Solvent Extraction Behavior of Metal Ions with Calixarene Derivatives by Using a Microreactor

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(Received August 30, 2013; Accepted September 24, 2013)

In this study, the extraction behavior of calixarene derivatives by using the multiphase parallel flow technique was investigated. Using a partially-modified microfluidic device, the extraction rate of silver and palladium ions from the aqueous phase with calix[4]arene derivatives was evaluated. As a result, the time necessary for silver ion to reach equilibrium was 15 s. In the case of palladium extraction, the extraction percentage was 80 % at 8 s reaction time. In the conventional batch method, the times necessary for silver and palladium extraction to reach equilibria were about 72 h and 5 min, respectively. These results showed that increasing the liquid-liquid interface area is effective in the solvent extraction of metal ions with calix[4]arene derivatives. The correlation between the difference in the functional groups of calix[4]arenes and their effect on the rate of extraction at the parallel flow liquid-liquid interface was considered.

1. Introduction

Recently, the industrial demand for rare metals has increased. However, the supply of these metals has been erratic due to unstable international situations and the fact that these metals are not widely located. Therefore, there is an increasing demand for the recycling of these metals [1,2]. Recovery of these metals from their source is complicated by the variety of other contained metals therefore, techniques for recovery should enable selective and effective metal separation. Many efforts have been made to develop recycling processes for rare metals. Calixarenes are phenolic cyclic oligomers which are well known as attractive and interesting host compounds. Their ability to recognize and discriminate between metal ions is one of their remarkable features. In particular, functional groups and ring size of calixarene derivatives are very important factors for selective and effective extraction [3-6]. These features of calixarenes make specific extraction of rare metals possible. For example, ketonic calix[4]arene specifically extracts silver from a solution comprising a mixture of silver and palladium ions with a corresponding concentration factor of 100 times [7]. However, in macroscale batchwise extraction, this compound required 72 h to reach equilibrium. The slow rate of the extraction is one of the issues to be resolved in using this compound as a solvent extractant reagent.

The microfluidic reactor has been found to be an efficient reaction apparatus in the chemical
engineering field. The microfluidic system has several advantages over conventional macroscale solvent extraction reaction processes [8-11]. For example, the microfluidic system has a larger surface/interface area per unit volume than that of conventional macroscale apparatuses. An increase in the interface area provides enhancement of extraction efficiency. Kitamori et al. reported efficient solvent-solvent extraction using parallel laminar streams [9-11]. By using such streams, it is possible to enhance the extraction efficiency of rare metals with calixarenes. In this study, we investigated the extraction behavior of calixarene derivatives by using multiphase parallel flow in a microfluidic reactor.

2. Experimental

2.1 Materials

Nitric acid, silver nitrate, palladium nitrate, and chloroform were purchased from Wako Pure Chemicals (Osaka, Japan). Reagents used for the analysis were of the highest purity. Ketonic and pyridyl calix[4]arenes were used as the extractants. The syntheses of the calix[4]arene derivatives have been described in previous papers [7,12]. The chemical structures of these derivatives are shown in Figure 1. Ketonic and pyridyl calix[4]arenes were used for extraction of silver and palladium ions, respectively. Organic solutions were prepared by dissolving the calixarene derivatives in chloroform. The concentration of the calix[4]arenes were 3.3 mM (M=\text{mol dm}^{-3}) and 5 mM, for the ketonic and pyridyl compounds, respectively. Aqueous solutions were prepared by dissolving silver and palladium nitrates. The concentration of the silver solution was 0.025 mM in 1.77 M HNO$_3$. The concentration of palladium solution was 0.1 mM in 0.1 M HNO$_3$. The extraction rate of silver and palladium ions from the aqueous phase by changing the contact time was evaluated.

![Figure 1. Chemical structures of the calix[4]arene derivatives.](image)

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R : CH_2COCH_3 \text{ (Ketonic derivative)}
\]

\[
CH_2N \text{ (Pyridyl derivative)}
\]

2.2 Fabrication of the microreactor

The microreactor was fabricated in Pyrex glass and silicon plates using a micromachining process followed by bonding the glass and silicon plates irreversibly [13]. In brief, a square microchannel structure was fabricated on each plate of glass and silicon by using a desktop numerical control-processing machine (MC-ATC-M01; PMT Corp., Fukuoka, Japan) equipped with Diamond Plated Points (Minitor Co. Ltd., Japan). Each channel structure (200 µm width; 100 µm depth) was confirmed using laser microscope analysis (VK-8510; Keyence Co., Osaka, Japan). Figure 2 shows an illustration of the microreactor. The
surface of the silicon-side microchannel was coated with 30 nm-thick titanium using a vapor deposition method, and then coated similarly with 50 nm-thick Au. The glass and silicon plates were laminated where the glass-sided and silicon-sided microchannels horizontally overlapped. These plates were then bonded irreversibly using an anodic bonding method. A microchannel (200 µm width; 200 µm depth) with glass surfaces and Au surfaces was formed on the silicon surface. The Au surface was rendered hydrophobic by surface treatment with 1 mM 1-octadecanethiol in ethanol solution. The length and inner volume of the micro-extraction region were 2 cm and 0.8 µL, respectively.

2.3 Extraction experiment

Figure 3 shows the microreactor system used in this study. Syringe pumps (Model 100, BSA, Tokyo, Japan) and gastight syringes (GASTIGHT 1001, Hamilton, Reno, NV, USA) were used to inject the reagents into the microreactor. The extraction using the micro reactor system was carried out at room temperature. For the extraction experiment, a three-fold greater volume of the organic phase compared to the aqueous phase was loaded to stabilize the interface horizontally [14,15]. The flow rates of aqueous phase were 1.6, 3.0, 4.0, and 6.0 µL min\(^{-1}\) for 15, 8, 6, and 4 s of the residence time, respectively. The extraction time was calculated based on the residence time of the aqueous phase. The recovered aqueous phase was subjected to inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 3300 DV) to estimate the amount of the extracted rare metal. The extraction percentage is defined as

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\%E = (1 - C / C_0) \times 100
\]

where, \(C\) represents the concentration of silver or palladium ions in the recovered aqueous phase, and \(C_0\) is the initial concentration of silver or palladium ions in the aqueous phase. For batchwise extraction, equal volumes (13 mL) of the aqueous phase and the organic phase were mixed and shaken at 303 K. After phase separation, the metal concentrations in the aqueous phase were also measured by ICP-OES.
3. Results and Discussion

The microchannel surfaces of the glass and silicon sides are hydrophilic and hydrophobic, respectively. The aqueous solution flowed through the glass side (upper side) of the microchannel while the organic solution flowed through the silicon side (lower side). First, the extraction of silver from the aqueous phase comprising a 0.025 mM AgNO$_3$ solution and 3.3 mM of the ketonic calix[4]arene in chloroform solution was examined. This compound specifically extracted silver from a mixture of silver and a 100 times larger concentration of palladium [7]. However, in the macroscale batchwise extraction, this compound required 72 h to reach equilibrium. We focused on microfluidic system which has a larger surface/interface area per unit volume than that of the conventional macroscale apparatuses. The large interface area made it possible to enhance the extraction efficiency. The time-course dependency of extraction rate was investigated by changing the flow rate. Figure 4 (a) shows the rate of silver extraction using the ketonic calix[4]arene in the microreactor. The extraction rate increased with increasing residence time. In addition, the extraction percentage was 80% at 15 s and almost reached equilibrium.

Next, the extraction of palladium from the aqueous phase using a 0.1 mM Pd(NO$_3$)$_2$ solution and 5.0 mM of pyridyl calix[4]arene in chloroform solution was investigated. Preliminary experiments were carried out and it was found that the extraction rate of pyridyl calix[4]arene was significantly faster compared with the ketonic calix[4]arene (data not shown). In the batchwise extraction, this compound needed up to 5 min to reach equilibrium achieving an extraction percentage of almost 98%. Figure 4 (b) shows the rate of extraction of palladium using pyridyl calix[4]arene in the microreactor. In the microreactor system, 74% of palladium was extracted within 15 s. However, in contrast to the above case, the extraction rate was not improved by the extended residence time. The extraction in the microreactor system was carried out at room temperature whereas the batchwise extraction temperature was 303 K. Although the extraction data are dependent on the temperature, the difference in temperature for both experiments can be neglected because of the extreme difference in the extraction rate.
These results suggest that the micro-extraction system dramatically improved the rate of extraction compared with the conventional batchwise method. The enhanced extraction rate was attributed to the increased liquid-liquid interfacial area and the smaller diffusion length of the microfluidic system. For the microreactor system, the inner volume and liquid-liquid interfacial area of the micro-extraction region were 0.8 μL and 0.04 cm$^2$, respectively. On the other hand, for the conventional batchwise method, the inner volume and liquid-liquid interfacial area were 26 cm$^3$ and 13 cm$^2$, respectively. Therefore, the interface to volume ratio for the micro-extraction system was calculated to be 50 cm$^{-1}$ which value was almost two orders of magnitude more than the value for the conventional batchwise method. In addition, the diffusion length was 200 μm which value was also two orders of magnitude less than the value for the batch method. Consequently, the metal extraction efficiency was dramatically improved. However, the extraction behavior of the two calixarene derivatives was slightly different. The extraction efficiency for silver using the ketonic compound was more enhanced compared with palladium using the pyridyl compound in micro-extraction. This may have resulted from the difference in the properties of each compound derived from their chemical structure. In particular, the adsorption and desorption behavior of the calixarene derivatives at the liquid-liquid interface was the main process in micro-extraction and affected the extraction efficiency. The pyridyl compound may be more adsorbed at the liquid-liquid interface than the ketonic compound. In the case of batchwise extraction, the extraction rate of silver using the pyridyl compound was considerably faster than the ketonic compound [7,12]. This result suggests that the ketonic compound does not exist to the same extent at the liquid-liquid interface. In other words, the pyridyl compound has greater amphiphilicity than the ketonic compound. For this reason, it was presumed that the extraction efficiency of the ketonic compound was more enhanced compared with the pyridyl compound by using parallel multiphase microflows. To confirm this hypothesis, further studies are required.
4. Conclusion

In the present study, the micro-extraction system was shown to be an effective tool that enables enhancement of the extraction rate of silver and palladium using calix[4]arene derivatives, by taking into account the characteristic larger liquid-liquid interface per unit volume. Silver extraction using the ketonic compound was strongly enhanced by the microreactor. Palladium extraction was also enhanced by the use of the microreactor as evidenced by the shorter time required (15 s) to reach equilibrium compared to the batchwise system (5 min). The difference in the extraction efficiency of the two calixarene derivatives suggests that enhancement of extraction is also influenced by the structure of the calixarene derivative. This study shows that the microreactor is a novel efficient apparatus for the extraction of silver and palladium with calixarene derivatives.

Acknowledgement

We thank Ms. Yuka Ishiji for her technical assistance. Part of this work was supported by The Environment Research and Technology Development Fund (3K-123022) from the Ministry of Environment of Japan, for MM and KO. One of the authors also acknowledges partial support by a Grant-in-Aid for JSPS Fellows.

References