Separation of Copper and Zinc Ions by Hollow Fiber Supported Liquid Membrane Containing LIX84 and PC-88A

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The separation of Cu²⁺ and Zn²⁺ in mixed solutions of zinc and copper sulfate has been studied using hollow fiber supported liquid membrane (HFSLM). The extractants for Cu²⁺ and Zn²⁺ were LIX84 (anti-2-hydroxy-5-nonyl acetonaphenoneoxime) and PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) which were diluted in kerosene, respectively. The effects of operational variables on the permeation rate and the separation factor of Cu²⁺ and Zn²⁺ were investigated. At metal concentrations in the feed solution between 1 to 200 mol·m⁻³ under pH 2.0, the permeation rate of Cu²⁺ by 10 mass% LIX84 HFSLM was 1 × 10⁻⁵ to 5 × 10⁻⁶ mol·m⁻²·s⁻¹ while that of Zn²⁺ with PC-88A was 10⁻⁶ to 10⁻⁵ mol·m⁻²·s⁻¹. By total recycle operation, copper sulfate solution with 99.6% purity and 99.9% pure zinc sulfate solution could be enriched from the dilute solution in which the concentrations of both Cu²⁺ and Zn²⁺ were 1 g/L, respectively.

Keywords: copper and zinc separation, permeation, hollow fiber supported liquid membrane (HFSLM), anti-2-hydroxy-5-nonyl acetonaphenoneoxime (LIX84), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A)

1. Introduction

The separation of Cu and Zn has long been an issue in hydrometallurgical processes. Simons and Veltman et al. introduced a chemical precipitation method in which the separation was achieved by precipitation of CuS as CuS.¹,² The cementation technique was another approach in which Cu²⁺ was removed by the reductive precipitation as metallic Cu.³⁻⁵ Both methods have several drawbacks as the generation of large waste solutions and moreover lack of high-separation capability which is essential for the fabrication of high-purity metals. To overcome these problems and separate the ions effectively, the solvent extraction technique has been introduced recently.⁶

To meet the strict environmental requirements nowadays, it is necessary to develop environment friendly solvent extraction methods more than ever. Efforts were made for new extraction technology with lower-energy consuming extraction device and effective back-extraction. The non-dispersive solvent extraction has been the subject of many researchers due to its advantages as low extractant consumption, the simultaneous extraction and back-extraction in a single process, and simpler device etc.⁷⁻¹⁰

Non-dispersive extraction is an extraction technique in which the metals are separated by the selective permeation while the dispersion between organic phase and aqueous phase is prevented using porous membrane. As means for contact between organic phase and aqueous phase, the membrane contactor,¹¹ the supported liquid membrane,¹² the contained liquid membrane¹³ were suggested. Among them, supported liquid membrane was the most studied due to its advantages in equipment, process cost, and extraction speed.

In this study, Cu²⁺ and Zn²⁺ were separated from the mixed solution of CuSO₄ and ZnSO₄ by the non-dispersive solvent extraction using the hollow fiber supported liquid membrane (HFSLM). For the separation of Cu²⁺, LIX84 (anti-2-hydroxy-5-nonyl acetonaphenoneoxime) was used as a extractant while PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) was used for Zn²⁺. As Cu²⁺ was extracted at low pH by LIX84 and Zn²⁺ was at pH higher than 5, the separation could be achieved by the prior extraction of Cu²⁺ at low pH.¹⁴ Since the extraction of Zn²⁺ by PC-88A started at pH 1.5 and that of Cu²⁺ at pH 3, they could be separated by adjusting the acidity of the solution between 1.5 and 3.¹⁵ The effect of pH and metal concentrations in the feed solution, and the extractant concentration in liquid membrane on the permeation rate and selective separation was investigated to obtain the optimum separation conditions for Cu²⁺ and Zn²⁺. In addition, Cu²⁺ and Zn²⁺ were separated and enriched by continuous recirculation of feed and stripping solutions through HFSLM.

2. Experiments

The extractants for the liquid membrane were LIX84 from Henkel Co. and PC-88A from Daibachi Chemical Industry Co. The diluent was EP-grade kerosene from Junsei Chemical Co. The liquid membrane supporter was the hollow fiber module from Hoechst Celanese Co. Their specifications are listed in Table 1. HFSLM was prepared by passing the organic liquid membrane solution through the tube side of fibers and soaking microporous fiber wall for over 30 minutes. The organic liquid membrane solution was prepared by diluting extractant in kerosene. Before soaking, the hollow fiber supports were dried at 100°C.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Specification of the hollow fiber module.</th>
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<tbody>
<tr>
<td>Fiber</td>
<td>Module</td>
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<tr>
<td>Material</td>
<td>polypropylene</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>16 cm</td>
</tr>
<tr>
<td>Diameter (I.D.) (µm)</td>
<td>240</td>
</tr>
<tr>
<td>Wall thickness (µm)</td>
<td>30</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>30</td>
</tr>
<tr>
<td>Potting material</td>
<td>epoxy</td>
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The solution was adjusted by 1 N H\textsubscript{2}SO\textsubscript{4} and ZnSO\textsubscript{4} solution of various concentrations and pH. The pH of the solution was adjusted by 1 N H\textsubscript{2}SO\textsubscript{4} or 1 N NaOH. In all experiments, 3 N H\textsubscript{2}SO\textsubscript{4} was used as the stripping solution. The feed solution and stripping solution were introduced at the speed of 1 L/min to the tube side and the shell side of fibers, respectively. The metal concentration was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, JOBIN YVON, JY 28+). Figure 1 shows the HFSLM set up used in the study.

3. Results and Discussion

3.1 Separation of Cu\textsuperscript{2+} by LIX84 HFSLM

In the separation of metal ions by supported liquid membrane, the permeation rate of each metal is an indication of separation efficiency. Figure 2 shows the effect of pH in feed solution and extractant concentration on the permeation rates of Cu\textsuperscript{2+} and Zn\textsuperscript{2+}, and the separation factor of Cu\textsuperscript{2+} at the LIX84 HFSLM. The separation factor (S\textsubscript{Cu, Zn}) is defined as follows:

\[
S_{\text{Cu, Zn}} = \frac{(J_{\text{Cu}}/[\text{Cu}^{2+}]_F)}{(J_{\text{Zn}}/[\text{Zn}^{2+}]_F)} = \frac{(J_{\text{Zn}}/[\text{Zn}^{2+}]_F)}{(J_{\text{Cu}}/[\text{Cu}^{2+}]_F)}
\]

Here, \(J_{\text{Cu}}\) and \(J_{\text{Zn}}\) are the permeation rates of Cu\textsuperscript{2+} and Zn\textsuperscript{2+}, respectively. [Cu\textsuperscript{2+}]\textsubscript{F} and [Zn\textsuperscript{2+}]\textsubscript{F} are the concentration in the feed solution.

The extraction of Cu\textsuperscript{2+} by LIX84 occurred at low pH as below 1 while that of Zn\textsuperscript{2+} started at high pH exceeding 5. The permeation rate of Cu\textsuperscript{2+} was almost constant regardless of pH due possibly to early saturation of LIX84 by Cu\textsuperscript{2+} at the feed-liquid membrane interface. The saturation of LIX84 at the feed-liquid membrane interface was rapid since the extraction equilibrium constant of Cu\textsuperscript{2+} with LIX84 was 1.7 that is about 100 times larger than the equilibrium constant of Zn\textsuperscript{2+} with PC-88A.\textsuperscript{15,16} The permeation rate of Zn\textsuperscript{2+} increased with pH. This occurred since the formation of complex increases with the decrease in H\textsuperscript{+} concentration in the feed solution at extraction equilibrium. The increase in permeation rate of Zn\textsuperscript{2+} results in the reduction of the separation factor of Cu\textsuperscript{2+}.

Figure 3 shows the effect of metal concentration in the feed solution on the permeation rate and separation factor. In the feed solution, the concentrations of Cu\textsuperscript{2+} and Zn\textsuperscript{2+} were adjusted to be the same in the range of 1~100 mol m\textsuperscript{-3}. The permeation rate Cu\textsuperscript{2+} was found unaffected by the variations in metal ion concentration in the feed solution. The permeation rate of Zn\textsuperscript{2+} decreased as metal concentration increased resulting in the improvement of the selective separation of Cu\textsuperscript{2+}. In general, the permeation rate of metal ions were affected by the metal concentration as long as the...
free extractant are not exhausted completely at the feed-liquid membrane interface or the loading of metal ions is not saturated regardless of the nature of rate determining step of the permeation. The condition that the permeation rate is not affected by metal ion concentration in the feed solution typically occurs when the extractant in the liquid membrane completes bonding with most of metal ions even at low metal concentrations due to strong affinity between them. Therefore, the zero order kinetics of Cu\(^{2+}\) concentration due to strong affinity between them. There-
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Figures 4 and 5 show the results of continuous recirculation of the feed and stripping solutions without discharging for the separation and enrichment of Cu\(^{2+}\) in the stripping solution. The initial concentration of Cu\(^{2+}\) and Zn\(^{2+}\) in the feed solution was 15.3 mol-m\(^{-3}\) and the volume of the feed solution and stripping solution was 1.25 L. The stripping solution was 3 N H\(_2\)SO\(_4\).

Figure 4 shows the enrichment and separation with time at pH 2.0 and pH 4.0 using 10 mass% LIX84 HFSLM. It demonstrates that Cu\(^{2+}\) enrichment could be easily achieved by the active facilitated transport, which is one of the advantages of supported liquid membrane. The rate of enrichment of Cu\(^{2+}\) is not affected by pH of the feed solution that agrees with the results already shown in Fig. 2. At lower pH, the selectivity of Cu\(^{2+}\) is improved as the permeation of Zn\(^{2+}\) in stripping solution diminishes with the decrease in pH of the feed solution.

Figure 5 shows the effect of extractant concentrations on the enrichment of Cu\(^{2+}\) in stripping solution at pH 2.0. The

3.2 Separation of Zn\(^{2+}\) by PC-88A HFSLM

Figure 6 shows the effect of pH in the feed solution and
extractant concentration in liquid membrane on the permeation rates of Zn$^{2+}$ and Cu$^{2+}$, and on the separation factor of Zn$^{2+}$ at the PC-88A HFSLM. The permeation rate of Zn$^{2+}$ and Cu$^{2+}$ increased with pH in the feed solution. This could be explained by the increase in complex formation at reaction equilibrium as hydrogen ion decreases in the feed solution as suggested by Nakashino et al.\textsuperscript{15)} However, in case of Zn$^{2+}$ this effect was diminished at pH ≥ 2.5 resulting in the nearly constant permeation rate as observed. This phenomenon might be related to the extractant saturation at feed-liquid membrane interface\textsuperscript{16)} and to the hydrogen transfer resistance in the boundary layer of feed.\textsuperscript{17)} The permeation rate with 30 mass% PC-88A was similar to that with 10 mass%. This result agrees with the results obtained by Youn et al. during the separation of Co and Ni.\textsuperscript{17)} The permeation rate increased with extractant concentration as they form more complexes with metal ions at the feed solution-membrane interface. In the meantime, this could increase the viscosity of liquid membrane that should counteract the permeation above a certain extractant concentrations as observed.

Figure 7 shows the effect of metal ion concentration in the feed solution on the permeation rate and separation factor. The permeation rate of Zn$^{2+}$ at the PC-88A HFSLM was 10$^{-6}$–10$^{-5}$ mol m$^{-2}$ s$^{-1}$ which agrees with the value obtained by Sato et al. using the membrane contactor.\textsuperscript{18)} The value of permeation rate in this study was for the permeation from feed solution to stripping solution via liquid membrane. Meanwhile, the value in Sato et al.’s experiment was the permeation from feed solution to liquid membrane. Considering the difference, the agreement of two permeation rates from both experiments appears to indicate that the permeation from liquid membrane to stripping solution may not alter the overall permeation rate. The separation factor of Zn$^{2+}$ was about 1000 and not affected by metal ion concentration. The value is similar to the value obtained by the conventional dispersive solvent extraction.\textsuperscript{15)} It would be remarked that the separation efficiency of Zn$^{2+}$ by supported liquid membrane is compatible to the conventional solvent extraction method.

In Figs. 8 and 9 the enrichments of Zn$^{2+}$ by total feed recycle at the HFSLM containing 10 mass% PC-88A. [Zn$^{2+}$]$\text{F}$ = [Cu$^{2+}$]$\text{F}$ = 15.3 mol·m$^{-3}$, volume of feed and stripping solution = 1.25 L.

Fig. 7 Effect of concentration of Zn$^{2+}$ and Cu$^{2+}$ in the feed on the permeation rate at the HFSLM containing 10 mass% PC-88A. [pH]$\text{F}$ = 2.0.

Fig. 8 Enrichment of Zn$^{2+}$ in the stripping solution by total feed recycle at the HFSLM containing 10 mass% PC-88A. [Zn$^{2+}$]$\text{F}$ = [Cu$^{2+}$]$\text{F}$ = 15.3 mol·m$^{-3}$, volume of feed and stripping solution = 1.25 L.

Fig. 9 Effect of PC-88A concentration on the enrichment of Zn$^{2+}$ in the stripping solution by total feed recycle at the HFSLM containing PC-88A. [pH]$\text{F}$ = 2.0, [Zn$^{2+}$]$\text{F}$ = [Cu$^{2+}$]$\text{F}$ = 15.3 mol·m$^{-3}$, volume of feed and stripping solution = 1.25 L.
5 mass% PC-88A and pH 2.0, only 55% of Zn\(^{2+}\) was separated in stripping solution the separation factor being about 500. The complete enrichment using 10 mass% PC-88A HFSLM was obtained in 150 minutes and the separation factor was 14,000 resulting in zinc sulfate solution with 99.9% purity. With increasing PC-88A concentration to 30 mass%, the operation time for complete enrichment was further reduced decreasing the separation factor to 3,000 resulting in 99.6% pure solution. For the successful separation and enrichment of Cu\(^{2+}\) and Zn\(^{2+}\) in the mixed solution, the operation variables such as the concentration of extractant, pH in feed solution, and enrichment duration should be properly selected considering the aim at the purity of metal and the degree of enrichment.

4. Conclusions

The separation and enrichment of Cu\(^{2+}\) and Zn\(^{2+}\) from the mixed solution of CuSO\(_4\) and ZnSO\(_4\) were studied using LIX84 HFSLM and PC-88A HFSLM, respectively. At the LIX84 HFSLM, the permeation rate of Cu\(^{2+}\) was higher than that of Zn\(^{2+}\) and was unaffected by the metal concentration in the feed solution and pH. The permeation rate of Zn\(^{2+}\) using PC-88A HFSLM was higher than that of Cu\(^{2+}\) and increased with the metal concentration in the feed solution and pH. At metal concentration in the feed solution of \(1 \sim 200 \text{ mol} \cdot \text{m}^{-3}\) and pH = 2.0, the permeation rate of Cu\(^{2+}\) at 10 mass% LIX84 HFSLM was \(1 \times 10^{-6} \sim 5 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\) and that of Zn\(^{2+}\) with PC-88A was \(10^{-6} \sim 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\). The separation and enrichment of Cu\(^{2+}\) and Zn\(^{2+}\) from dilute solution of 1 g/L of their ions were possible by total recycle process. Copper sulfate solution with 99.6% purity was recovered by 30 mass% LIX84 HFSLM at pH of 2.0 and 99.9% pure zinc sulfate solution was recovered by 10 mass% PC-88A HFSLM. For the successful separation and enrichment of Cu\(^{2+}\) and Zn\(^{2+}\) in the mixed solution, the concentration of extractant, pH in feed solution and enrichment duration should be properly selected considering the aim at the metal purity and degree of enrichment.

REFERENCES