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Facilitated ion transport through cellulose triacetate-based polymer inclusion membranes: A promising method for treatment of nuclear wastewater

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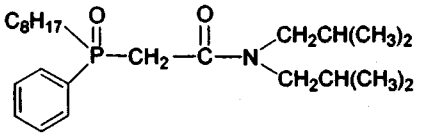
1. Introduction

The large quantity of liquid wastes from nuclear industries such as nuclear power plants would become a serious storage problem in view point of the environmental safety. The liquid wastes should be concentrated to a smallest possible volume before the storage. The use of supported liquid membranes (SLMs) for this purpose is very attractive [1,2], however loss of solvent and carrier in the surrounding solutions limits the stability of SLMs and hinders their commercial application in the industries. The instability problem is related to the structure of SLM, which consists of solvent and carrier impregnated in the pores of a macroporous membrane. In this work, in order to develop stable membranes, we prepared polymer inclusion membranes (PIMs) based on cellulose triacetate (CTA) using 2-nitrophenyl n-octyl ether (NPOE) as a solvent. Here, the solvent acts as a plasticizer for the polymer to result in a stable organo gel [3]. Shinbo *et al.* have studied the long-term stability of PIM, and reported that almost no change in the transport performance was observed during about one month of continuous experiment [4]. Other work also confirmed the stability of PIM during more than three months operation [5]. The carriers used to develop the present PIMs were octyl(phenyl)-N,N-diisobutyl carbamoylmethylphosphine oxide (CMPO) and N,N,N',N'-tetraoctyl-3-oxapentane-diamide (TODGA), which are known as excellent extraction agents for actinides [1,6]. An aqueous acidic solution containing cerium(III) nitrate was used as a model for the low level radioactive wastewater, and the facilitated transport of cerium(III) ions through the PIMs was investigated experimentally.

2. Experimental

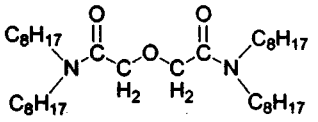
CMPO was purchased from Hokko Chem. Ind., Japan. TODGA was synthesized in our laboratory using a synthetic route, which was a modification of that initially proposed by Sasaki *et al.* [6]. The chemical structures of CMPO and TODGA are shown in Figures 1 and 2.

To prepare a PIM, two grams of CTA (Eastman Kodak Co. USA, 43.6% acetyl content, product no.: CAT114 4476) was dissolved in 98 g of chloroform by stirring for 5 h at room temperature. NPOE (Dojindo, Japan) and the CTA solution was then mixed with a weight ratio of NPOE : CTA of 3:1. CMPO or TODGA was added and the solution was stirred for 2 h at room temperature to obtain a homogenous solution. The amount of CMPO or TODGA added into the solution was adjusted to obtain PIMs containing 5 - 15 wt% carrier. The solution was then cast onto glass petri dishes (64 mm of diameter), and chloroform was allowed to evaporate slowly at room temperature for one day. Finally, the membranes were carefully peeled off the dishes. The resulted PIMs showed a good mechanical strength and were completely clear with thicknesses varying from about 30 to 150 μm.



Octyl(phenyl)-N,N-diisobutyl carbamoylmethylphosphine oxide (CMPO)

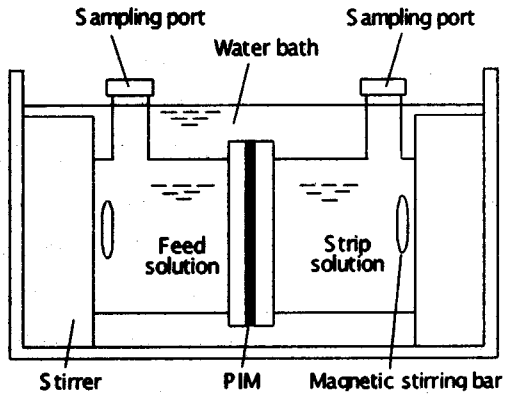
Fig.1 Chemical structure of CMPO.



N,N,N',N'-tetraoctyl-3-oxapentane diamide (TODGA)

Fig.2 Chemical structure of TODGA.

For the transport experiment, the membrane was clamped between two compartments of a permeation cell as shown in Figure 3. The effective membrane area was 7.1 cm^2. The feed compartment was filled with 20 ml of an aqueous feed solution containing 100-1800 ppm $Ce(NO_3)_3$, 0.05 M HNO_3 and 2.95 M $NaNO_3$. The receiving (strip) compartment was filled with 20 ml of distilled and deionized water. The cell was placed in a water bath, and both compartments were stirred at 600 rpm. The temperature was varied from 25°C to 40°C. Samples of the feed and strip solutions were periodically taken and analyzed by inductively coupled plasma (ICP) spectroscopy.



F ig. 3 Apparatus for transport experiment.

3. Results and discussion

The result of the transport experiment using the PIM without carrier showed that no change in cerium concentration was observed during the 5 h experiment, indicating that in the absence of carrier the transport of cerium ions from the feed phase to the strip phase did not occur. This result established that the PIM without carrier served as a barrier to ion permeation. Figure 4 shows the transport of cerium ions through the PIM containing 15 wt%

CMPO for different temperatures. The feed solution was an aqueous solution of 200 ppm $Ce(NO_3)_3$ in 0.05 M HNO_3/ 2.95 M $NaNO_3$. It can be seen that cerium ions were completely removed from the acidic aqueous feed solution to the strip solution within 5 h. The increase in temperature was effective to increase the transport rate of cerium against its concentration gradient. A similar tendency was also obtained for the PIM containing 15 wt% TODGA as shown in Fig. 5.

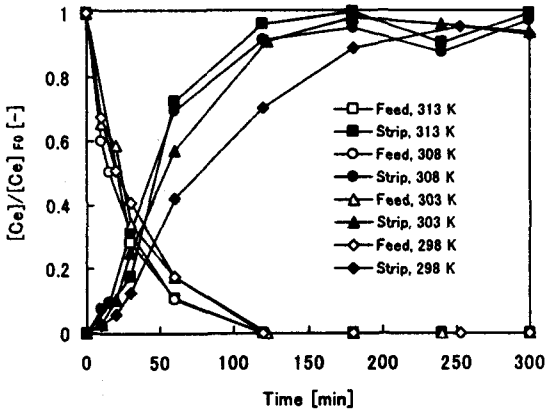


Fig.4 Transport of cerium through CMPO-containing PIM for different temperatures.

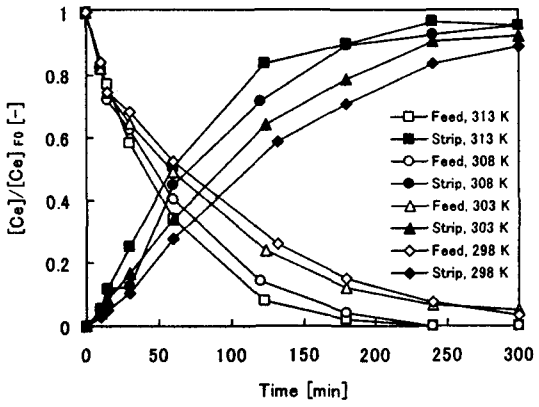


Fig.5 Transport of cerium through TODGA-containing PIM for different temperatures.

In order to determine the permeate flux of cerium accurately, the transport experiments were performed by circulating a feed solution from a reservoir to the feed compartment of the cell. Here, since the change of the feed concentration is negligible, we can expect a linear relationship between the concentration of cerium in the strip phase and the time after a steady state condition is attained. The permeate flux can be then calculated from the slope of the fitted line and the known membrane area. Figure 6 shows the permeate flux as a function of carrier concentration for the PIM containing TODGA. Here, the feed solution was an aqueous solution of 200 ppm $Ce(NO_3)_3$ in 0.05 M HNO_3/ 2.95 M $NaNO_3$. It can be seen that the permeate flux was zero in the absence of carrier, and increased with increasing carrier concentration, indicating that carrier-mediated transport occurred in the PIM. At high carrier concentrations, the curve became a plateau since the high carrier concentration affected the diffusivity of the carrier and increased the viscosity of the membrane solution.

Transport experiments were then performed using PIMs with various membrane thicknesses. Figure 7 shows the reciprocal of permeate flux as a function of the membrane thickness. As seen, a straight line through the origin was obtained for the relationship between the reciprocal of permeate flux and the membrane thickness. This result is consistent with a diffusion-limited transport mechanism like those common to SLMs [7]. Thus, it can be concluded that the rate-limiting step of the transport process in the present PIMs is the diffusion of the cerium ion-carrier complex in the membrane.

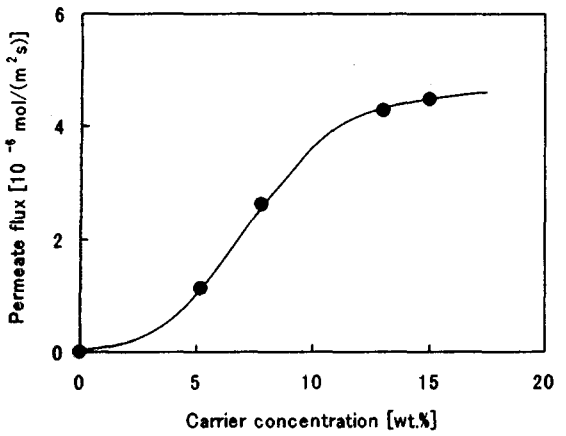


Fig.6 Effect of carrier concentration on permeate flux of cerium through TODGA-containing PIM.

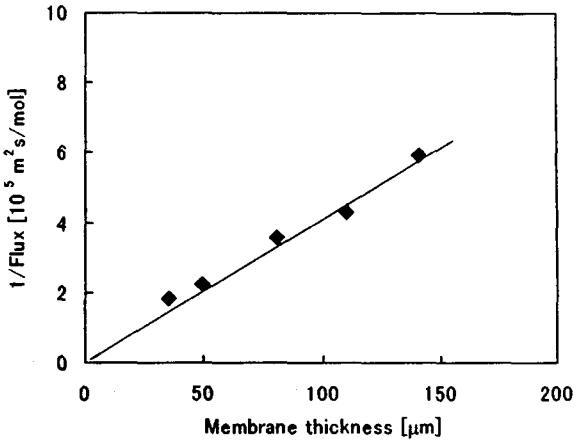


Fig.7 Effect of membrane thickness on permeate flux of cerium through PIMs containing 15 wt% TODGA.

4. Conclusion

We developed PIMs consisting of CTA as a polymer matrix, NPOE as a solvent and CMPO or TODGA as a carrier, and found that the PIMs were very effective for the facilitated transport of cerium(III) ions. The results of this work suggest that the present PIMs have a potential application for the treatment of nuclear wastewater.

Acknowledgment

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