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Facilitated Transport of Zinc Chloride through Hollow Fiber Supported Liquid Membrane. Part 2. Membrane Stability

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Abstract

The stability of a hollow fiber supported liquid membrane of tri-*n*-octylamine diluted in *n*-dodecane with 2-ethylhexyl alcohol was examined for the facilitated transport of zinc chloride. The liquid membrane was unstable when the feed and the strip aqueous solutions were not saturated with the organic phase used as the liquid membrane. This was found to be due to the dissolution of relatively soluble 2-ethylhexyl alcohol to the aqueous phases. When both aqueous phases were presaturated with the organic phase used, a rather constant flux could be maintained for a long time by the reimpregnation of the organic phase approximately once a day. The continuous impregnation of the organic phase to the support membrane drastically increased the stability of the liquid membrane, even without presaturation of the two aqueous phases with the organic phase.

INTRODUCTION

One of the biggest problem which makes supported liquid membrane operation difficult as an industrially feasible operation is the instability of the liquid membrane (*1-9*). The factors which affect this stability have been studied by many workers. The organic phase is sustained in the micropores of the support membrane. Therefore, the small pressure difference across the membrane and the large interfacial tension increase membrane stability (*4, 8*). The size of the micropores should be small, but a too small diameter hinders diffusion, which in turn makes the permeation flux low (*10*). Support membranes with micropores

between 0.1 to 1 μm are usually considered to be appropriate. Increased viscosity (*11*) and the use of a relatively thick support membrane wall (*4–6, 8*) increases the lifetime of a liquid membrane. The dissolution loss of the organic solvent or carrier to the aqueous phases is known to decrease the lifetime of a liquid membrane (*4, 8, 11, 12*).

The system employed in the present series of papers is the facilitated transport of zinc chloride through the liquid membrane of *n*-dodecane with 2-ethylhexyl alcohol which contains tri-*n*-octylamine as the carrier. The solubility of this alcohol is relatively large, and it is apt to be lost to the aqueous phases. Our interest was to study the stability of the present system and to develop a method which permits stable operation with this system.

EXPERIMENTAL

The apparatus and the procedure used for the experimental study of permeation of phenol and zinc chloride are the same as before (*13*). In the experiments on phenol permeation, a liquid membrane of *n*-dodecane with or without 2-ethylhexyl alcohol (EHA) was used. The feed aqueous solution of phenol runs through the inside of the polyethylene hollow fiber. The strip solution outside the fiber was 0.4 kmol/m^3 aqueous sodium hydroxide solution. The membrane phase in the experiments of zinc chloride facilitated transport was *n*-dodecane with 6 vol% EHA which contained tri-*n*-octylamine (R_3N) as the carrier. The feed aqueous solution was a 1.0 kmol/m^3 hydrochloric acid solution which contained zinc chloride ($\sim 2.5 \times 10^{-4}$ kmol/m^3), and the strip solution was 0.1 kmol/m^3 aqueous hydrochloric acid solution. A trace amount of lithium chloride was added to the strip solution to check for film breakage. All experiments were carried out at 298 K.

RESULTS AND DISCUSSIONS

Phenol Permeation Experiments

Figure 1 shows the time course change of the phenol flux, J_{Ph}, through a liquid membrane of *n*-dodecane with 6 vol% EHA. In the case when both aqueous phases were carefully presaturated with the organic phase (a), a high constant flux level was maintained for 4 days. The observed overall

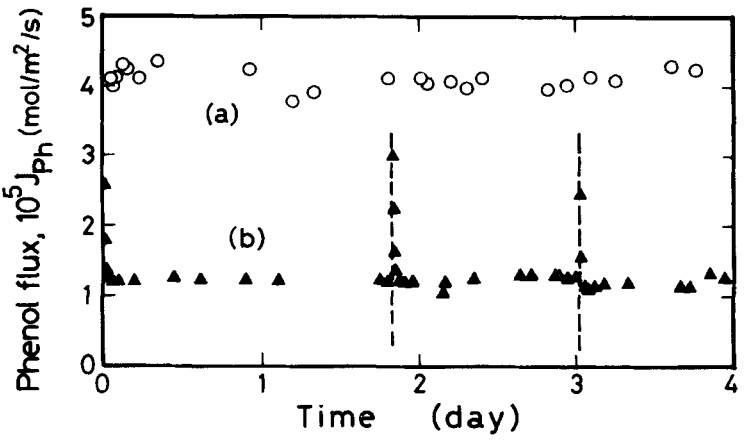

FIG. 1. Time course change of phenol flux through HFSLM of *n*-dodecane with 6 vol% EHA at 298 K. (a): When both aqueous phases were presaturated with the organic phase. (b): Without presaturation. Vertical dashed lines indicate the reimpregnation of the organic phase.

resistance approximately agreed with the sum of the inside film resistance and the membrane resistance with the distribution coefficient $K_{D,Ph}$ = 1.42 and a tortuosity factor of 1.4 (*13*). When the aqueous phase without presaturation with the organic phase was used (b), the original high flux rapidly decreased to a lower constant level. The vertical dashed lines indicate the reimpregnation of the organic phase. The flux retained the high level but again rapidly decreased to the same lower level. The phenol flux with *n*-dodecane without EHA as the membrane phase is shown in Fig. 2. The flux level is stable and coincided with the lower level in Fig. 1(b). This suggests that the rapid decrease of flux in Fig. 1(b) is due to the rapid dissolution of EHA, whose solubility is relatively high (~0.1 wt% at 298 K), into the aqueous phases.

To understand the difference in flux levels with and without EHA, the distribution equilibrium of phenol between water and *n*-dodecane with different EHA contents was examined. Figure 3 shows the result. Obviously, EHA works as an extractant of phenol and increases the distribution coefficient as a linear function of EHA content. With *n*-dodecane only, $K_{D,Ph}$ is low (= 0.14), which increases the membrane resistance approximately 10 times compared with the case with 6 vol% EHA ($K_{D,Ph}$ = 1.42). The total resistance in the case of lower flux levels in Fig. 1(b) and in Fig. 2 agrees with the one calculated with the membrane resistance with $K_{D,Ph}$ = 0.14.

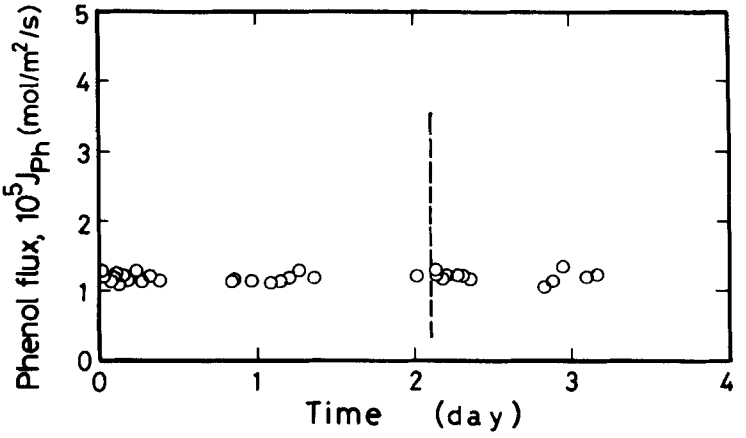

FIG. 2. Time course change of phenol flux through HFSLM of *n*-dodecane only at 298 K. Vertical dashed line indiates the reimpregnation of the organic phase.

Zinc Permeation

Examples of the fluxes of zinc chloride, J_Z, through a liquid membrane of R_3N (0.1 kmol/m^3) in *n*-dodecane with 6 vol% EHA are shown in Fig. 4. The feed is an aqueous solution of zinc chloride ($\sim 2.5 \times 10^{-4}$ kmol/m^3) and hydrochloric acid (1 kmol/m^3). The strip solution on the outside of the hollow fiber was an aqueous solution of 0.1 kmol/m^3 hydrochloric

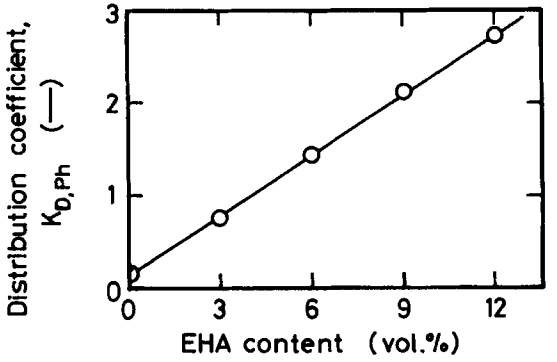

FIG. 3. Distribution equilibrium of phenol at 298 K between water and *n*-dodecane with EHA.

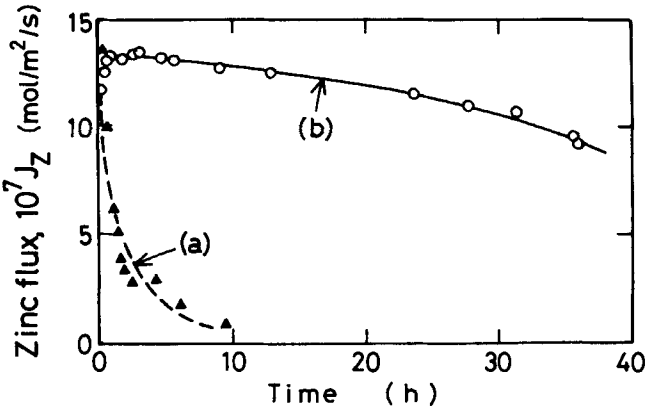

FIG. 4. Zinc chloride flux through HFSLM of *n*-dodecane with 0.1 kmol/m^3 R_3N and 6 vol% EHA at 298 K. $C_{H,1}$ = 1.0 kmol/m^3, $C_{H,2}$ = 0.1 kmol/m^3. (a): When both aqueous phases were not presaturated with the organic phase. (b): When both aqueous phases were presaturated with the organic phase.

acid. Throughout the experiments, lithium chloride was not detected in samples of the exit raffinate solution, which indicates that breakage of the liquid membrane is negligible.

Curve (a) in Fig. 4 results when both aqueous solutions are not presaturated with the organic phase of *n*-dodecane with 6 vol% EHA. The flux rapidly decreases. This would again be due to the dissolution of EHA into the aqueous phases. This would cause the formation of complicated complexes of hydrochloric acid and of zinc chloride with R_3N. Curve (b) in Fig. 4 results when both aqueous phases are presaturated with the organic phase used. The membrane is much more stable, although it still decreases gradually. The initial flux level agreed well with the calculated one from the two films and the membrane phase resistances (*13*).

It has been shown by many workers that reimpregnation of the organic phase to the support membrane recovered the original flux level (*3*, *4*, *6*, *7*, *9*, *14*). The result of a long time experiment with reimpregnation of the organic phase by running it through the inside of the hollow fiber for a short period of time approximately once a day is shown in Fig. 5. The reimpregnation recovered the original flux level, and a rather stable operation was possible for 24 d. Both aqueous phases used were presaturated with the organic phase.

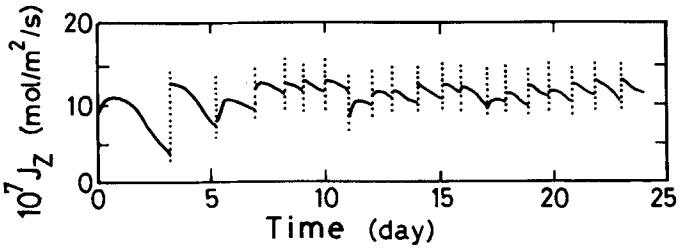

FIG. 5. Effect of reimpregnation of the organic phase approximately once a day in the zinc chloride flux through HFSLM of *n*-dodecane with 0.1 kmol/m^3 R_3N and 6 vol% EHA at 298 K. $C_{H,1}$ = 1.0 kmol/m^3, $C_{H,2}$ = 0.1 kmol/m^3. Both aqueous phases were presaturated with the organic phase.

Continuous Impregnation of Organic Phase

Even though stable operation for a long period of time was demonstrated in Fig. 5, presaturation of the aqueous phase is not practical for an industrial operation. The liquid membrane system was modified as shown in Fig. 6, so that the organic phase could be continuously fed to the micropores of the hollow fiber wall. Application of an additional head pressure on the organic phase in the left compartment over the feed solution (~20–30 cm) and a slight vacuum in the other compartment was enough to ensure the flow of the organic phase. The flow rate of the organic phase was approximately 0.7 cm^3/d, which is less than 1% of the flow rate of the feed aqueous solution.

The result of experiments with this continuous impregnation is illustrated in Fig. 7. A high constant flux, which agreed with the initial level in Fig. 4, could be maintained for 9 d even though both aqueous phases were not presaturated with the organic phase. This continuous impregnation succeeded in increasing the stability of the liquid

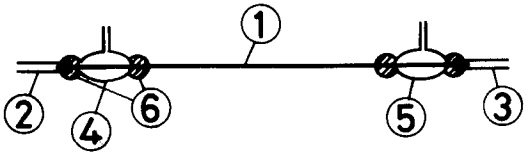

FIG. 6. Continuous impregnation of the organic phase. ① Hollow fiber. ②, ③ Glass tube. ④ Glass compartment for the continuous feeding of the organic phase. ⑤ Glass compartment for vacuum. ⑥ Adhesive epoxy resin.

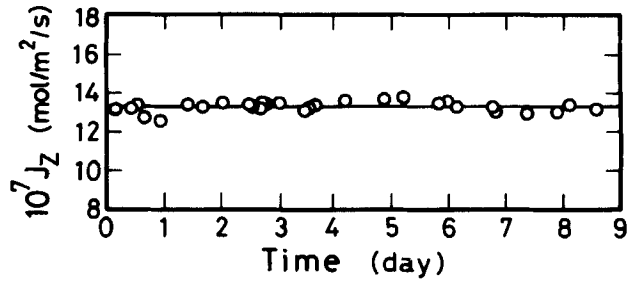

FIG. 7. Stabilization of zinc chloride flux through HFSLM of *n*-dodecane with 0.1 kmol/m^3 R_3N and 6 vol% EHA at 298 K by continuous impregnation. $C_{H,1}$ = 1.0 kmol/m^3, $C_{H,2}$ = 0.1 kmol/m^3. Both aqueous phases were not presaturated with the organic phase.

membrane operation drastically. Similar continuous impregnations have been reported (*7*, *12*).

Figure 8 illustrates the phenol flux with the same continuous impregnation of *n*-dodecane with 6 vol% EHA. Even without presaturation of the aqueous phases, the high flux level which approximately coincided with Fig. 1(a) could be maintained for 5 d.

Note that the system employed in the present work is principally very unstable due to the high solubility of EHA. There have been reported cases where liquid membranes are much more stable (*5–9*, *14*). Even in

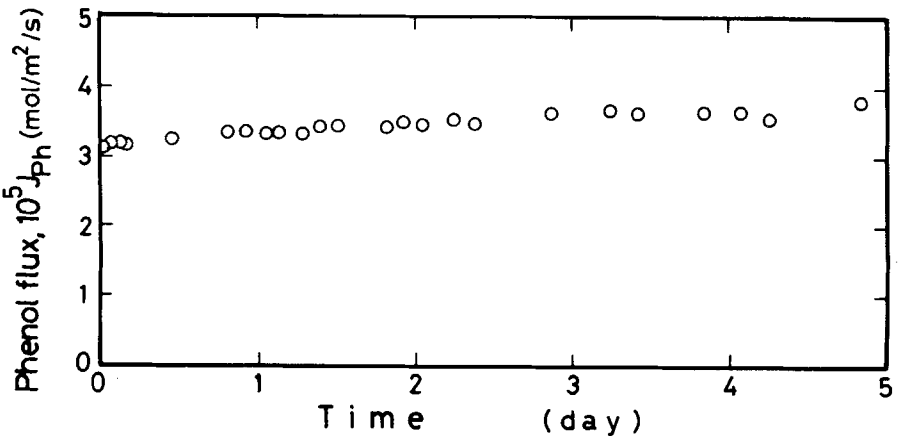

FIG. 8. Phenol flux through HFSLM of *n*-dodecane with 6 vol% EHA at 298 K with continuous impregnation. The aqueous phases were not presaturated with the organic phase.

these cases, a gradual decrease in flux is usually observed, so the present continuous impregnation would help to make the lifetime considerably longer. It would also make possible the use of extractants and additional reagents whose solubility to the aqueous phases are relatively high. Systematic work on the optimal pressure to be applied to the organic phase for continuous impregnation of the support membrane and the vacuum to be applied to the other side is necessary.

CONCLUSIONS

The liquid membrane with EHA was unstable unless both aqueous phases were not presaturated with the organic phase used. This was found to be due to the relatively high solubility of EHA into the aqueous phases. When aqueous phases presaturated with the organic phase were used, a rather constant flux could be maintained by the reimpregnation of the organic phase once a day. The continuous impregnation of the organic phase drastically increased the stability of the liquid membrane. Even without presaturation, a high constant flux could be maintained for days.

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