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# Selective and Simultaneous Extractions of Zn and Cu Ions by Hollow Fiber SLM Modules Containing HEH(EHP) and LIX84

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## ABSTRACT

The selective extractions of $Zn^{2+}$ and $Cu^{2+}$ from their mixed solutions of sulfate medium have been studied using hollow fiber supported liquid membranes (HFSLM). The HFSLM contained two kinds of extractants; one contained 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester [HEH(EHP)], the commercial name of which is PC88A, for Zn extraction; the other contained the hydroxy oxime reagent LIX84 for Cu extraction. Individual runs of each HFSLM were made to determine the effect of operational variables on the permeation rates of metal ions and their separation factors. In addition, the simultaneous and selective extractions of both $Zn^{2+}$ and $Cu^{2+}$ from their mixed solutions were demonstrated using the PC88A and LIX84 HFSLMs together. The performance of simultaneous extraction was compared with those of the individual runs.

## INTRODUCTION

The selective separations of zinc and copper from their mixed solution or from solutions containing other metal ions are of great interest in hydrometallurgical processes. They are now gaining more importance due to increasing demands to recycle metal ions not only to avoid possible environmental pollution problems but also for finding secondary metal resources. Nondispersive solvent extraction technology, namely membrane solvent extraction, has attracted attention as a future technology which will meet the requirements for

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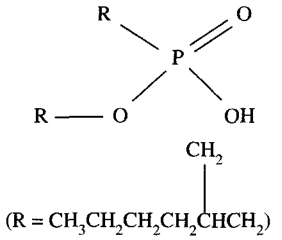
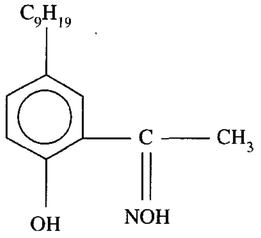
performance and economics compared with conventional ore processing. Several different configurations are currently applicable to obtain nondispersive contact between immiscible liquids by the aid of a porous solid support such as a membrane contactor (1), a supported liquid membrane (2), and a contained or flowing liquid membrane (3, 4). Among those, the supported liquid membrane (SLM) has been the most widely employed by researchers due to its outstanding features of system compactness, overall cost, extraction rate, etc. However, the instability of SLMs is a major bottleneck for their commercial applications, and this problem remains to be solved at an acceptable level. Much effort, including our previous works, have focused on this subject (5–7).

In the present study the SLM extraction of $Zn^{2+}$ or $Cu^{2+}$ from their mixed solutions as a sulfate medium was studied using a phase contact module of high density hollow fibers from Hoechst Celanese Corporation. Two different kinds of extractants were used for the selective extraction of each component. 2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (henceforth referred to by the commercial name PC88A) was used for $Zn^{2+}$ extraction. The recently available hydroxy oxime reagent (*anti*-2-hydroxy-5-nonyl acetophenoneoxime, henceforth referred to as LIX84) was used for $Cu^{2+}$ extraction.



PC88A



LIX84

Individual runs of each hollow fiber supported liquid membrane (HFSLM) at steady-state conditions were made to determine the effects of operational variables on the permeation rates of metal ions as well as their separation factors: the hydrogen and metal concentrations in the feed solution, and the carrier concentration in the liquid membrane. The enrichment of each component in the stripping solution was also achieved by total recycle of the feed solution.

One of the interesting properties of the two extractants is that their extractions of each metal ion occur with a very similar feed acidity. According to basic extraction equilibrium studies (8, 9), the remarkable loading of $Zn^{2+}$ into PC88A was found at pHs higher than 1.5 and that of $Cu^{2+}$ at pHs higher than 3. On the other hand, loading of $Cu^{2+}$ into LIX84 was found at pHs higher than 0.5 and that of $Zn^{2+}$ at pHs higher than 5.5. Therefore, if we maintain the pH between 1.5 to 3 in the feed solution, then the simultaneous and selective extractions of both ions from their mixed solutions could be achieved using the above two SLM modules together. This distinctive feature of simultaneous SLM extraction originated from its nondispersive contacting operation between the organic and aqueous phases. Simultaneous extraction has been demonstrated, and the performance has been compared with that of the individual runs.

## EXPERIMENTAL

PC88A from Daihachi Chemical Industry Co. and LIX84 from Henkel Co. were used as extractants without further purification. Kerosene of commercial EP grade from Junsei Chemical Co. was used as the diluent. A hollow fiber module made by Hoechst Celanese Co. (Liqui-Cel. Material, polypropylene; number of fibers, 3600; fiber length, 16 cm; fiber I.D., 24 μm; total surface area, 0.4 $m^2$; fiber wall thickness and porosity, 30 μm and 30%) was used as the liquid membrane support. The HFSLM was prepared by flowing the organic liquid membrane solution through the tube side of fibers and soaking the microporous fiber walls at least 30 minute. The liquid membrane solutions were prepared by diluting the extractants in kerosene at a predetermined weight ratio. The zinc and copper sulfate solutions were used as feed phases after adjusting the acidity by the addition of NaOH or $H_2SO_4$. A sulfuric acid solution of 3 N was used as the stripping solution at all times. The feed and stripping solutions passed through the tube side and shell side of fibers, respectively. The flow rate for each was 1 L/min. The concentrations of metal ions in the aqueous phase were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, JOBIN YVON, JY 38+). Figure 1 is a schematic diagram for the simultaneous and selective separation of zinc and copper ions by two parallel HFSLMs.

## RESULTS AND DISCUSSION

### Permeation Rate

Figures 2 and 3 show the effect of hydrogen concentration in the feed solution ($[H^+]_F$) and the extractant concentration in the liquid membrane on both permeation rates of $Zn^{2+}$ and $Cu^{2+}$, and their separation factors at the PC-88A and the LIX84 HFSLMs. The separation factor (Sf) was defined by the equation

$$\mathrm{Sf} = \frac{J_{M1}/[M1]_F}{J_{M2}/[M2]_F} \tag{1}$$

where $J_{M1}$ and $J_{M2}$ are the permeation rates of major and minor transporting components, respectively. $[M1]_F$ and $[M2]_F$ are their feed concentrations. The

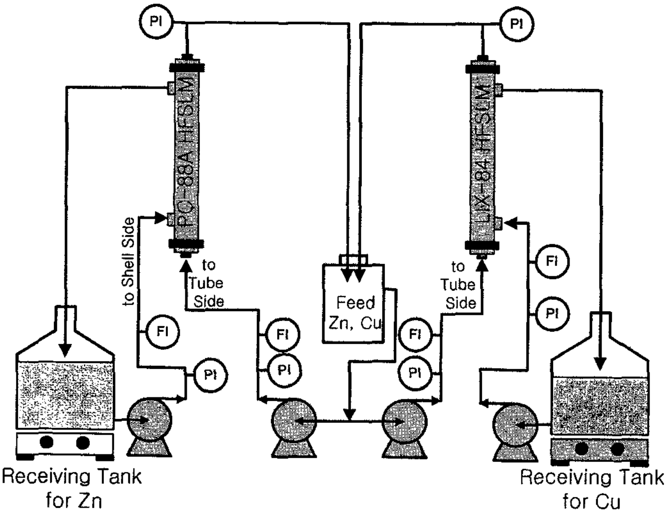


FIG. 1 Apparatus for the simultaneous and selective extractions of $Cu^{2+}$ and $Zn^{2+}$. PI: pressure indicator, FI: flowmeter.

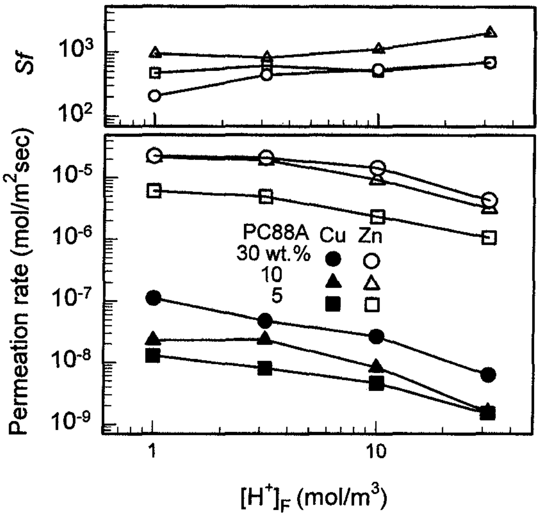


FIG. 2 Effect of $[H^+]_F$ and PC88A concentration on the permeation rates of $Zn^{2+}$ and $Cu^{2+}$ at the PC88A HFSLM. $[Cu^{2+}]_F = [Zn^{2+}]_F = 15.3$ mol/m$^3$.

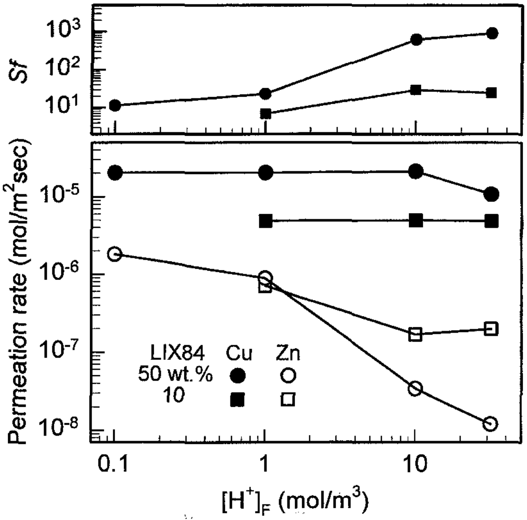


FIG. 3 Effect of $[H^+]_F$ and LIX84 concentration on permeation rates of $Zn^{2+}$ and $Cu^{2+}$ at the LIX84 HFSLM. $[Cu^{2+}]_F = [Zn^{2+}]_F = 15.3$ mol/m$^3$.

permeation rates of metal ions, except the case of $Cu^{2+}$ permeation at the LIX84 HFSLM, increased with decreasing $[H^+]_F$ and became stationary. This can be easily explained by their extraction equilibria described elsewhere (8, 9). The permeations of minor transporting components were enhanced further, and thus the separation factors appeared to decrease with decreasing $[H^+]_F$. The permeation rate of $Cu^{2+}$ in the LIX84 HFSLM was monotonous with a change of $[H^+]_F$, which is due to the early saturation of LIX84 molecules with $Cu^{2+}$ at the feed–membrane interface. This phenomenon will be discussed later in detail together with the effect of feed concentrations. For extractant concentrations in the liquid membranes, the permeation rates increased with increasing extractant concentration because more molecules of the extractant could react with metal ions at the feed–membrane interface. However, the effect weakened, as shown in the $Zn^{2+}$ permeations of Fig. 2, because the membrane phase became more viscous (10).

Figures 4 and 5 show the effect of metal concentrations in the feed solution. Equimolar amounts of $Zn^{2+}$ and $Cu^{2+}$ were present in the feed solution. For the case of the PC88A HFSLM, the permeations rates of both $Zn^{2+}$ and $Cu^{2+}$ were monotonously increased by increasing their feed concentrations. The permeation rates were expected to reach a plateau along with the saturation of extractant at the feed–membrane interface as is usually observed in most liquid membranes. The value of the $Zn^{2+}$ permeation rate was found about $10^{-6}$–$10^{-5}$ mol/m$^2$·s at a feed concentration of 1–100 mol/m$^3$. This value is

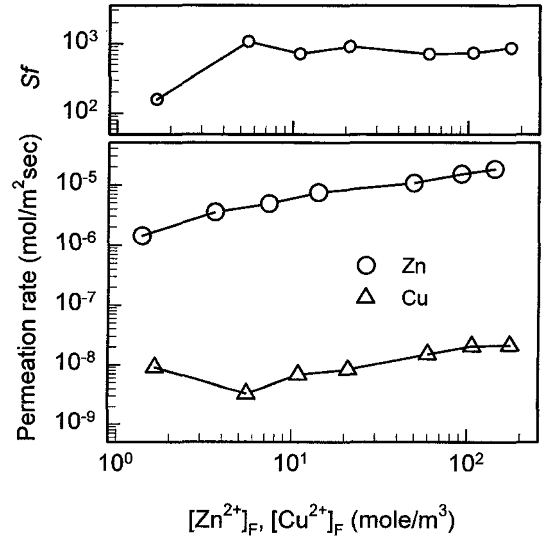


FIG. 4 Effect of $[Cu^{2+}]_F$, $[Zn^{2+}]_F$ on their permeation rates at the PC88A HFSLM. PC88A = 10 wt%, $[H^+]_F = 10$ mol/m$^3$.

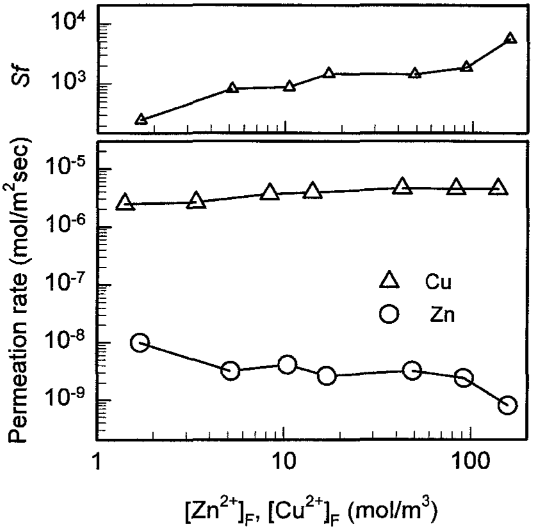


FIG. 5 Effect of $[Cu^{2+}]_F$, $[Zn^{2+}]_F$ on their permeation rates at the LIX84 HFSLM. LIX84 = 10 wt%, $[H^+]_F = 10$ mol/m$^3$.

equivalent to that obtained by Sato (4) with a membrane extractor in which our stripping step was not included. The separation factor was about the third order of magnitude and its value was similar to that which could be obtained by conventional solvent extraction (8). For the case of the LIX84 HFSLM, the permeation of $Cu^{2+}$ was only slightly affected by its feed concentration and the permeation of $Zn^{2+}$ decreased with increasing metal concentrations in the feed solution. According to current knowledge on the permeation mechanism through an SLM, the permeation rates of metal ions are controlled by three major mass transfer steps: mass transfer resistances in the aqueous boundary layer and in the liquid membrane phase, and the extraction reaction rate at the feed–membrane interface. Depending on the system of interest, one of these steps will be the major controlling step for the permeation rate. However, whatever the controlling step is, the metal concentration in the feed phase should affect its permeation rate unless the free extractants at the feed–membrane interface are totally exhausted and the loading of metal ions becomes saturated. Therefore, the zero-order kinetics of $Cu^{2+}$ permeation on its feed concentration and also on $[H^+]_F$ in Fig. 3 can be explained by the fast saturation of LIX84 even with a very low $Cu^{2+}$ concentration due to its high extraction equilibrium constant. The value of the equilibrium constant available from previous work is 1.7, which is a hundred times higher than that of $Zn^{2+}$ for PC88A (8, 11). The decrease of the $Zn^{2+}$ permeation rate with increasing metal concentrations at the LIX84 HFSLM can be explained by the gradual decrease of the portion of extractant saturation for $Zn^{2+}$ because it was replaced by increasing $Cu^{2+}$ which has more affinity with LIX84.

## Enrichment in the Stripping Solution

In Figs. 6 to 9 the enrichments of $Zn^{2+}$ or $Cu^{2+}$ in the stripping solution obtained by total recycle of the feed solution are shown. The initial concentration of each metal ion in the mixed feed was 15.3 mol/m$^3$ with a volume ($V_F$) of 1.25 L. The stripping solution was 3 N $H_2SO_4$, and the volume ($V_S$) was the same as that of the feed solution. Enrichment of metal ions could be easily achieved by the SLM's capability of active uphill transport. For the case of the PC88A HFSLM, most $Zn^{2+}$ in the feed solution was recovered within 150 minutes with 10 wt% of PC88A in the liquid membrane and a $[H^+]_F$ of 10 mol/m$^3$. When the PC88A concentration was increased to 30 wt%, the process could be finished much sooner but the separation factor decreased by an order of magnitude. Also, improvement in selectivity could not be achieved by increasing $[H^+]_F$ higher than 10 mol/m$^3$ as shown in Fig. 6. The rate of enrichment of $Cu^{2+}$ with the LIX84 HFSLM was not affected by $[H^+]_F$ as shown in Figure 8. This confirms the results in Fig. 4. A better selectivity could be obtained however, with a higher $[H^+]_F$. By increasing the LIX84 concentration up to 50 wt%, most of the $Cu^{2+}$ in the feed solution could be recovered within

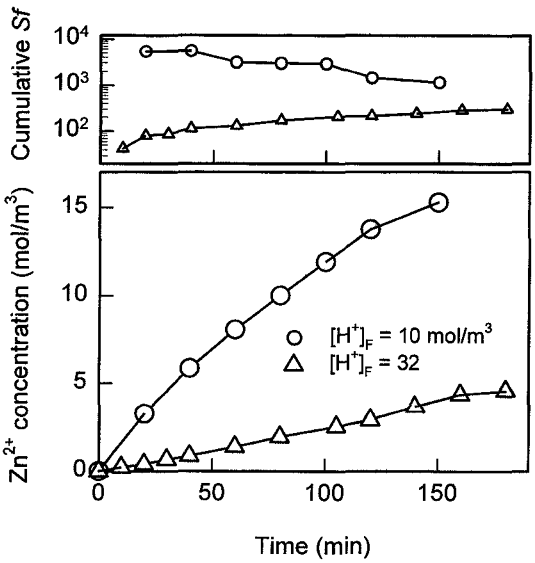


FIG. 6 Enrichment of $Zn^{2+}$ in the stripping solution by total feed recycle at the PC88A HFSLM. PC88A = 10 wt%, $[Cu^{2+}]_F = [Zn^{2+}]_F$ = 15.3 mol/m³, $V_F = V_S$ = 1.25 L.

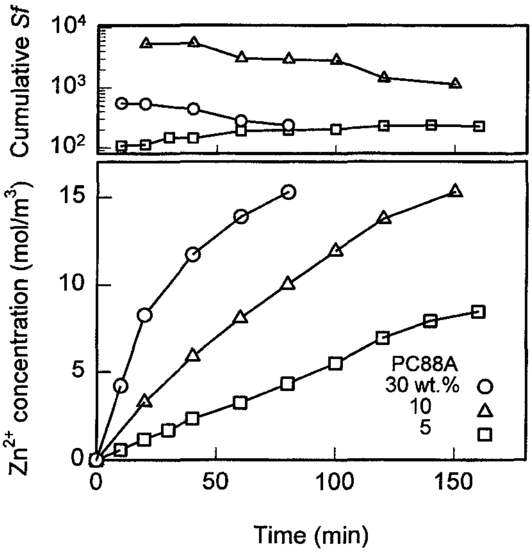


FIG. 7 Enrichment of $Zn^{2+}$ in the stripping solution by total feed recycle at the PC88A HFSLM. $[H^+]_F$ = 10 mol/m³, $[Cu^{2+}]_F = [Zn^{2+}]_F$ = 15.3 mol/m³, $V_F = V_S$ = 1.25 L.

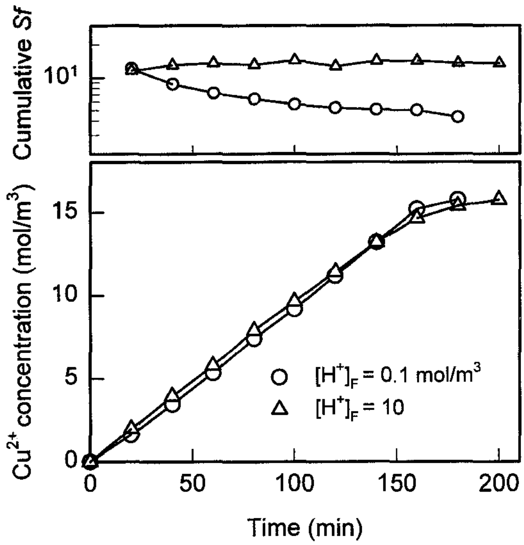


FIG. 8 Enrichment of $Cu^{2+}$ in the stripping solution by total feed recycle at the LIX84 HFSLM. LIX84 = 10 wt%, $[Cu^{2+}]_F = [Zn^{2+}]_F = 15.3$ mol/m$^3$, $V_F = V_S = 1.25$ L.

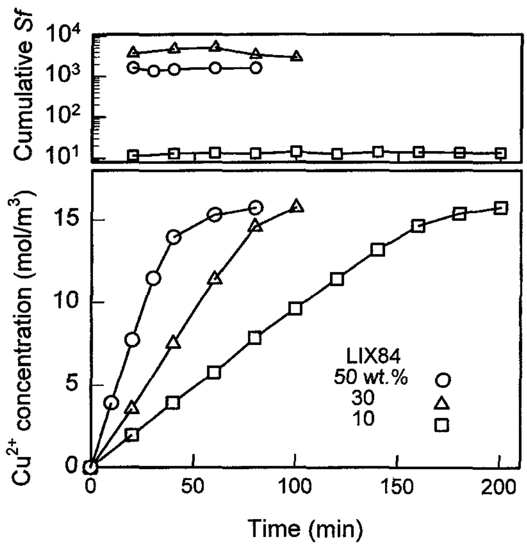


FIG. 9 Enrichment of $Cu^{2+}$ in the stripping solution by total feed recycle at the LIX84 HFSLM. $[H^+]_F = 10$ mol/m$^3$, $[Cu^{2+}]_F = [Zn^{2+}]_F = 15.3$ mol/m$^3$, $V_F = V_S = 1.25$ L.

80 minutes, as shown in Fig. 9. A slight decrease in selectivity was observed when the concentration of LIX84 was increased from 30 to 50%.

## Simultaneous and Selective Extraction

Figure 10 shows the metal concentrations in the stripping solutions during the simultaneous enrichments of $Zn^{2+}$ and $Cu^{2+}$. Both PC88A and LIX84 HFSLMs were connected parallel to the feed vessel, and the feed solution was circulated through two HFSLMs simultaneously. The initial concentration of each metal in the mixed feed was 15.3 mol/$m^3$ with a volume of 2 L. The volume of the receiving solution was 1.25 L. Based on the results of the individual runs for each HFSLM, the conditions of the simultaneous extraction were chosen as a $[H^+]_F$ of 10 mol/$m^3$, a PC88A concentration of 10 wt%, and a LIX84 concentration of 50 wt%; these values were used in this experiment. By comparing the results with the individual runs shown in Figs. 7 and 9, it can be seen that the rate of enrichment in each stripping solution is similar to those of the individual runs. However, the separation factor, especially that for $Zn^{2+}$ in PC88A HFSLM, decreased greatly due to contamination of the extractant with LIX84 during feed circulation through two HFSLMs. Repeating the simultaneous experiments several times led to the conclusion that the SLM could not avoid contamination by a different kind of extractant even when it

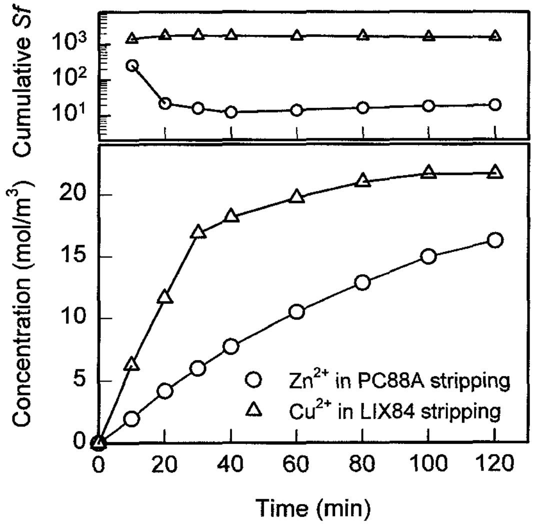


FIG. 10 Simultaneous and selective extractions of $Zn^{2+}$ and $Cu^{2+}$ using the PC88A and LIX84 HFSLMs together. $[H^+]_F$ = 10 mol/$m^3$, $[Cu^{2+}]_F = [Zn^{2+}]_F$ = 15.3 mol/$m^3$, $V_F$ = 2 L, $V_S$ = 1.25 L, PC88A = 10 wt%, LIX84 = 50 wt%.

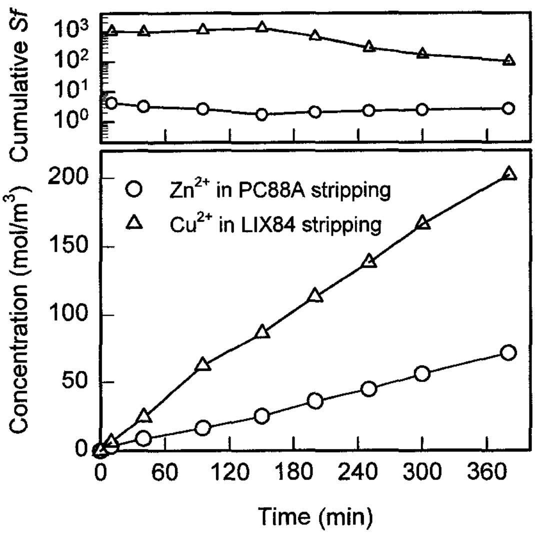


FIG. 11 Simultaneous and selective extractions of $Zn^{2+}$ and $Cu^{2+}$ with periodic injections of membrane solutions into the circulation lines of stripping solutions. $[H^+]_F = 10$ mol/m$^3$, $[Cu^{2+}]_F = [Zn^{2+}]_F = 15.3$ mol/m$^3$, $V_F = 20$ L, $V_S = 1.25$ L, PC88A = 10 wt%, LIX84 = 50 wt%.

existed in a very small amount in the aqueous feed phase. It was nearly impossible to exclude completely the entrainment of extractants into the feed phase whether it was caused by leakage of extractants from the pores of support fiber walls or by insufficient cleaning after the initial organic soaking.

Figure 11 shows the results of long-term operation for simultaneous enrichments of $Zn^{2+}$ and $Cu^{2+}$. A feed solution of 20 L containing 15.3 mol/m$^3$ of each metal ion was concentrated in a stripping solution of 1.25 L. For long-term operation the organic extractants were injected periodically into the circulation lines of stripping solutions to refresh the depleted SLM. This technique was developed for continuous operation of an SLM in our previous study (7). The permeation rate of each component was similar to the individual runs and previous short-term operation, but the separation factor was worse. This was because some extractants injected into the circulation lines of the stripping phase leaked into the feed phase.

The main advantages of simultaneous extraction would be a scale down of the system and a reduction in processing time. An additional advantage would be improvement in selectivity through the simultaneous removal of minor extracting components. However, in reality, the selectivity may not be improved or may even be made much worse due to possible contamination of the liquid membranes by entrainment of organic extractants into the feed solution. More studies are needed to exclude the extractants from the feed phase by inserting a small organic trap in the feed circulation line.

## CONCLUSIONS

The selective and simultaneous extractions of $Zn^{2+}$ and $Cu^{2+}$ from their mixed solutions of sulfate medium were studied using PC88A and LIX84 HFSLMs. From each individual extraction it was concluded that the permeation rate of $Zn^{2+}$ at the PC88A HFSLM increases with either increasing its feed concentration or decreasing $[H^+]_F$, and approaching a maximum value afterward. The permeation rate of $Zn^{2+}$ was about $10^{-6}$–$10^{-5}$ mol/m$^2$·s at a feed concentration of 1–100 mol/m$^3$ and a $[H^+]_F$ of 10 mol/m$^3$ with a PC88A concentration of 10 wt%. The separation factor of the PC88A HFSLM was not much affected by the feed metal concentration and could be obtained up to the third order of magnitude. On the other hand, the permeation rate of $Cu^{2+}$ at the LIX84 HFSLM was not affected by its feed concentration or $[H^+]_F$. A permeation rate about two times higher than that of $Zn^{2+}$ could be obtained at the PC88A HFSLM. There was a similar separation factor when the LIX84 concentration was increased to 50 wt%. The simultaneous extraction of both ions was achieved by using two HFSLMs together with a $[H^+]_F$ of 10 mol/m$^3$, a PC88A concentration of 10 wt%, and a LIX84 concentration of 50 wt%. It was found that the extraction rates of both $Zn^{2+}$ and $Cu^{2+}$ were similar to those of their individual runs, but the separation factor, especially for $Zn^{2+}$ in PC88A HFSLM, was greatly decreased because the extractant was contaminated with another extractant during feed circulation through the two HFSLMs.

## ACKNOWLEDGMENT

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