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The Effect of Porous Support Composition and Operating Parameters on the Performance of Supported Liquid Membranes

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Abstract

Factors, such as porous support composition and operating parameters, that influence the performance of supported liquid membranes (SLMs) were investigated. SLMs of varying porous support compositions and structures were studied for the transport of metal ions. A microporous polybenzimidazole support was synthesized and prepared in the form of an SLM. This SLM, containing the selective extractant di-(2-ethylhexyl)phosphoric acid, was evaluated for the transport of copper and neodymium. Dramatically improved performance over that of commercially available membranes was found in tests for removing the metal ions from solution. Metal ion transport reaches near completion in less than 3 h, whereas Celgard-polypropylene and Nuclepore-polycarbonate reaches only 50% completion even after 15 h. The transport driving force for acidic extractants is a pH gradient between the feed and strip solutions. Polybenzimidazole, an acid- and radiation-resistant polymer, has two protonatable tertiary nitrogens per repeat unit that may help sustain the pH driving force. Another factor may be the ability of the polybenzimidazole to hydrogen bond with the extractant. Transport through the flat-sheet SLMs was tested by using a unique cell design. Countercurrent flow of the feed and strip solutions was established through machined channels in half-cell faceplates that are in a spiral, mirror-image pattern with respect to each other, with the flat-sheet SLM interposed between the two channeled solutions. Advantages comprised in the design of the two clamped half-cells (tangential entry, zero primary pressure, zero pressure differential, controlled flow regimes, no sharp turns, and channeled flow) give operating parameters that will not physically dislodge the liquid membrane from the porous support; consequently, the lifetime of the support is increased. Permeability coefficients remained unchanged after a month of daily use versus 20 to 100% declines for membranes in other cell configurations.

INTRODUCTION

High-performance supported liquid membranes (SLMs) are being investigated for their future use in the recovery of actinide metal ions found at low concentrations in aqueous process streams. Many studies have demonstrated SLMs as a viable alternative over the more conventional processes based on solvent extraction and ion exchange (*1*, *2*). An SLM is composed of an extractant containing organic solution adsorbed within the pores of a thin microporous support. The SLM is placed between an aqueous feed solution containing the permeating metal ions and an aqueous strip solution. A chemical potential gradient between the two solutions, such as pH, drives the transport for acidic extractions. The use of SLMs offers the possibility of high selectivities, high concentration factors, negligible solvent entrainment, utilization of small quantities of extractant, and energy efficiency.

The actual use of SLMs in process applications, however, has been very limited. The major problem is their physical instability. This instability is attributed to a number of mechanisms (*1*), such as solvent or carrier loss by solubility in the aqueous phase, feed-strip pressure differentials, and emulsion formation.

In the present study, some factors which may influence SLM stability and performance have been examined. The effect of the porous support has been examined by studying metal ion transport behavior using five supports of different chemical composition. This study resulted in a new and significantly improved SLM consisting of a polybenzimidazole porous support. The effect of structural aspects of the porous support such as porosity and pore size were also studied. The effect of liquid membrane composition was examined for its support wettability and concomitant transport function. Permeability coefficients were measured to determine if operating parameters, such as cell and transport apparatus design, contributed to the membrane lifetime.

EXPERIMENTAL

Reagents

All reagents were analytical grade products. The aqueous copper feed solution used in all experiments initially contained 1×10^{-3} *M* copper nitrate hydrate (Aldrich Chemical Co.) in a solution of 1.9 *M* sodium acetate and 0.1 *M* acetic acid, at pH 6.0. For neodymium transport experiments, the aqueous feed solution contained 1×10^{-3} *M* neodymium nitrate hexahydrate (Aldrich Chemical Co.) in 1.9 *M* sodium acetate and 0.1 *M* acetic acid. The aqueous strip solution contained 2.0 *M* nitric acid.

Two types of organic solutions were used as liquid membranes. The first consisted of 0.5 *M* di-(2-ethylhexyl)phosphoric acid (HDEHP) (Alfa Products) in dodecane. This liquid membrane was used when the support was composed of a hydrophobic polymer. The second type of liquid membrane was an oil-in-water emulsion. This was prepared by adding 10 g of the organic solution, 0.5 *M* HDEHP in dodecane, into 90 g of an aqueous surfactant solution consisting of 3% by weight Brij 30 (polyoxyethylene lauryl ether). The mixture was stirred for 30 min, then bath-sonicated at 30°C for 3 h. The resulting oil-in-water emulsion was used as a liquid membrane for hydrophilic supports.

Polymeric Membrane Support Materials

Hydrophobic and hydrophilic polymeric supports were used in this work. Most of the experiments were performed using a Celgard membrane (Celanese Plastics). Celgard is a microporous hydrophobic polypropylene film, 25 μm thick with a nominal porosity of 45% and an effective pore size of 0.04 μm. The other hydrophobic support material used in this work was a microporous Nuclepore 111703 polycarbonate membrane (Nuclepore Corp.). It is 6 μm thick with a nominal porosity of 2% and an effective pore size of 0.05 μm. Unlike Celgard membranes, the Nuclepore membranes are nontortuous with capillary pores of a defined size. The Nuclepore membranes are rendered hydrophobic by pretreatment with 1.0 *N* acetic acid in a sonicator bath for 30 min followed by rinsing in deionized water to remove the hydrophilic polymer coating (polyvinylpyrrolidone).

The three hydrophilic polymeric support materials were used. Two were commercial membranes and one was synthesized using a procedure described below. The two commercial membranes were Celgard 3401 and Nuclepore polycarbonate 111703. The two membranes are identical in physical structure to their hydrophobic counterpart membranes described above; however, they are factory treated with surfactants and made available in a hydrophilic form.

The hydrophilic polybenzimidazole membrane support was prepared by a phase inversion process. A 10 wt% polybenzimidazole (Celanese Corp.) solution in *N*-methylpyrrolidone was chilled and knife-cast at 170 μm onto a glass plate. The film was then immersed into a nonsolvent bath containing 30% by weight of water in *N*-methylpyrrolidone. The temperature of the precipitation bath was 7°C. After 1 h in this bath, the membrane was transferred to a pure water bath. The membrane structure was examined with a S520 Hitachi electron microscope. Micrographs were obtained from the top surface, the bottom surface, and the cross section of the membrane. Figure 1 shows the micrographs of the polybenzimidazole membrane. The

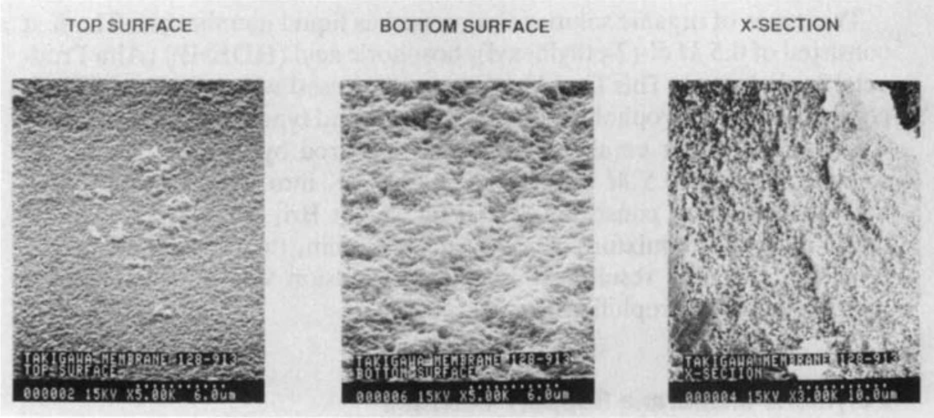

FIG. 1. Micrographs of polybenzimidazole membrane.

membrane was considered to be microporous due to the detection of pores in the top layer.

Supported Liquid Membrane

The SLMs were prepared by soaking the polymeric support in the appropriate organic solution for a few minutes followed by placing the contents under vacuum for a few hours. The membrane was then rinsed with deionized water and gently blotted with paper.

Cell Transport Apparatus

The SLM was placed and clamped between two half-cell faceplates. The faceplates are spiral, machined channels that are the mirror image of each other, with an inlet at the beginning of the spiral and an outlet at the end. The channel is 0.16 cm deep and 0.32 cm wide. The end-to-end length of the entire spiral is 98.5 cm. The feed solution was pumped into one of the channels from a 250-mL feed reservoir by digital drive pumps (Ismatec) and recirculated from the outlet back into the feed reservoir for the entire course of the experiment. The strip solution was similarly recirculated from a 250-mL strip reservoir through the adjacent channeled half-cell faceplate. Feed and strip sides of the apparatus were equipped with flowmeters and pressure gauges for monitoring the flow and pressure of both solutions as they traversed the respective channels. The solutions were pumped in a countercurrent flow, each at 240 mL/min with zero primary pressure and zero pressure difference between feed and strip sides.

Transport Measurements

Metal ion transport across the membrane was monitored by measuring the change in concentration of the feed solution. At regular time intervals, an aliquot of the feed solution was taken and prepared for spectrophotometric analysis. For copper, an aliquot from the feed solution was taken and mixed with a Cuver 1 Hach reagent (Hach Co.) and measured spectrophotometrically at 560 nm. For neodymium, the reagent arsenazo III (Aldrich) was mixed with an aliquot of the feed to give a complex reaction which was monitored spectrophotometrically at 658 nm (*3*).

Permeability Coefficient Measurements

The permeability coefficients were determined by applying Fick's diffusion law as previously described by Danesi (*1*):

$$J = PC = -dC/dt(V/A)$$

$$\ln C/C_0 = -A/V(Pt)$$

where J = membrane flux, P = permeability coefficient (cm/s), C = feed metal concentration at time t, C_0 = initial feed concentration, V = volume of feed solution, and A = membrane area. The permeability coefficient was calculated from the slope of the plot of $\ln C/C_0$ vs t.

The permeability coefficient of the SLMs was measured daily. Each day, the feed and strip solutions from the previous day were removed and the entire apparatus was cleaned by rinsing and recirculating with deionized water. A new feed and strip solution was placed in the appropriate reservoir and the transport experiment conducted. These experiments were carried out for 8 h and usually stopped overnight.

RESULTS AND DISCUSSION

Hydrophobic SLM Supports

Figure 2 shows the transport of copper from an aqueous feed solution, pH 6.0, into the 2.0 *M* nitric acid strip solution through a Celgard 2400 SLM containing 0.5 *M* HDEHP in dodecane. The copper content in the feed solution decreased with time while that in the strip solution increased. The symmetrical curves suggest that copper is efficiently released into the strip solution without remaining in the SLM. This also indicates that the diffusion time inside the membrane is small compared with the extraction time into the membrane. Control experiments in which the support contained only solvent and no extractant showed no transport of copper (Fig. 3). At 50% extraction, the transport stops because of the equivalence of

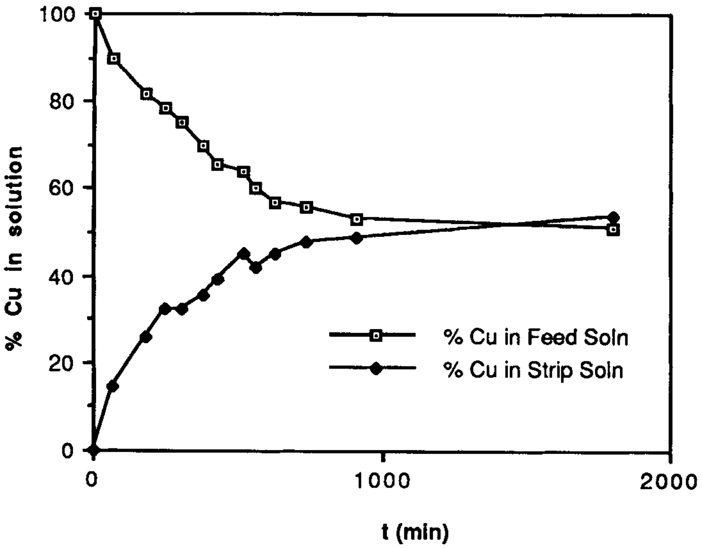

FIG. 2. Copper transport from feed and strip solutions. Initial $C_{Cu,feed}$ = 10^{-3} *M* and C_{HNO_3} $_{,strip}$ = 2 *M*. Extractant: 0.5 *M* HDEHP. Celgard 2400 was used as the membrane support.

pH in the feed and strip solutions. The equal distribution of metal species between the two solutions may indicate that the membrane behaved only as a porous diaphragm, without facilitated transport. In our case, however, the transport mechanism is indeed facilitated transport as shown in Fig. 4.

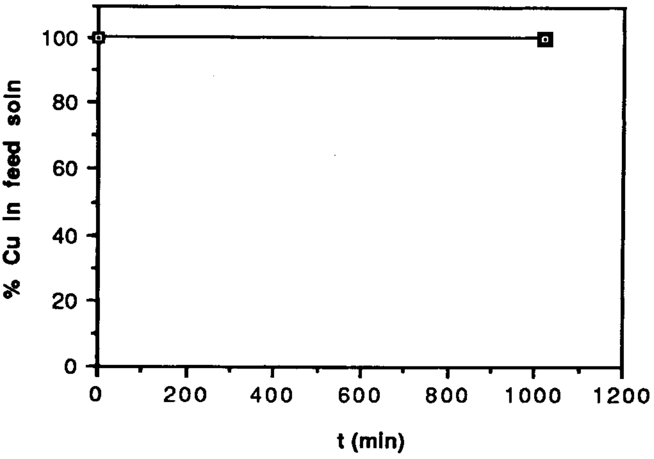

FIG. 3. Control experiment. Celgard support contains only dodecane solvent, no extractant.

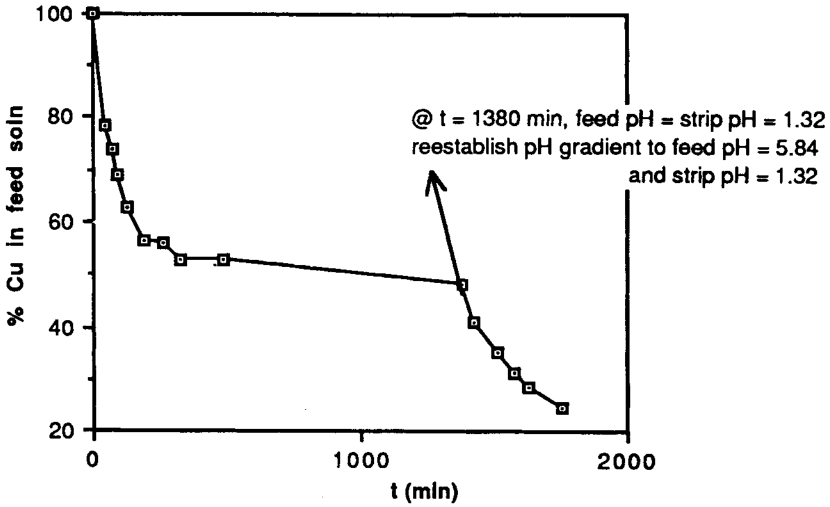

FIG. 4. Copper transport through Celgard SLM. Achieve continuous extraction only by titrating the feed solution and reestablishing the chemical potential gradient.

When the feed solution is titrated to pH 5.84, the pH chemical potential gradient is reestablished and the transport resumes. For acidic extractants, such as di-(2-ethylhexyl)phosphoric acid, this pH gradient must be maintained in order to drive the metal ion transport to completion. A similar transport profile has been observed for hydrophobic Nuclepore 11174 SLM containing 0.5 *M* HDEHP in dodecane (Fig. 5).

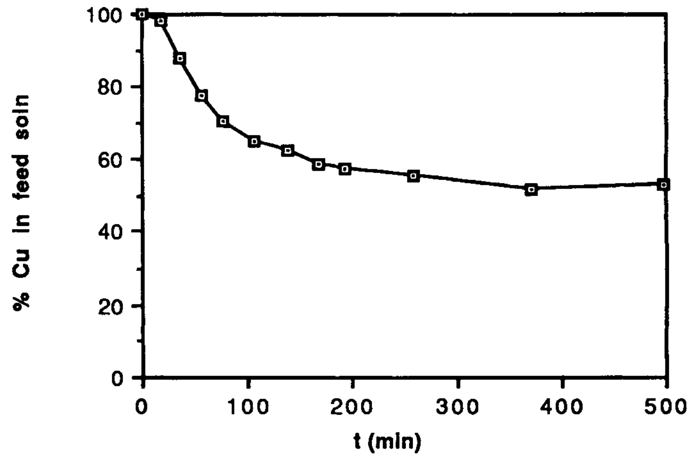

FIG. 5. Copper transport through Nuclepore, hydrophobic SLM. Initial $C_{\mathrm{Cu,feed}} = 10^{-3}$ *M*. Extractant: 0.5 *M* HDEHP.

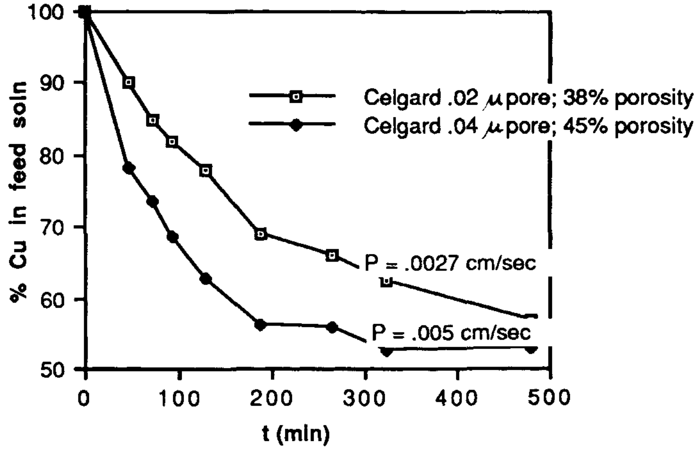

FIG. 6. Effect of support pore size and porosity. Initial $C_{Cu,feed} = 10^{-3}$ *M*. Extractant: 0.5 *M* HDEHP.

Structural characteristics of the porous support can play an important role in metal transport behavior. Figure 6 shows that when the pore size and porosity are greater, the transport occurs more efficiently. A Celgard membrane with a pore size of 0.04 μm and 45% porosity was found to have a much higher permeability than a similar Celgard membrane with a pore size of 0.02 μm and 38% porosity.

Permeability Coefficient Measurements

One of the goals of this work was to increase the stability and lifetime of the SLM. Figure 7 plots the permeability coefficient of Cu^{2+} through a Celgard 2400 SLM containing 0.5 *M* HDEHP in dodecane over 27 days of operation. The permeability coefficient stays constant, suggesting no decline in membrane performance. Many reasons may account for this stable performance. Controlled operating parameters such as equivalent ionic strength between feed and strip solutions gave zero osmotic pressure gradients across the SLM. This is a problem commonly observed to affect stability of SLMs (*4*). Solubility of the extractant and organic solvent in water, which also affect SLM stability, were also minimized by using the appropriate reagents. The solubility of the extractant HDEHP in aqueous solutions is very limited: $[\text{HDEHP}]_{\text{octane}}/[\text{HDEHP}]_{\text{water}} = 4 \times 10^4$ (*5*).

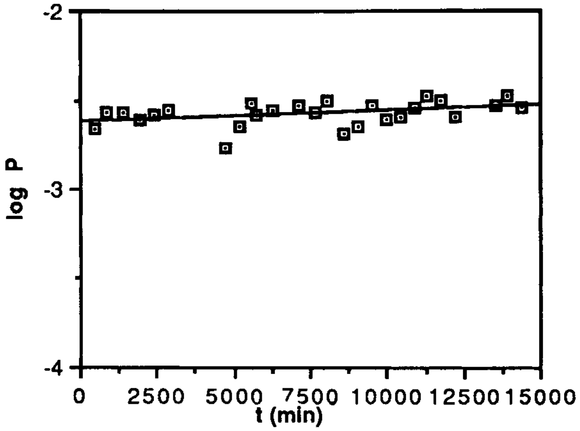

FIG. 7. Lifetime study of Celgard SLM. Permeability coefficient of Celgard SLM taken over a 30-day period.

It is believed, however, that the design of the transport apparatus (Fig. 8) was significant in reducing the problems of pressure-drop dislodge of the liquid membrane. Similar experiments in which the permeability of Eu^{3+} was determined using a Celgard SLM imbibed with HDEHP in dodecane showed a 20% decline in the permeability coefficient during a similar period of about a month (*3*). Those experiments were carried out using stirred feed and strip cells in which the SLM is interposed between the two aqueous compartments. Boundary layer or concentration polarization problems are associated with such an apparatus design (*6*). The transport apparatus design used in our work eliminates stirring problems: the feed and strip are pumped into the respective cells at a tangential entry by digital drive pumps. Controlling the flow rate allows the solutions to flow in the turbulent or laminar region. After many attempts to design a cell which would eliminate pressure-drop dislodge problems with the SLM, the spiral-channeled design (Fig. 9) we found to work the best. It gave operating parameters of zero primary pressure and zero pressure differential between both sides of the SLM, tangential entry, no sharp turns, and controlled flow regions.

Hydrophilic SLM Supports

The chemical composition of the porous support plays an important role in metal ion transport. When identical transport experiments were performed with Celgard 3401, which is the hydrophilic form of Celgard 2400, poor transport was obtained (Fig. 10). Poor wettability and immobilization

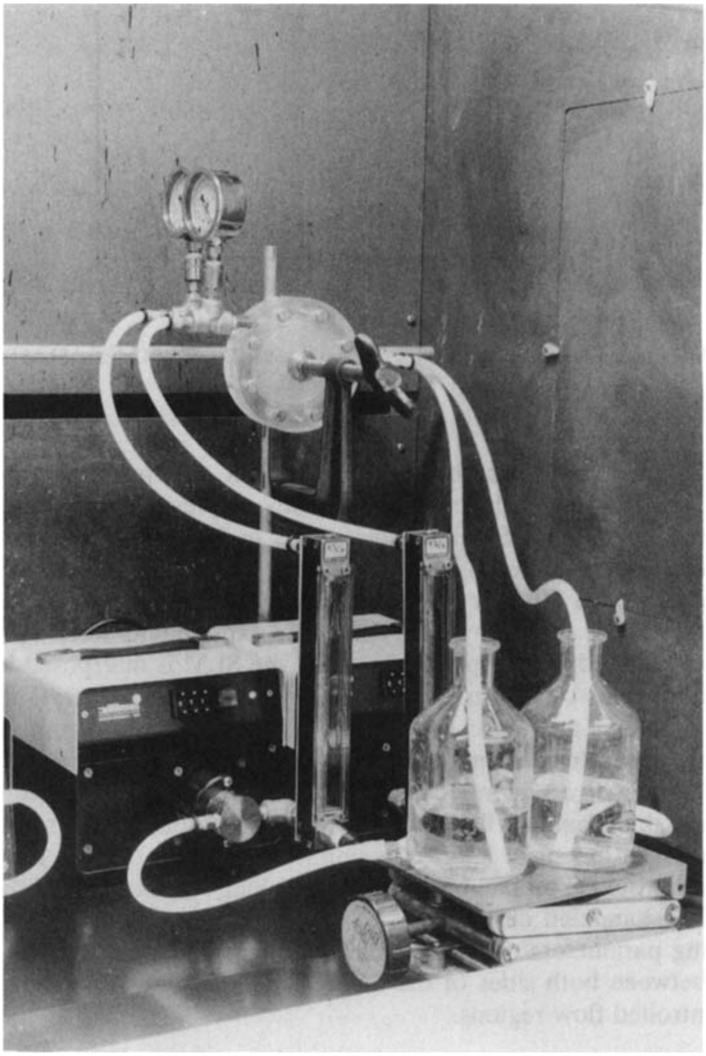

FIG. 8. Transport apparatus for flat-sheet SLM studies.

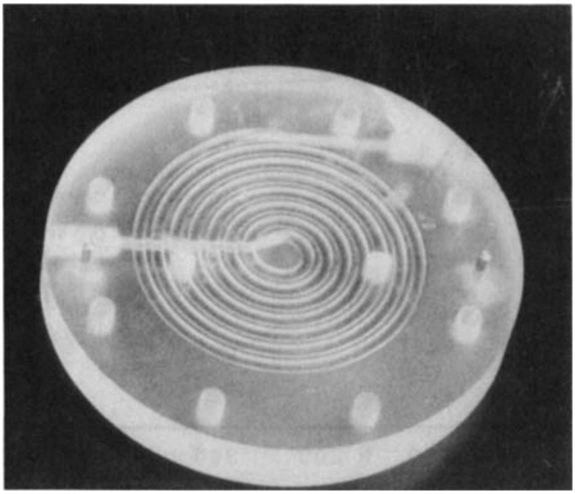

FIG. 9. Half-cell faceplate. Tangential entry and exit. Dimensions of spiral flow channel: 0.16 cm × 0.32 cm × 98.5 cm.

of the hydrophobic liquid membrane, 0.5 *M* HDEHP in dodecane into a hydrophilic support, is the most probable cause. An evaluation of the extractant content by electron microprobe analysis showed no detectable levels of phosphorus. A solution to this problem was devised by preparing the liquid membrane in an oil-in-water emulsion containing the same

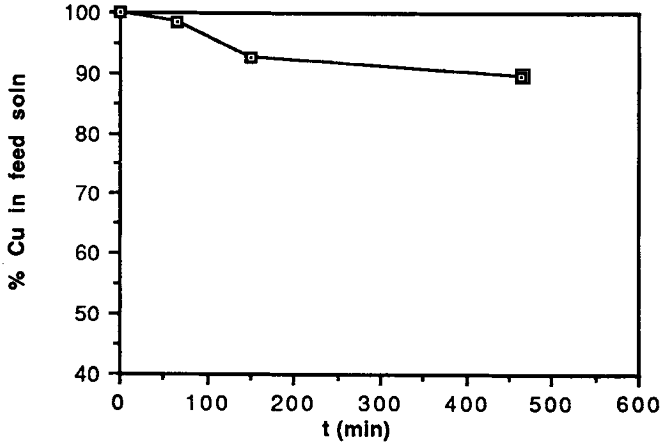

FIG. 10. Copper transport through hydrophilic Celgard 3401 SLM. Initial $C_{Cu,feed} = 10^{-3}$ *M*. Extractant: 0.5 *M* HDEHP.

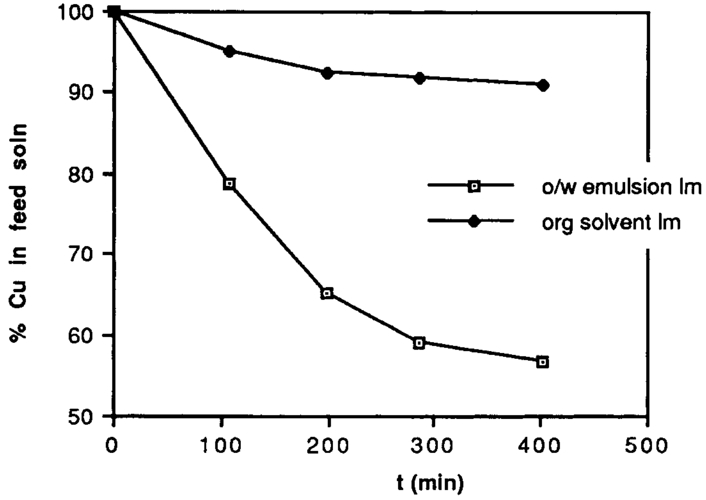

FIG. 11. Effect of oil-in-water emulsion liquid membrane containing 0.5 *M* HDEHP immobilized in a hydrophilic support. Celgard 3401 was used as the support.

amount of extractant. In an oil-in-water emulsion, the outer region is polar and thus wettable to polar or hydrophilic supports. The significance of immobilizing a wettable fluid into the support for enhancing the resistance to transmembrane pressure has been discussed (7).

The significant improvement in transport, upon employing the oil-in-water liquid membrane in Celgard 3401, is shown in Fig. 11. This supported liquid membrane remained stable, with no variation in the permeability coefficient, after many consecutive days of operation.

Similar improvement of transport behavior was observed for hydrophilic Nuclepore 11174 when immobilized with the hydrophilic oil-in-water emulsion.

Polybenzimidazole SLM

A hydrophilic polybenzimidazole membrane, whose preparation is discussed in the Experimental Section, was also immobilized with the oil-in-water emulsion. Polybenzimidazole is an acid- and radiation-resistant polymer; thus it is well-suited for its use in actinide recovery operations. The transport behavior of this SLM is shown in Fig. 12. The transport goes to near completion in less than 3 h. This is quite remarkable in that the transport through Celgard and Nuclepore SLM membranes stopped at 50% extraction even after 15 h of operation. The pH gradient between feed and strip was self-maintained, unlike the other two commercial membranes.

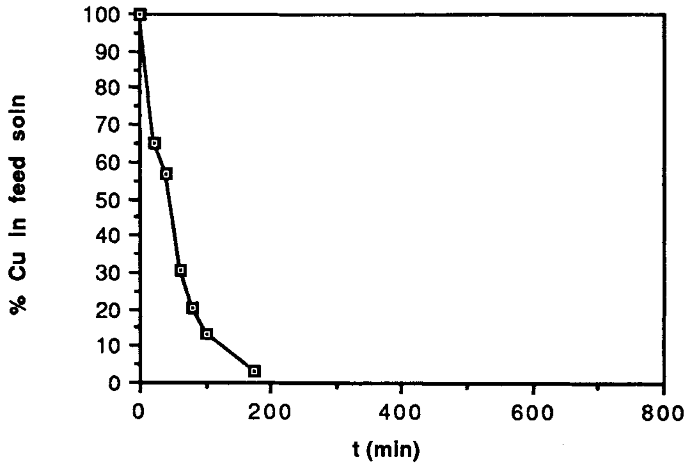

FIG. 12. Copper transport through polybenzimidazole SLM. Initial $C_{Cu,feed} = 10^{-3}$ *M*. Extractant: 0.5 *M* HDEHP in oil-in-water emulsion form.

Polybenzimidazole has two protonatable tertiary nitrogens per repeat unit which may help sustain the pH driving force. Electron microprobe analysis of phosphorus content (from extractant) in the membrane cross-section showed 4 to 10 times more phosphorus in the PBI membrane than in Celgard or Nuclepore. Unlike Celgard and Nuclepore, the chemical structure of PBI enables it to participate in hydrogen bonding interactions with

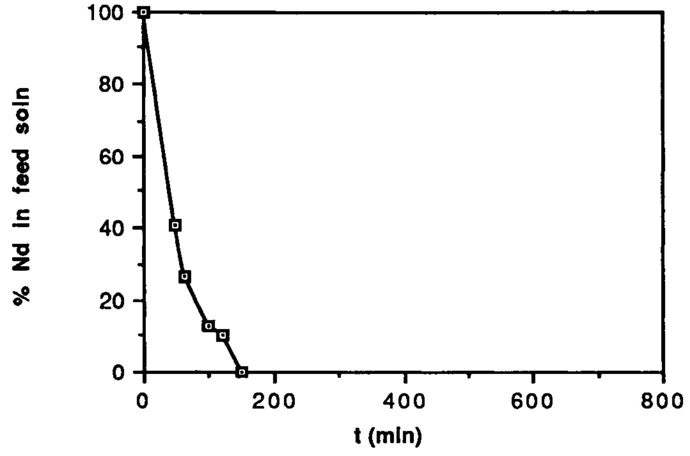

FIG. 13. Neodymium transport through polybenzimidazole SLM. Initial $C_{Nd,feed} = 10^{-3}$ *M*. Extractant: 0.5 *M* HDEHP in oil-in-water emulsion.

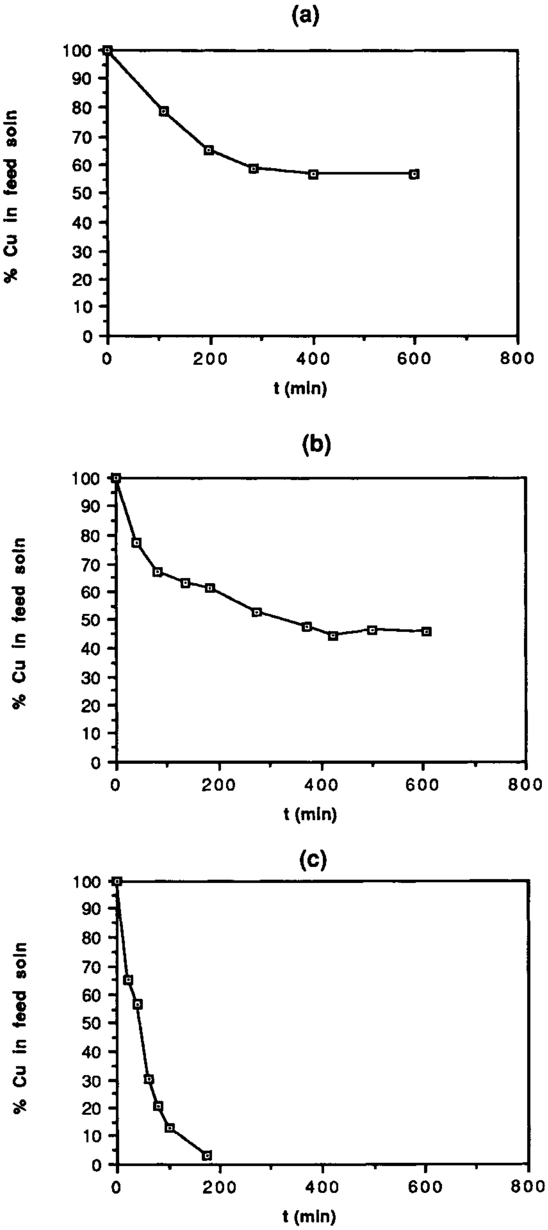

FIG. 14. Comparison of copper transport through 3 SLMs: (a) hydrophilic Celgard support, (b) hydrophilic Nuclepore support, (c) hydrophilic polybenzimidazole support, Initial $C_{\mathrm{Cu,feed}} = 10^{-3}$ *M*. Extractant: 0.5 *M* HDEHP in oil-in-water emulsion form.

the di-(2-ethylhexyl)phosphoric acid which may help enhanced extractant immobilizaton. Similar transport results have been observed for neodymium, an analog of the actinide, americium (Fig. 13). Transport studies using polybenzimidazole SLMs for other actinides and lanthanides are anticipated.

CONCLUSION

Chemical composition of the support has been shown to play a significant role in metal ion transport through SLMs. Hydrophilic membranes can behave as well as the hydrophobic membranes if immobilized with the appropriate support-wetting liquid membrane. Hydrophobic extractants can be immobilized into hydrophilic supports by preparing the liquid membrane in an oil-in-water emulsion form. Structural properties of the support, such as pore size and porosity, were also observed to play an important role. As illustrated in Fig. 14, microporous polybenzimidazole membrane supports for SLMs have shown superb transport properties over commerically available membranes and may hold promise for the future development of improved SLM supports.

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