metal separation is difficult because the diffusion rate is not so different among the metals. Here, we noticed the diffusion rate. The extraction rate, J_M , which was found to be proportional to the metal concentration (data not shown), can be approximated by the equation, $J_M = K_M C_M$. Under the high pH range, the overall mass transfer coefficient, K_M , is practically the mass transfer coefficient of metal ion in the aqueous phase, k_M . The value of k_M roughly estimated to be 4×10^{-5} (m/s) by the equation above, the value of J_M and the metal concentration was larger than that obtained for the ordinal size extractor ($\sim 1 \times 10^{-5}$ (m/s)). [8,9]

It was confirmed that the extraction and back-extraction of metals satisfactorily proceed in the microchannel and the effect of scale down of the device was appeared in a molecular diffusion rate.

3.3 Raising the productivity

The characteristic extraction behavior of rare earth metals with PC-88A could be successfully observed on the microchannel extractor. The extraction degree of metals, E , were 10~20% under the present conditions because the phase contacting time estimated by V_{aq}/v_{aq} (V_{aq} : the volume of the aqueous phase) was less than 1 sec, although the short contacting time is one of the advantages of this system. Increase in the extractability is required for the application of the microchannel extractor to the metal production. The values of E measured by the extractor having a long extraction section and a large specific interfacial area (extractor 2) at v_{aq} 1.4×10^{-10} m³/s were compared to that by the extractor 1 mentioned above. As shown in Fig. 4, it was observed that the complete extraction was achieved for Y and Eu on the extractor 2, where the phase contacting time was less than 2 sec. This result suggests that the productivity of this system can be attained by the optimum design of the extractor and demonstrates the possibility of the application of the microdevice to the solvent extraction.

Fig. 4 Raising the extraction degree

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