Immobilized Extractants: Selective Transport of Magnesium and Calcium from a Mixed Chloride Solution via a Hollow Fiber Module

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Synopsis

A supported liquid membrane process was used for the selective transport of alkali earth cations from solutions containing a mixture of alkali and alkali earth chlorides. Bis-trimethylpentylphosphinic acid (HDTMPP), an organophosphorous acid, was used as the carrier in the liquid membrane supported by a polypropylene fiber. It was found that the porous structure of polypropylene fiber suffered significant irreversible changes due to the formation of an inorganic salt of HDTMPP. This caused a reduction in the cation fluxes and the final failure of the supported liquid membrane.

INTRODUCTION

In our previous work on immobilized extractants, the liquid organic extractant was immobilized into a polymer or an inorganic support in the form of beads or irregular particles during the process of polymerization.[1-3] The solid extractant-containing polymer was then used to extract metallic species from dilute solutions by the column process, combining, in this way, the advantages of highly selective, commercially available liquid extractants with those of the well-established ion exchange technology. The present work is based on a new technique that has emerged in the past few years—that of the supported liquid membrane (SLM).[4-8] The development of SLM is an outcome of the idea of adsorbing the liquid ion exchanger or extractant into a polymeric material in the form of flat sheet or hollow fiber. SLM offer a potentially attractive alternative to conventional separation processes in that they combine the steps of extraction, stripping, and regeneration into a single stage.

A SLM may be described as a thin microporous polymer film containing an organic solution immiscible in water. The organic solution is composed of a diluent that is impermeable to the dissolved species and a carrier (extractant) capable of undergoing reversible reaction with a particular inorganic species. The transfer of material from one boundary of an SLM to the other occurs by facilitated transport. Facilitated transport is a separation process by which an active chemical carrier will selectively bind with a permeate, transport the permeate across a liquid film, and then release the permeate at the other boundary. In an SLM a thin layer of organic phase with a carrier reagent is immobilized on a microporous hydrophobic support (flat sheet or hollow fiber) interposed between two aqueous phases. A metal-containing feed solution and an aqueous solution capable of stripping the permeable species are arranged on opposite

sides of the membrane. In general, the same reagents that are used for selective metal separations in liquid–liquid extraction can be applied as selective metal carriers in SLM operations.
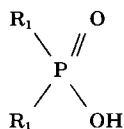
The SLM system has been modeled by a number of investigators in terms of diffusion and chemical reaction parameters, and the validity of such models has been tested for various metal–extractant combinations. In our study we used the approach developed by Danesi,[5] and adopted by other workers, to describe the transport of divalent cations through the SLM containing an acidic organophosphorous extractant. We used bis-trimethylpentylphosphinic acid (HDTMPP) produced by American Cyanamid under the trade name of Cyanex 272 as the liquid carrier. HDTMPP has been extensively studied as an extractant for Co/Ni separations[7-11] but has, to the best of our knowledge, never been used for alkali earth and alkali cation separations. The chemistry of the extracting species, the equilibria in chloride and sulfate media, and the selective Co^{2+} transport across liquid membrane have been described. In addition, the lifetime of the SLM and the factors determining the operating life have also been studied.[12] It is widely accepted that the loss of the liquid membrane phase (extractant or/and diluent) resulting from water transport is probably one of the more important factors contributing to SLM instability. However, very little is known about the effect of the nature, structure, and morphology of the polymer material on the performance of the SLM. A general picture of the importance of the porous structure of the polymer is available, but no systematic study has been performed on the behavior of the polymeric support during the separation process or on the polymer–extractant–metal relationship.

In this work, a hollow fiber module was used to study the separation of alkali earth cations from alkali cations. Our preliminary results in liquid–liquid extraction experiments with a hexane solution of HDTMPP have shown that about 30–35% of Ca^{2+} and Mg^{2+} can be selectively extracted from Dead Sea brine at a suitable pH.[13] The objectives of the current project work were (1) to demonstrate the selective transport of alkali earth cations from chloride solutions of alkali and alkali earth cations via a hollow fiber module and (2) to study the transformations of the polymer support during the separation process.
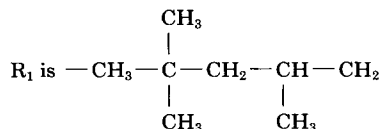
EXPERIMENTAL

Membrane and Reagents

Microporous polypropylene hollow fibers (Celgard 2500, Celanese) were used as the polymeric support throughout this study. This type of fiber has an internal diameter of 0.4 μm, a wall thickness of 0.025 mm, a porosity of 45%, and an average pore size of approximately of 0.04 μm. HDTMPP, the structural formula of which is

$$\begin{array}{ccc} R_1 & & O \\ & \diagdown & \mathbin{/\!/} \\ & P & \\ & \diagup \;\; \diagdown & \\ R_1 & & OH \end{array}$$

where

$$R_1 \text{ is } -CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2$$

was obtained from American Cyanamid with a purity of approximately 93%. It was further purified by the method of McDowell.[14] Toluene was supplied by Merck. Other reagents used were commercial AR grade.

A 15% (w/w) membrane solution was prepared by diluting HDTMPP in toluene. The feed solution was prepared by dissolving $CaCl_2$ and $MgCl_2$ in distilled water or by diluting the Dead Sea brine. The pH of the feed solution was maintained by continuous addition of ammonia acetate–acetic acid buffer (pH 10) with a Titroprocessor 686 (Metrohm) device. HCl was used as the stripping reagent.

Membrane Module

The membrane module comprised a bundle of 35 fibers with a working length of 75 cm. The hollow fibers were first extracted in a soxhlet apparatus with hexane, then immersed in a toluene solution of Cyanex 272 for impregnation, and finally washed with water. Excess water was removed with filter paper, the fibers were weighed, and the percentage of impregnation was calculated as the difference between the weight of the original fibers and the weight of the impregnated fibers.

The fibers were arranged into bundles, and the ends sealed into a perspex tube to provide a rigid sleeve that acted as a seal between the feed and stripping solutions. The bundle was inserted into a plastic sleeve to produce a shell construction in which the feed solution was circulated through the lumen of the fibers, while the stripping solution was circulated around the fibers.

① Hollow-fiber module
② Overflow pipe
③ Flow meter
④ Constant flow pump
⑤ Reservoir for tube-side solution
⑥ Reservoir for shell-side solution
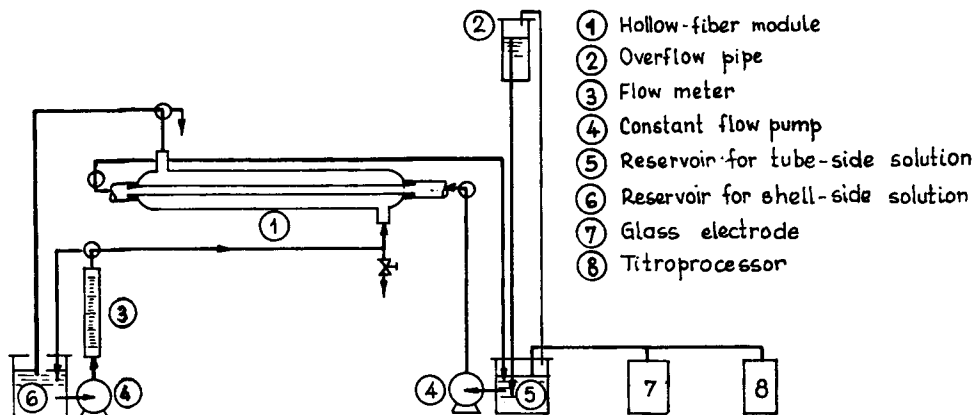⑦ Glass electrode
⑧ Titroprocessor

Fig. 1. Schematic diagram of the experimental apparatus for the study of hollow-fiber-supported liquid membranes.

In our experiments the module, which is schematically described in Figure 1, operated in a recycling mode. The feed solution from reservoir 5 was circulated by means of pump 1. The stripping (or product) solution was circulated by means of pump 4 from reservoir 6. As can be seen from the figure, the pH was measured in the feed, while the cation–extractant complex formation and subsequent extraction occurred at the membrane/solution interface. Therefore, fluctuation of pH was inevitable at this stage of study. After steady-state conditions had been reached, samples (0.5–1 cm^3) were taken from the both vessels. Calcium and magnesium were analyzed by titration against EDTA, and sodium and potassium by flame photometry.

The experimental results were plotted as a concentration/time relationship, and the slopes of straight lines were determined. The slope of any straight line was determined by a least-square linear regression analysis. The fluxes were determined by multiplying these quantities by the aqueous volume and dividing by the membrane surface area. The flux values presented were calculated using the entire surface area of the membrane. The aqueous volume in both phases was 200 mL and the membrane surface was 360 cm^2.

Scanning Electron Microscopy

The morphology of the fibers was examined by electron microscopy. Images of the fiber surface or cross sections were obtained after gold evaporation coating using a scanning electron microscope (JOEL JSM-38CF Japan) and an X-ray device.

RESULTS AND DISCUSSION

Transport of Alkali Earth Cations

Before we started our experiments with diluted Dead Sea brine some preliminary experiments were carried out with synthetic solutions containing only magnesium or calcium chloride. The effect of changes in pH and initial cation concentration was first studied, and a phenomenon of "uphill" transport was observed.

1. *Effect of pH on cations flux.* A series of permeation experiments was performed to investigate the effect of pH on the transport of Ca^{2+} and Mg^{2+}. We then applied the liquid–liquid extraction data as a guide in order to determine the range of feed pH at which to carry out further experiments. For this purpose, solutions of CaCl$_2$ (0.025 M) and MgCl$_2$ (0.1 M) were tested. The stripping (product) solution was HCl (1.0 M). The results presented in Figure 2 show that the fluxes of both cations increase as the pH rises. The fluxes of Ca^{2+} were lower, obviously due to its lower initial concentration.

2. *Effect of cation concentration on flux.* The effect of the Ca^{2+} and Mg^{2+} concentration in the feed solution on the fluxes was determined, and the results are given in Figure 3. The flux of Mg^{2+} increased gradually with increasing Mg^{2+} concentration. Ca^{2+} flux increased sharply at first and then reached a limiting value at concentrations of almost 1.0 mol/L. It seems to us that this limiting effect is due to saturation of the organic phase with a calcium–Cyanex 272 complex. It was also observed that a white, water-insoluble, organic-soluble
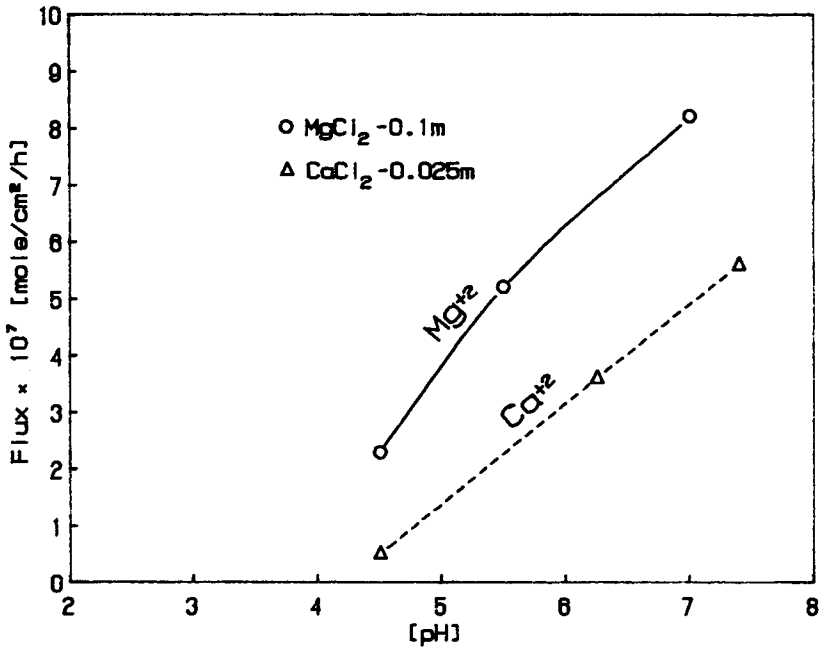
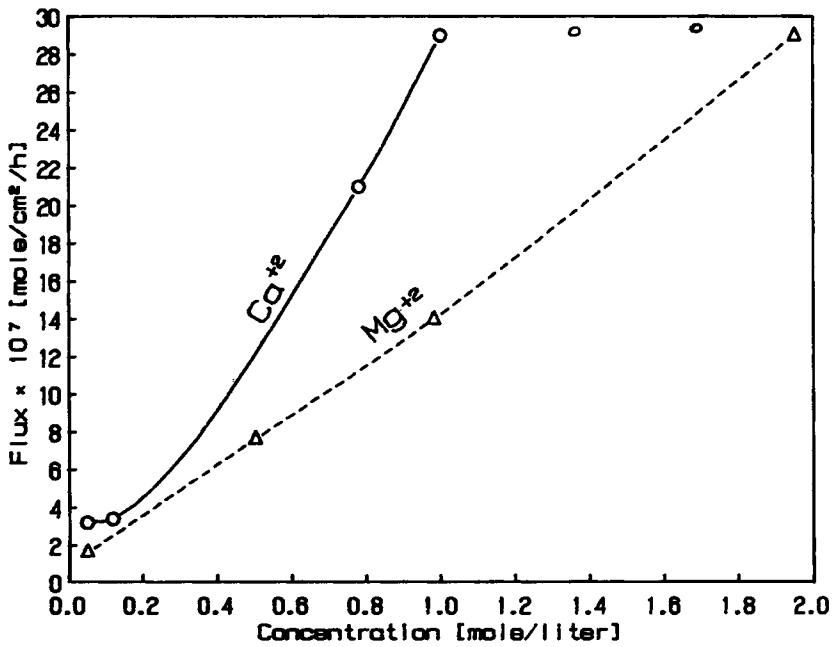Fig. 2. Ca^{2+} and Mg^{2+} flux as a function of pH.

Fig. 3. Ca^{2+} and Mg^{2+} flux as a function of cation concentration in the feed solution.

precipitate formed at the feed solution/membrane interface in some experiments. The appearance of this precipitate was accompanied by the retardation of fluxes, and as a result final failure of the whole process occurred. As in other works[15] the water transport from feed to product solution was observed.

3. *Demonstration of "uphill" transport.* In the next series of experiments mixed Ca^{2+} and Mg^{2+} chloride solutions were tested. The total cation concentration was 0.012 *M,* and the concentration of HCl in the stripping solution was 0.05 *M.* The pH was kept at 7.5. The results were plotted as a concentration/time dependence for the alkali earth cations in both the feed and stripping phases. (Figs. 4 and 5). We can see that the concentrations of Mg^{2+} and Ca^{2+} in the feed solution were gradually reduced, while in the stripping solution there was a constant increase in the cation concentration. The increase of concentrations in the product solution proceeded until almost all alkali earth cations were present there. This indicates that the "uphill" process does indeed occur (i.e., cations moved from the low concentration zone to the high concentration zone against a concentration gradient).

Transport of Cations from Diluted Dead Sea Brine

A set of experiments with diluted Dead Sea brine was performed under conditions favorable to the transport of alkali earth cations, i.e., pH 7.5, cation concentration of approximately 0.02 *M,* and 0.05 *M* HCl. The results are presented in Figure 6 as cation variation in the feed solution vs. time. It is clearly shown that amounts of K^+ and Na^+ cations did not change, while Ca^{2+} and Mg^{2+} disappeared completely. In addition to the evidence for uphill transport,
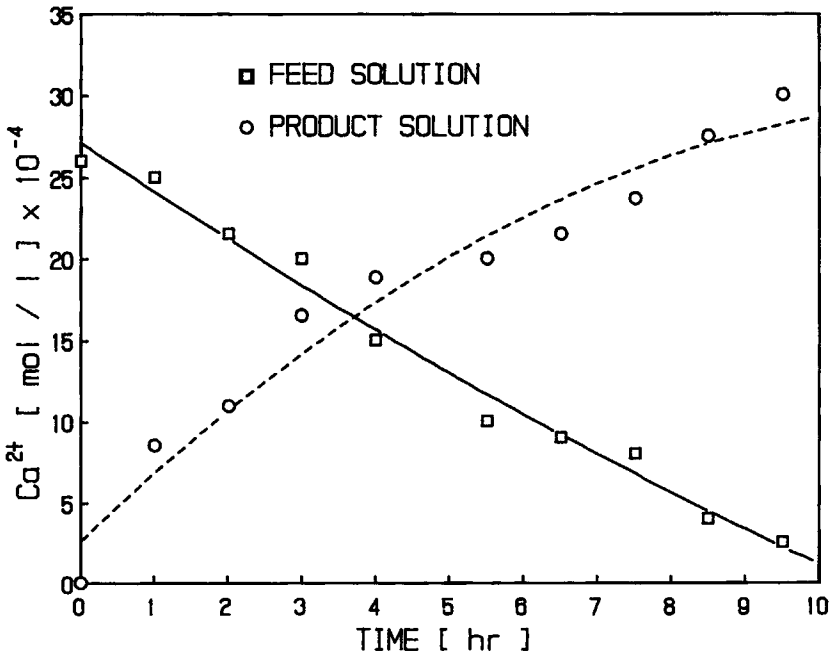

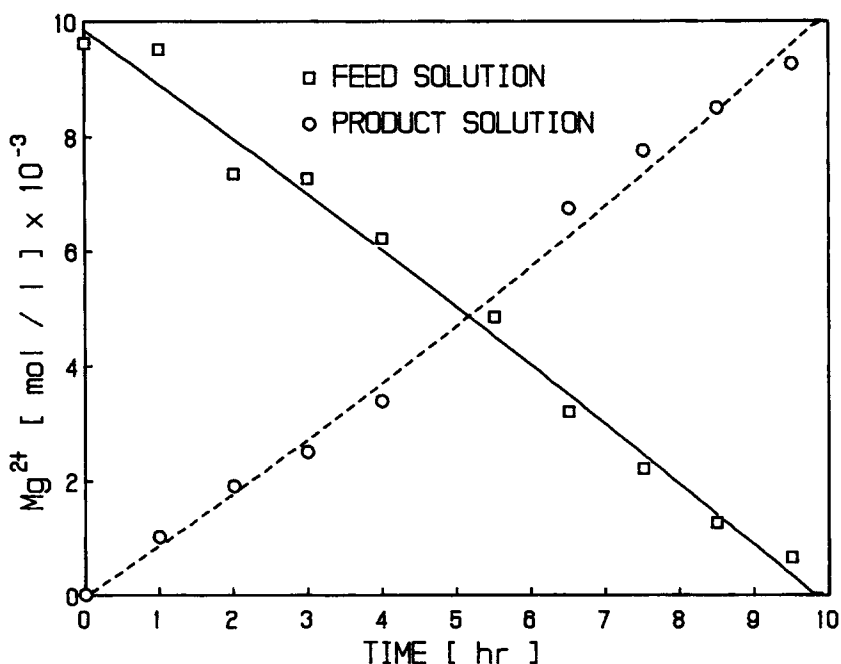Fig. 4. Concentration of Mg^{2+} ions vs. time in the feed and stripping solutions.

Fig. 5. Concentration of Ca^{2+} ions vs. time in the feed and stripping solutions.

we can see that the selective separation of Mg^{2+} and Ca^{2+} takes place in this case. In these experiments, the white precipitate was observed floating on the surface of the feed solution, as previously described. A similar phenomenon has been reported,[15] where insoluble brown specks of a Cu^{2+} extractant complex were formed. Our feeling is that our product is a Ca salt of the organophosphorous acid. The analysis of the precipitate will be the subject of another study. In the present article the effect of this product on the structure and texture of polypropylene fiber was studied with SEM.

MORPHOLOGY STUDY

We began the examination of morphology and texture of polymer support at the preparation step in which the liquid (solvent and extractant) was incorporated into the fiber. The fibers were examined by SEM, and micrographs are presented in Figures 7–10.

It is worthwhile remembering here the microporous structure of Celgard fibers formed during extrusion, annealing, and stretching of isotactic polypropylene. Micrographs of the membrane surface of the original fiber, presented in Figure 7(a), reveal the typical structure of a Celgard porous fiber with areas of large pores surrounded by a nonporous lamillar matrix. Each large elliptical pore is composed of several small pores divided by thin partitions. The surface area of an impregnated fiber is shown in Figure 7(b) and (c). We can clearly see that the surface is now covered by a film with large holes that look like volcanic craters and have much bigger dimensions than those of the original
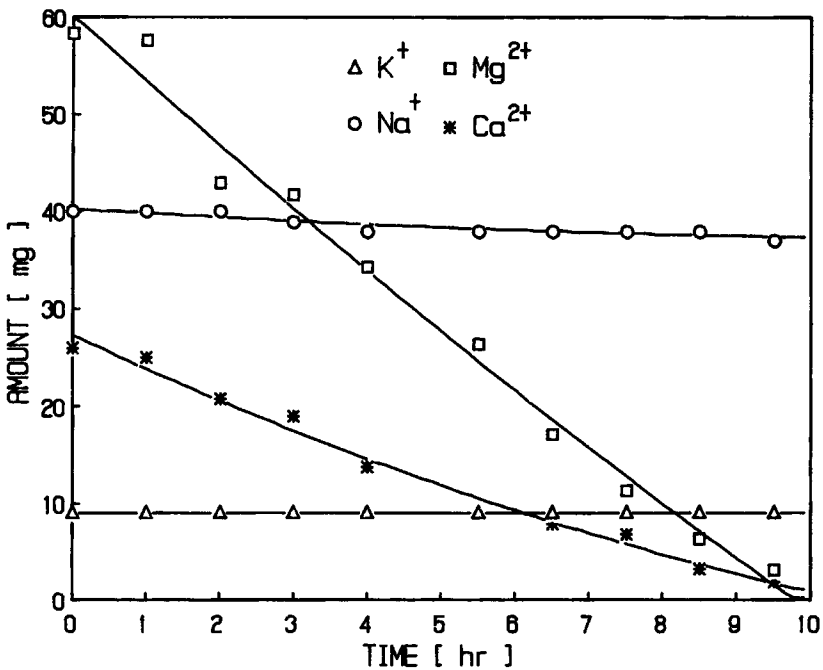
Fig. 6. Variation in cation concentrations vs. time in feed solution.

fiber. These holes were probably formed in places in which groups of pores were present in the original fiber and seem to be responsible for the fast fluxes.

The next series of photographs shows the appearance of fiber after the separation process was terminated and the module was taken apart to remove the fibers (Fig. 8). It is evident that once again the appearance of the fibers has undergone a remarkable change. The surface area is totally closed and covered with numerous round shaped "globules." In one of the experiments the formation of a large domain consisting of "globules" was observed. X-ray analysis of this domain showed that a significant amount of calcium is present with smaller amounts of phosphorous. This analysis supplies evidence for the existence of an organophosphorous salt. From the SEM photographs it can also be seen that the formation of a coating tightly bound to the surface of the fiber has occurred.

In order to obtain additional information about the structural transformation of polypropylene fibers the following experiment was setup. The module was allowed to work as a membrane permeator, i.e., the organic phase loaded with cations was constantly circulated inside the fibers, and the aqueous strip solution was circulated outside the fibers. In this way, only one step (i.e., stripping) was performed using organic phase loaded with cations. Photographs of the fiber taken from this permeator are presented at three magnifications (Fig. 9). We can see that the surface area of the fiber shows the existence of two different areas running along the length of the fiber: one consists of semicovered large holes, very similar to those in Fig. 8, and the other is a rather smooth area with small "bumps." The appearance of the semiclosed holes is characterized by protruding ring-like forms that are made up of a number of layers. The buildup
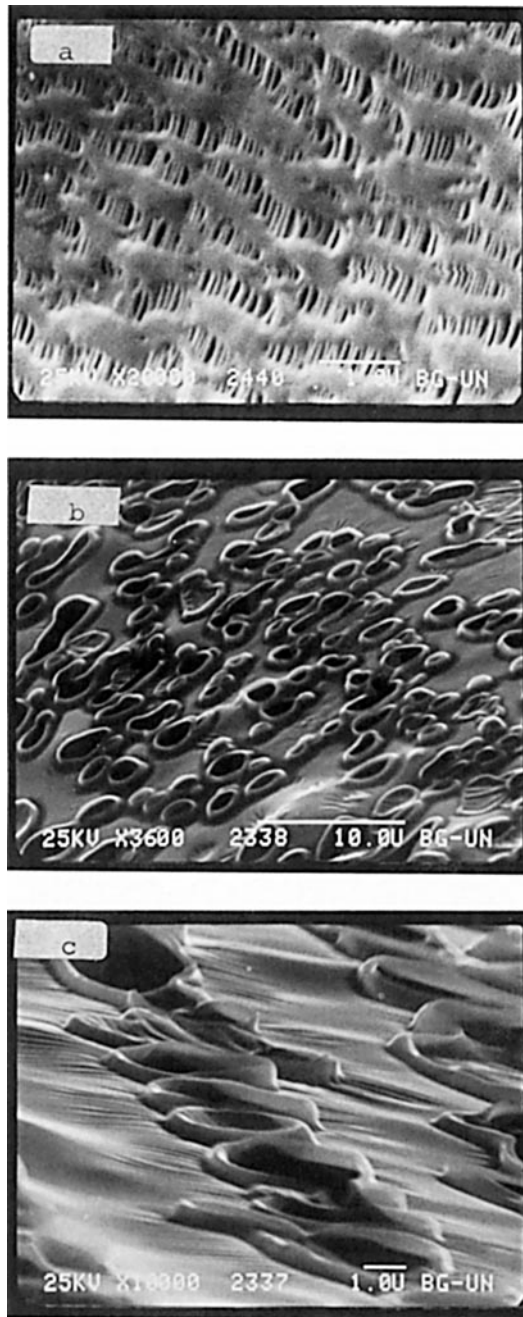
Fig. 7. Scanning electron micrographs of original (a) and impregnated (b, c) fibers.

of the layers continues as the process proceeds and eventually leads to the complete closing of the pore. Another observation is that cracks and fissures have been created on the surface of the coated fiber. All these findings indicate that during the separation process the fiber underwent significant deformation.
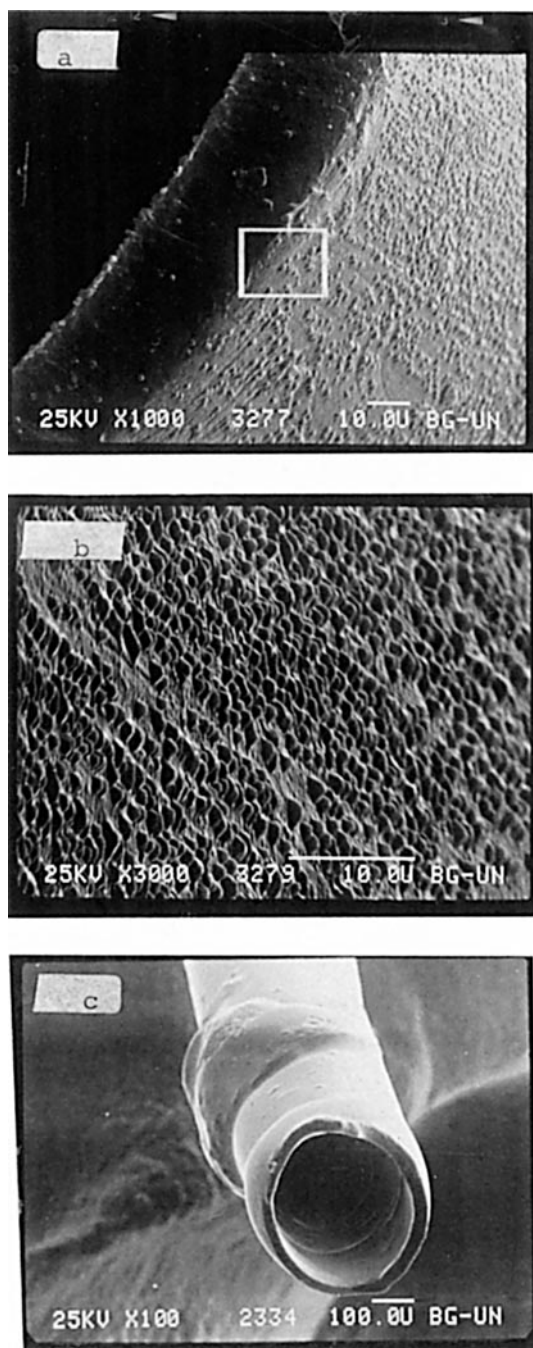
Fig. 8.   Scanning electron micrographs of the fiber after termination of the separation process: (a) appearance of surface area, with window indicating the boundary layer; (b) magnification of the window shown in (a); (c) general view.
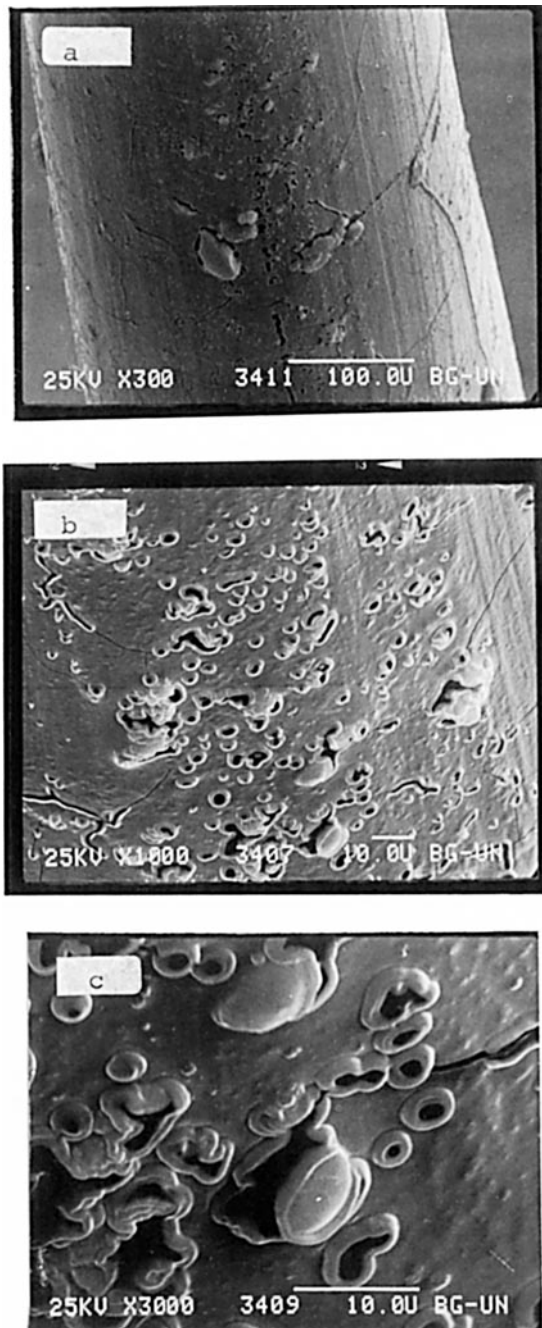
Fig. 9. Scanning electron micrographs of fiber from the permeator at three different magnifications.
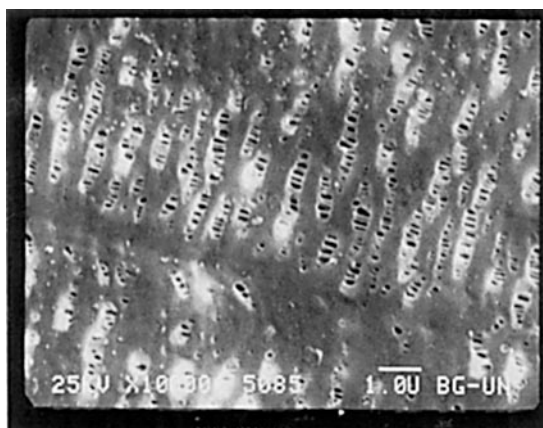
Fig. 10.   Scanning electron micrograph of acetone-treated fiber.

Several attempts were made to recover the original morphology of the fibers. For example, extraction with acetone or butanol was performed (Fig. 10). As we can see acetone extraction produced a fiber with a texture bearing some similarity to that of the original in that elliptical pores consisting of small pores and partitions reappeared. However, a significant part of the surface remained closed.

In conclusion, it is evident that the transport of cations via a liquid membrane that is incorporated in a polypropylene support caused significant interaction between the cation–extractant complex and the polymer. As a result, the fluxes dropped markedly, and the SLM failed. However, we cannot ignore the fact that this interaction may have resulted from unfavorable transport conditions, such as pressure differences, ionic strength, or high cation concentration in the feed. These points require clarification, and the subject is currently under study. Obviously, modification of polymer so as to prevent unfavorable deformations is another point that requires further research.

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