



SEPARATION OF LANTHANIDES USING MICRO SOLVENT EXTRACTION SYSTEM

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ABSTRACT

A micro solvent extraction system for the separation of lanthanides has been investigated. The micro flow channel is fabricated on a poly(methyl methacrylate) (PMMA) plate, and solvent extraction progresses by feeding aqueous and organic solutions into the channel simultaneously. The extraction equilibrium is quickly achieved, without any mechanical mixing, when a narrow channel (100 μm width and 100 μm depth) is used. The results of solvent extraction from the Pr/Nd and Pr/Sm binary solutions revealed that both lanthanides are firstly extracted together, and then, the lighter lanthanide extracted in the organic solution alternatively exchanges to the heavier one in the aqueous solution to achieve the extraction equilibrium. The phase separation of the aqueous and organic phases after extraction can also be successively achieved by contriving the cross section of the flow channel, and the extractive separation of Pr/Sm is demonstrated.

Keywords: Micro solvent extraction, Separation, Light lanthanide, Middle lanthanide

INTRODUCTION

Separation and recovery of metals constitute the current issues which are expected to support the advanced technology. Solvent extraction as well as ion exchange have been applied on an industrial scale. Along with the progress in studying the separation of metals, solvent extraction has been

found out to be more selective than ion exchange, even when they exploit similar functional groups. One disadvantage, however, is that a large amount of an organic solvent is needed to dissolve both the extractant and the extracted species. The encapsulation of the extractant into the polymer matrix was therefore investigated, as the second generation of the extraction system, to prevent losing the organic solvent into the aqueous phase [1-4]. Although the microcapsules with the extractant possess the equivalent potential for separation ability when compared to the original extractant, some other properties, e.g.: loading capacity and/or extraction rate, are reduced [4]. When the solvent extraction process is considered, reduction of the organic solvent should be taken into account.

Along with the progress in microfabrication, the micro chip technology has recently attracted much attention, especially in the field of analytical chemistry [5], and micro total analysis system (μ TAS) has been advocated. The μ TAS generally includes pre-treatment of sample, reaction of sample with reagent, and sensitive detection. Additionally, solvent extraction was started to be applied as a separation technique in the pre-treatment step of the trace metal assay [6,7]. These studies showed that a micro flow channel is suitable for the interfacial reaction of solvent extraction, since the micro flow channel increases the ratio of the interface area (between aqueous and organic phases), to the volume of the aqueous and organic phases. This potential was also supported by simulation [8,9] and kinetic research [10-12]. In addition, the liquid membrane operation with three phase flows was recently achieved on a micro flow channel [11], and extraction as well as stripping were carried out simultaneously [13]. There are, however, relatively few reports concerning the process of metals separation on a micro chip with solvent extraction.

In the present work, a micro solvent extraction system under practical operating conditions was therefore developed. The micro solvent extraction chip was fabricated on a PMMA plate, and the extraction property of lanthanide was investigated. The separation of lanthanides (Pr/Nd and Pr/Sm) was then performed on the micro extraction chip, and compared with a conventional extraction system. In addition, separation of two phases after the extraction, without modification of the channel interface, was developed for the practical separation process. The separation of the above lanthanides was conducted with the micro solvent extraction chip developed.

EXPERIMENTAL

The commercial extractant, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA, marketed as PC-88A by Daihachi Chemical Industry Co. Ltd.), was used as received. All inorganic chemicals were supplied by Wako Pure Chemical Industries as analytical-grade reagents. Aqueous feed solutions were prepared by dissolving appropriate amounts of lanthanide chlorides in deionized water. The organic solution was prepared

by dissolving EHPNA in kerosene. In the case of conventional extraction system, the mixed aqueous and organic solutions, at the organic/aqueous (O/A) volume ratio of 1:1, were shaken and equilibrated at 298 K for 1 h. The pH value of the aqueous feed solution was adjusted by adding appropriate amount of NaOH to a lanthanide chloride solution. Weighed samples of the organic solution were stripped by 3 mol/L HCl at the O/A ratio of 0.5. The lanthanide concentrations in aqueous phase samples were analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin Elmer Optima 4300DV Cyclon). The aqueous pH was measured with a pH meter (Horiba F-23).

The micro solvent extraction chip was made on the 3 cm \times 7 cm PMMA plate using a table type NC detailed processing machine (PMT Corporation Co. Ltd.). The channel was adhered with the PMMA plate cover in a constant temperature oven at 393 K. In the present study, two kinds of micro solvent extraction chips were prepared, as shown in Figure 1.

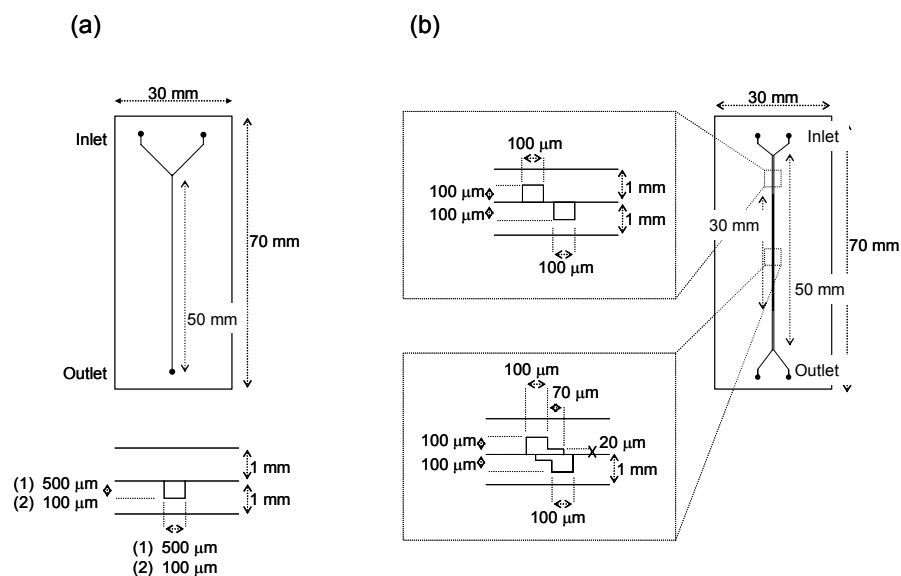


Fig. 1. Micro solvent extraction chip.

In the case when the extraction property was tested, the Y-type micro flow channel, with a normal cross section, was used (Figure 1a). In this case, the organic and aqueous feed solutions were fed into the micro flow channel via two inlets at the same flow rate using a programmable syringe pump (Harvard, PHD 2000-M). The mixture of the solutions was then collected at the outlet of the chip, and weighed organic samples were stripped by 3 mol/L HCl. In the case of a micro solvent extraction process, the micro flow channel with a complicated cross section, as shown in

Figure 1b, was used to achieve the phase separation after extraction. In this case, the organic and aqueous feed solutions were fed from two inlets, respectively. The resulting aqueous and organic solutions were separated and fed out from the two inlets. The weighed organic samples were stripped by 3 mol/L HCl. The resulting aqueous samples were analyzed using the ICP-AES.

RESULTS AND DISCUSSION

Extraction Equilibrium

The extraction equilibrium for the lanthanides with EHPNA in kerosene, up to high loading ratios, were described in previous papers [14,15]. It is well known that the aggregated species appear when the metals are extracted with acidic organophosphorus compounds. The maximum loading ratio ($[\overline{\text{Ln}}]/[\overline{(\text{RH})}_2]_{\text{feed}}$) of the lanthanides with EHPNA is 0.4, which suggests that an aggregated species contains a dimeric extractant and a lanthanide with the molar ratio of 5:2. The extraction equilibrium of the lanthanides is therefore expressed as:

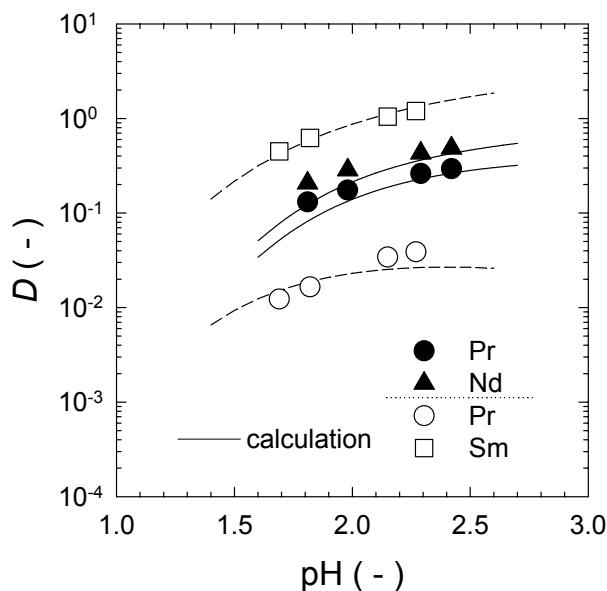
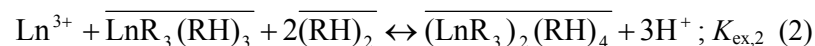
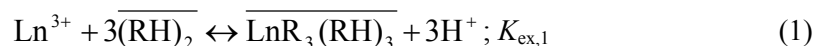


Fig. 2. Effect of pH on distribution ratio for the lanthanides in binary system. Closed keys show Pr/Nd system, and open keys show Pr/Sm system. $[\overline{(\text{RH})}_2]_{\text{feed}} = 0.05 \text{ mol/L}$ and $[\text{Ln}_i^{3+}]_{\text{feed}} = 0.025 \text{ mol/L}$.

The extraction constants, $K_{ex,1}$ and $K_{ex,2}$, were determined by the application of nonlinear least square method to fit the experimental data. The extraction equilibrium formulations can be applied to a binary metals system when interaction between two metals is negligible. Figure 2 shows the experimental distribution ratio of Pr/Nd and Pr/Sm, as a function of pH, together with the predicted values calculated from the extraction equilibrium formulations.

Extraction Properties on the Micro Solvent Extraction Chip

The extraction of single Pr^{3+} was carried out using the Y-type micro solvent extraction chip (Figure 1a), and the extraction properties in the micro flow channel were investigated. Figure 3 shows the effect of linear velocity, which is defined as the ratio of flow rate [m^3/min] to the cross sectional area of the flow channel [m^2], on the distribution ratio, together with the extraction equilibrium data obtained from the conventional extraction system. The extraction equilibrium is hardly achieved even with very slow flow rate in the case of $w = 500 \mu\text{m}$ and $d = 200 \mu\text{m}$ (Figure 3a), while it is easily achieved in the narrow micro flow channel of $w = 100 \mu\text{m}$ and $d = 100 \mu\text{m}$ (Figure 3b). These results suggest that the ratio of interface area between aqueous and organic phases to the volume of each phase dramatically increases in the case of the narrow flow channel chip. The process of metals separation with solvent extraction at equilibrium state can be easily carried out using a very narrow flow channel just by feeding each phase into the micro solvent extraction chip.

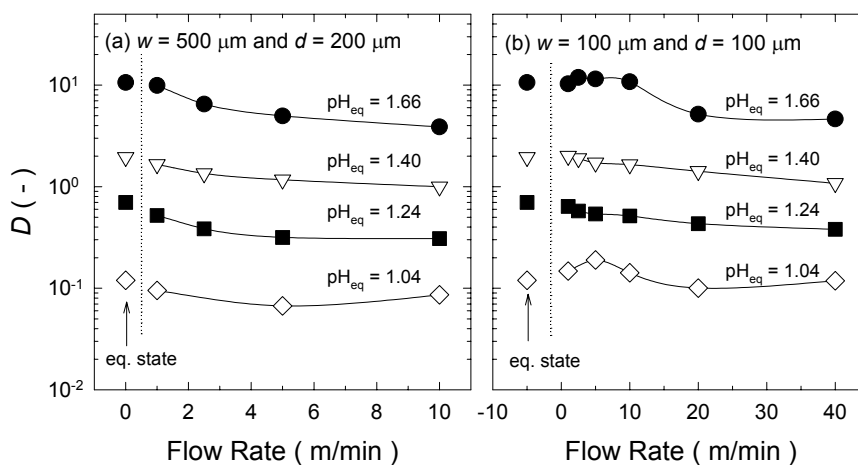


Fig. 3. Effect of flow rate on the Pr^{3+} distribution ratio with EHPNA on the micro solvent extraction chip of (a) $w = 500 \mu\text{m}$ and $d = 200 \mu\text{m}$ and (b) $w = 100 \mu\text{m}$ and $d = 100 \mu\text{m}$. $[(\text{RH})_2]_{\text{feed}} = 0.25 \text{ mol/L}$ and $[\text{Pr}^{3+}]_{\text{feed}} = 0.01 \text{ mol/L}$.

The separation of binary lanthanides (Pr/Nd and Pr/Sm) on the micro solvent extraction chip ($w = d = 100 \mu\text{m}$) was carried out. In these cases, the aqueous solution containing higher concentration of each lanthanide rather than that of the extractant was used from the practical operation point of view. Figure 4a shows the effect of linear velocity on the distribution ratios of each metal in the Pr/Nd binary system. At low pH ($\text{pH}_{\text{eq}} = 1.81$), the distribution ratios of Pr^{3+} and Nd^{3+} increase with a decrease in linear velocity. At high pH ($\text{pH}_{\text{eq}} = 2.42$), the distribution of Pr^{3+} decreases with a decrease in velocity, while that of Nd^{3+} increases. This suggests that the exchange reaction between Pr^{3+} in the organic phase and Nd^{3+} in the aqueous phase progresses to reach the extraction equilibrium state. Such exchange reaction between one metal extracted to the organic solution and another one existing in the aqueous solution has already been reported in a column separation process [3]. Figure 4b shows the results of the micro solvent extraction in the Pr/Sm system. The exchange reaction was also observed in this system. The highly effective separation can be achieved at low linear velocity.

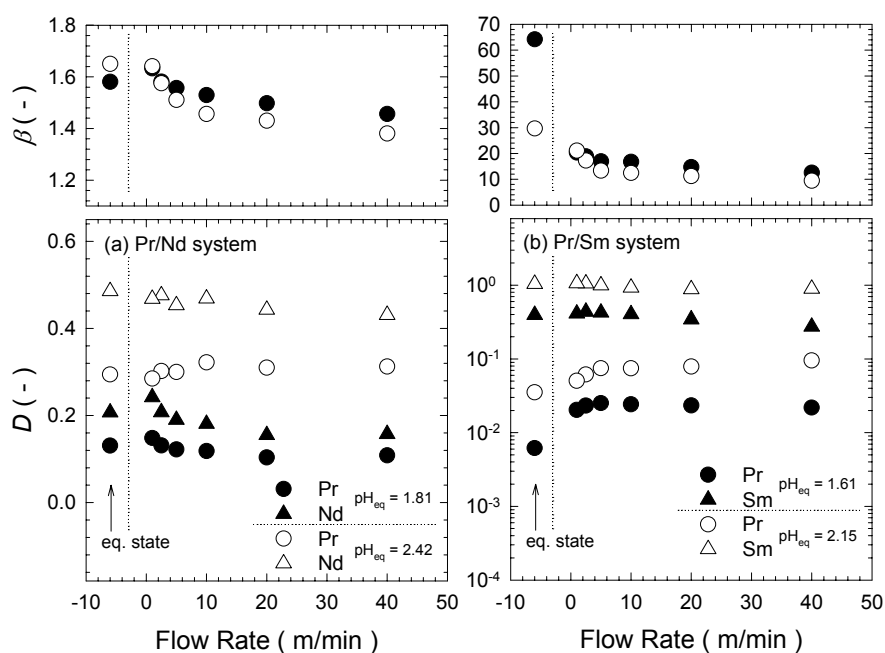


Fig. 4. Effect of flow rate on the distribution ratio of (a) Pr/Nd and (b) Pr/Sm with EHPNA on the micro solvent extraction chip of $w = 100 \mu\text{m}$ and $d = 100 \mu\text{m}$.

$$[(\text{RH})_2]_{\text{feed}} = 0.05 \text{ mol/L and } [\text{Ln}_i^{3+}]_{\text{feed}} = 0.025 \text{ mol/L.}$$

Separation Process of Lanthanides with Micro Solvent Extraction Chip

When the extractive separation process is considered, the phase separation of the two phases after extraction is one of the key factors. A modification of the chip surface with the hydrophobic group is generally carried out to enhance the phase separation [13]. In this method, however, the combined hydrophobic group is easy to remove during the operation. In the present work, therefore, the alternative method, involving the use of a complicated cross section for the phase separation was developed. Figure 1b shows the micro flow channel used and its cross section. The organic/aqueous solution is successively separated at the outlet of the flow channel. The separation of Pr/Sm was then carried out using that micro solvent extraction chip. The extraction equilibrium, however, is difficult to achieve, since the interface area to the volume of each phase ratio decreases. The slow flow rate was therefore used as the operation condition for that solvent extraction chip. Figure 5 shows the effect of linear velocity on Pr³⁺ and Sm³⁺ distribution ratios. The effective separation could be carried out at low linear velocity, as expected from the results with the Y-type chip.

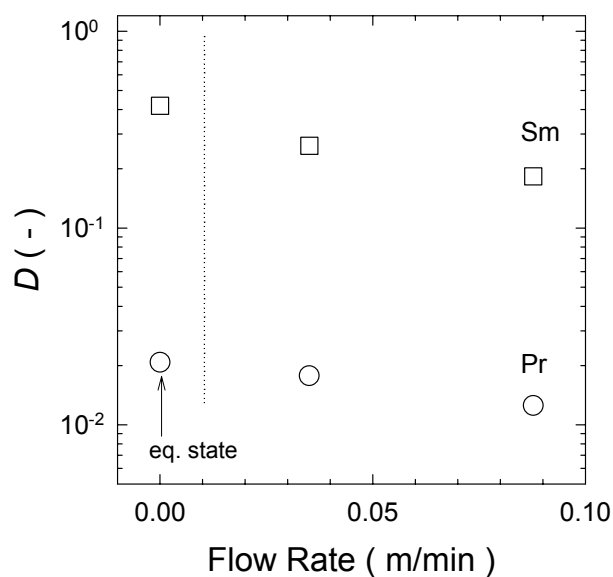


Fig. 5. Effect of flow rate on the Pr/Sm distribution ratio with EHPNA on the micro solvent extraction chip shown by Figure 1b. $[(\text{RH})_2]_{\text{feed}} = 0.05 \text{ mol/L}$, $[\text{Ln}_i^{3+}]_{\text{feed}} = 0.025 \text{ mol/L}$, and $\text{pH}_{\text{eq}} = 1.65$.

CONCLUSION

Separation of lanthanides in a micro solvent extraction system has been investigated, with the following results: (1) A micro solvent extraction system can be developed on a PMMA chip by mechanical fabrication, and extraction equilibrium can be achieved when a narrow micro flow channel is used. (2) The exchange reaction between a lighter lanthanide in the organic phase and a heavier lanthanide in the aqueous phase proceeds along with a decrease in the flow rate, and effective separation can be achieved under low linear velocity conditions. (3) The phase separation of the aqueous and organic phases after extraction can be carried out by changing the cross section of the micro flow channel.

ACKNOWLEDGEMENT

The ICP-AES measurement of the lanthanides was performed at the Instrumentation Center, The University of Kitakyushu. This research was supported by a Grant-in Aid for Science Research (No.15760571) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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