Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Saito, Takashi(1992) 'Deterioration of Liquid Membrane and Its Improvement in Permeation Transport of Zn(II) Ion through a Supported Liquid Membrane Containing a Bathocuproine', Separation Science and Technology, 27: 1, 1 — 9

To link to this Article: DOI: 10.1080/01496399208018861

URL: http://dx.doi.org/10.1080/01496399208018861

SEPARATION SCIENCE AND TECHNOLOGY, **27**(1), pp. 1–9, 1992

Deterioration of Liquid Membrane and Its Improvement in Permeation Transport of Zn(II) Ion through a Supported Liquid Membrane Containing a Bathocuproine

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Abstract

Investigations were made on the deterioration of liquid membrane in the permeation transport of zinc ion through a supported liquid membrane (SLM) as well as on its improvement. An SLM made of a porous polypropylene membrane impregnated with a dibenzyl ether solution of bathocuproine (4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline) as the carrier and a composite membrane (SLM-DM) made of the said SLM sandwiched between two dialysis membranes were prepared to make zinc ion permeation tests on both membranes. The permeation velocities of zinc ions increased with increasing temperature with both membranes. With the SLM every 1°C increase in temperature brought an increase in the permeation velocity of a zinc ion of 4.90×10^{-11} mol/cm^2·s and with the SLM-DM 1.21×10^{-11} mol/cm^2·s. For the SLM, a deterioration of the liquid membrane with time took place and resulted in a loss of its ability to function as a membrane in 60, 50, and 20 h at 25, 40, and 50°C, respectively. On the other hand, for the SLM-DM which lost more of its initial permeation velocity of the zinc ion compared to the SLM, a constant permeation velocity was maintained for a long time, which led to an increase in the durability of the liquid membrane.

Key Words: Zinc ion; Supported liquid membrane; Dialysis membrane; Temperature dependence; Deterioration of liquid membrane

INTRODUCTION

Permeation transport methods of a permeation species through an SLM containing a carrier are now under investigation for various metal ions. Because the extraction process through an SLM requires less consumption of the extraction solvent (liquid membrane solvent) and chelating agent than does the conventional liquid–liquid extraction process, the former is available at a lower cost. Moreover, because both normal and back-extractions take place simultaneously, it is possible to obtain continuous separation and the concentration of metal ions in an aqueous solution through a membrane into an aqueous phase. These SLMs can be structurally classified into various types such as flat, hollow fiber, and spiral. However, these SLMs suffer from because the extraction solvent and chelating agent are gradually exfoliated into the aqueous phase with time. Accordingly, the permeation velocity of the product decreases with time, finally becoming incapable of transporting the permeating species. Reports on the deterioration of this liquid membrane and its control have rarely appeared. Control of liquid membrane deterioration has been made by periodically reimpregnating the membrane with the extraction reagent (*1*, *2*) or by continuously supplying the liquid membrane solvent (*3–12*). Neither of these, however, constitutes a solution for the exfoliation phenomenon.

We prepared membranes composed of the extraction solvent and a ligand fixed by using polyvinyl chloride, and we investigated the permeation transport of copper ion through them, which revealed that these membranes do not deteriorate substantial, thereby verifying the improvement in liquid membrane durability reported previously (*13*). In the process, however, the low diffusion velocity of the permeation species through the membrane brought about a considerable reduction in permeation velocity.

Accordingly, in the present study, for the purpose of retaining the fluidity of the SLM membrane solvent and controlling the exfoliation of the membrane solvent and ligand, an SLM-DM comprised of an SLM sandwiched between hydrophilic dialysis membranes was prepared (*14*, *15*). The SLM-DM and ordinary SLM were compared in an investigation of the deterioration of these liquid membranes in the permeation of zinc ions.

EXPERIMENTAL

Reagents and Apparatus

Bathocuproine (used as the ligand of the zinc ion), zinc sulfate, lithium chloride, and dibenzyl ether were obtained as analytical pure grade from Wako Pure Chemical Industries Co.

The experimental apparatus for the permeation transport of zinc ion was the same as that used in an earlier paper (*16*).

SLM and SLM-DM

The supporting membrane to hold an organic solvent containing a ligand was a microporous polypropylene membrane, Celgard 2500 (Daicel Chemical Industry Co.), with a pore size of 0.04–0.4 μm, a porosity of 45%, a density of 0.49 g/cm^3, and a thickness of 25 μm. The membrane was cut into circular pieces of 8 cm diameter. It was impregnated with 50 μL bathocuproine solution (1×10^{-2} mol/L) in dibenzyl ether at the center to give a circle of 6 cm diameter as the SLM. Two dialysis membranes, cut into circular pieces of 8 cm diameter, were wetted with a little deionized water, and then the SLM was sandwiched between the dialysis membranes as the SLM-DM. The dialysis membrane used was cellophane, type D-T (Biomed Instruments Inc.), with a pore size of 1.5 nm and a thickness of 15 μm. The concentration of bathocuproine in the SLM and SLM-DM was 6.37×10^{-6} g/cm^2.

Measurements

An SLM or SLM-DM was placed between two cylindrical 150 mL glass cells, one filled with a solution of 2×10^{-4} mol/L zinc sulfate and 0.1 mol/L lithium chloride as the normal extraction side and the other with 150 mL deionized water as the back-extraction side. The contents of both cells were stirred with waterproof magnetic stirrers at 500 rpm in a water bath at constant temperature. Solutions of 1 mL were taken from each of the cells at definite time intervals. The concentrations of zinc ions were determined by atomic absorption spectrophotometry by using a Shimadzu AA-680 instrument.

RESULTS AND DISCUSSION

Permeation Transport of Zn^{2+} Ion through an SLM and SLM-DM

Changes with time in the concentrations of Zn^{2+} ion in the back-extraction side solutions in the course of permeation transport of Zn^{2+} ion through an SLM and an SLM-DM at 25°C are given in Fig. 1. For the permeation model of Zn^{2+} ion in the present process, the previous report shall be referred to (*16*). The initial concentrations of Zn^{2+} and Cl^- ions in the normal extraction side solution were 2×10^{-4} and 0.1 mol/L, respectively. For the SLM, about 50 min after the beginning of the permeation experiment, the Zn^{2+} ion concentrations in the normal and back-extraction side solutions were equal. The concentrations of both phases were later reversed, resulting in the Zn^{2+} ions being concentrated in the back-extraction side solution. After 3 h, all the Zn^{2+} ions in the normal extraction side solution were transported to the back-extraction side.

On the other hand, for the SLM-DM, the rate of Zn^{2+} ion permeating through the SLM-DM was less than that through the SLM. The Zn^{2+} ion concentrations in both phases was equal after about 4 h. Thereafter, the

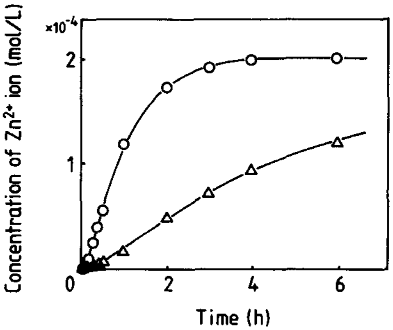

FIG. 1. Concentration of Zn^{2+} ion as a function of time for solutions on the back-extraction side at 25°C. (○) SLM, (△) SLM-DM.

concentrations in the phases were reversed. The initial permeation velocity of Zn^{2+} ion, N, was obtained by

$$N = (\Delta[Zn^{2+}]/\Delta t)/A \qquad (mol/cm^2 \cdot s)$$

where $[Zn^{2+}]$ is the Zn^{2+} ion concentration in the back-extraction side solution (mol/L), t is the permeation time (s), and A is the effective area of the SLM and SLM-DM (28.3 cm^2). Calculations made on the permeation velocity of Zn^{2+} ion through the SLM or SLM-DM under the conditions given in Fig. 1 revealed permeation velocities of 1.20×10^{-9} and 2.58×10^{-10} $mol/cm^2 \cdot s$, respectively.

The reproducibility of the values for the permeation velocity obtained by a permeating transport experiment of Zn^{2+} ion according to the present process was such that the relative standard deviations obtained in tests repeated three times under the same conditions were 4.5 and 3.0%, respectively, for the SLM and SLM-DM. Because the SLM-DM membrane became 2.2 times as thick as the SLM membrane, a reduction in permeation velocity took place, bringing the latter down to 1/4.6.

Relationship between Permeation Velocity of Zn^{2+} Ion and Temperature

Changes in the concentration of Zn^{2+} ion permeating through an SLM or SLM-DM in the back-extraction side solution are related to temperature as shown in Figs. 2 and 3, respectively. The concentrations of Zn^{2+} and Cl^- ions were the same as in Fig. 1. An increase in temperature resulted in an increase in the rate of Zn^{2+} ion transport by permeation through the membrane for either SLM or SLM-DM.

About 3 h were required at a temperature of 25°C with the SLM for

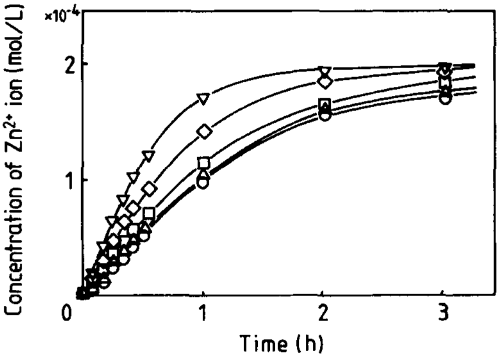

FIG. 2. Concentration of Zn^{2+} ion as a function of time against temperature through an SLM. (○) 25°C, (△) 30°C, (□) 35°C, (◇) 40°C, (▽) 50°C.

Zn^{2+} ion to be totally transported from the normal to the back-extraction side. On the other hand, with a temperature of 50°C, transport of Zn^{2+} ion was completed in about 1.5 h. With the SLM-DM, elevation of the temperature from 25 to 50°C nearly trebled the rate of Zn^{2+} ion permeation.

Arrhenius plots of the relationship between the temperature and the permeation velocities of Zn^{2+} ion through an SLM and SLM-DM are given in Figs. 4 and 5, respectively. Linear relations were established between the temperature and the permeation velocities of Zn^{2+} ion with both membranes, which revealed a temperature dependence of the permeation velocity. The permeation of Zn^{2+} ion through the SLM displayed an increase in permeation velocity of 4.90×10^{-11} mol/cm²·s per temperature increase

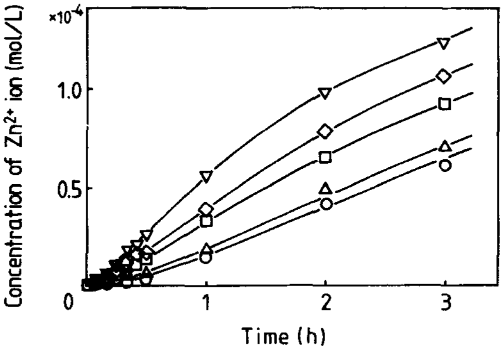

FIG. 3. Concentration of Zn^{2+} ion as a function of time against temperature through an SLM-DM. (○) 25°C, (△) 30°C, (□) 35°C, (◇) 40°C, (▽) 50°C.

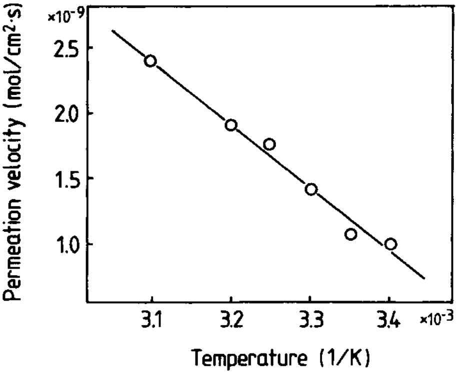

FIG. 4. Arrhenius plot of the permeation velocity of Zn^{2+} ion through an SLM.

of 1°C. On the other hand, that through the SLM-DM displayed an increase of 1.21 × 10^{-11} mol/cm²·s. The chief factors for the permeation velocity increase of Zn^{2+} ion with increasing temperature are the fact that an increase in temperature activates the diffusion of Zn^{2+} and Cl^- ions within the normal extraction side solution and that it also increases the solubility of the zinc–bathocuproine complex into organic solvents in an SLM or SLM-DM and thus accelerates the diffusion velocity of the zinc–bathocuproine complex within liquid membranes. Thus, it is extremely important to take temperature into account when constructing a membrane separation system with high transport efficiency.

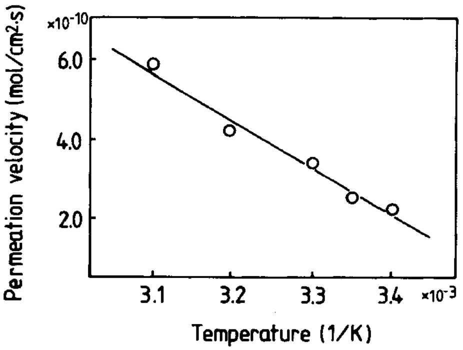

FIG. 5. Arrhenius plot of the permeation velocity of Zn^{2+} ion through an SLM-DM.

Deterioration of Liquid Membrane

Deterioration of the liquid membrane for an SLM and SLM-DM was investigated. A 150-mL solution containing 3 × 10^{-4} mol/L of $ZnSO_4$ along with 0.1 mol/L of LiCl was placed in the normal extraction side, and 150 mL deionized water was placed in the back-extraction side. A 3-h Zn^{2+} ion permeation test was made. The normal and back-extraction side aqueous solutions were subsequently removed. The SLM and SLM-DM were washed twice with deionized water and normal and back-extraction side solutions similar to those given above were placed in the permeating test cell. After a 3-h permeation test, the aqueous solutions in both cells were renewed in order to repeat the permeation tests. This operation was repeated, and the permeation velocities of Zn^{2+} ion at 3-h intervals were calculated.

Figure 6 gives the change in the permeation velocity of Zn^{2+} ion through the SLM with time. The permeation velocity value at 25°C was 1.60×10^{-9} mol/cm²·s immediately after the beginning of the permeation test, it decreased with time to as low as 9.10×10^{-11} mol/cm²·s after 60 h. At higher temperatures the reduction ratio of the permeation velocity was accelerated; it was reduced from 2.25×10^{-9} to 5.00×10^{-12} mol/cm²·s in the course of 21 h at 50°C. One of the reasons for this reduction is that the higher the temperature, the higher the solubility of the liquid membrane solvent in the aqueous phase as well as of the bathocuproine retained within the membrane pores. As stated above, at 25, 40, and 50°C it is clear that deterioration of the liquid membrane takes place in such a degree, resulting in a loss of the ability of the functional membrane to inhibit the transport of Zn^{2+} ion. On the other hand, Fig. 7 shows the change with time of the

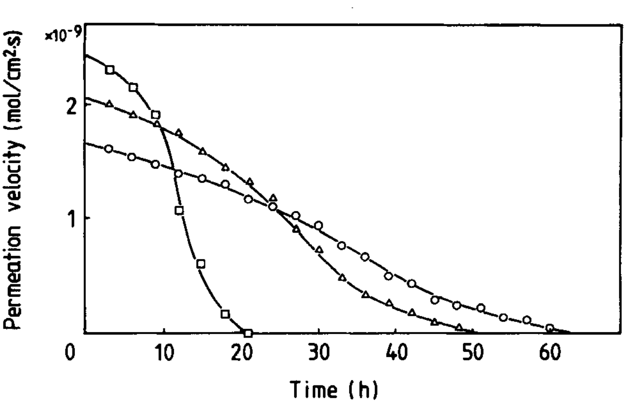

FIG. 6. Change with time in the permeation velocity of Zn^{2+} ion through an SLM. (○) 25°C, (△) 40°C, (□) 50°C.

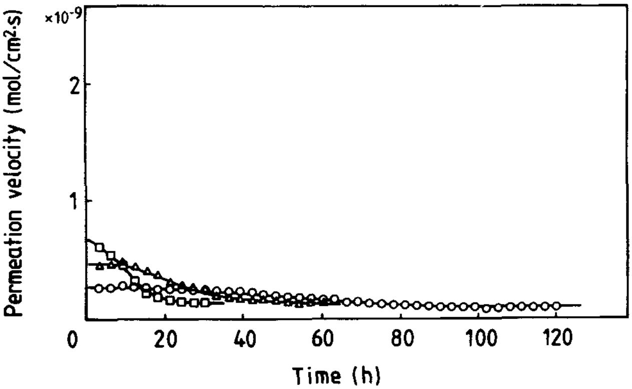

FIG. 7. Change with time in the permeation velocity of Zn^{2+} ion through an SLM-DM. (○) 25°C, (△) 40°C, (□) 50°C.

permeation velocity of Zn^{2+} ion through the SLM-DM. At 25°C the permeation velocity, which had been 2.93×10^{-10} mol/cm²·s at the beginning of the permeation test, was 1.58×10^{-10} mol/cm²·s after 60 h, which corresponds to a decrease of about 54%, whereas for there was a 5.7% decrease for the SLM under the same conditions. Moreover, the SLM-DM had no substantial reduction in permeation velocity after 120 h.

The transport of Zn^{2+} ion through the SLM-DM at 40 and 50°C remains nearly constant after a velocity of about 1.1×10^{-10} mol/cm²·s is attained. At 50°C it was observed that the SLM-DM maintained a permeation velocity 25 times as fast as that of the SLM after 21 h.

CONCLUSION

An SLM-DM constructed by sandwiching an SLM between dialysis membranes was prepared to test liquid membrane deterioration. Although the SLM-DM showed a decrease in the initial permeation velocity of Zn^{2+} ion, it controlled the exfoliation of the liquid membrane solvent and the carrier from the SLM and retained the function of the liquid membrane for a long time. In the future, it is expected that an SLM-DM will be used as a long life liquid membrane which retains its properties.

REFERENCES

1. T. Shiode, M. Tanigaki, M. Ueda, and W. Eguchi, *Reprints of the 19th Autumn Meeting of the Chemical Engineering Society*, 1985, p. 190.
2. M. Teramoto, H. Tanimoto, Y. Yoshida, and Y. Miyake, *Reprints of the 16th Autumn Meeting of the Chemical Engineering Society*, 1982, p. 502.

3. H. Adachi, I. Akiba, M. Hozawa, and K. Fujinawa, *Reprints of the 19th Autumn Meeting of the Chemical Engineering Society,* 1985, p. 189.
4. M. Hozawa, M. Akiyama, and K. Fujinawa, *Reprints of the 52nd Meeting of the Chemical Engineering Society,* 1987, p. 44.
5. I. Akiba, H. Adachi, M. Hozawa, and K. Fujinawa, *Ibid.,* p. 487.
6. M. Hozawa, M. Akiyama, A. Syono, N. Imaishi, and K. Fujinawa, *Reprints of the 53rd Meeting of the Chemical Engineering Society,* 1988, p. 314.
7. M. Tanigaki, T. Shiode, S. Okumi, and W. Eguchi, *Sep. Sci. Technol., 23,* 1171 (1988).
8. M. Nakano, K. Takahashi, and M. Takeuchi, *Reprints of the 52nd Meeting of the Chemical Engineering Society,* 1987, p. 50.
9. M. Teramoto and H. Tanimoto, *Sep. Sci. Technol., 18,* 871 (1983).
10. M. Teramoto, H. Matsuyama, H. Takaya, and S. Asano, *Ibid., 22,* 2175 (1987).
11. M. Teramoto, H. Matsuyama, H. Takaya, and N. Tohno, *Reprints of the 52nd Meeting of the Chemical Engineering Society,* 1987, p. 47.
12. S. Furusaki, *Reprints of the 21st Autumn Meeting of the Chemical Engineering Society,* 1988, p. 361.
13. T. Saito, R. Matsui, K. Tanabe, and A. Iguchi, *Reprints of the 56th Spring Meeting of the Chemical Society of Japan,* 1988, p. 748.
14. T. Saito, Y. Miyamoto, and A. Iguchi, *Reprints of the 47th Debating Society of the Japan Society for Analytical Chemistry,* 1986, p. 241.
15. T. Saito and T. Sugiyama, *Reprints of the 58th Spring Meeting of the Chemical Society of Japan,* 1989, p. 699.
16. T. Saito, *Sep. Sci. Technol., 25,* 581 (1990).

Received by editor November 5, 1990