Selectively-Permeable Ultrathin Film Composite Membranes Based on Molecularly-Imprinted Polymers

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Membrane-based chemical separations constitute an emerging research area and industrial technology. The objective is to develop membranes that selectively transport a particular target molecule and reject (or transport at much lower rates) other molecules that might be present in the feed solution. This paper describes a new approach for preparing highly selective composite membranes for pharmaceutical or biomedical separations. This approach entails photopolymerization of a "molecularly-imprinted polymer film" across the surface of a microporous support to form a new type of ultrathin film composite membrane. Composite membranes based on polymers that were imprinted on the bronchodilator theophylline were prepared. The rate and selectivity of theophylline transport across these ultrathin film composites were investigated.

Introduction

Membrane-based chemical separations constitute an emerging research area and industrial technology.[1−5] The objective is to develop membranes that selectively transport a particular target molecule and reject (or transport at much lower rates) other molecules that might be present in the feed solution or gas. Potential applications exist in industrial gas separations[1,5] and in pharmaceutical and petrochemical separations.[2] Membrane-based processes are potentially less energy intensive than competing separations technologies and, as such, can be viewed as an example of "green chemistry." However, materials with higher chemical selectivity for the desired target molecule that can be incorporated into geometries that offer high flux of this molecule are required.

We have been investigating both of these issues of higher chemical selectivity and higher flux. In the area of enhancing flux, we have been developing methods for preparing ultrathin film composite membranes.[5−7] These composites consist of an ultrathin (in our case as thin as 40 nm[5]), defect-free skin of a chemically selective polymer coated onto the surface of a highly permeable microporous support. Since flux of the target molecule through the chemically selective polymer film is, in general, inversely proportional to film thickness, this ultrathin film composite approach ensures that net flux through the composite membrane is maximized. In the area of chemical selectivity, we are developing new highly selective polymeric materials, with particular emphasis on industrial gas separations[8−10] and liquid−liquid separations.[11−13]

More recently, we have become interested in biomedical and pharmaceutical separations. It seemed likely that for such separations, the well-known "molecular-imprinting polymerization" method[14−17] might provide a general approach for preparing membrane materials with high chemical selectivity. This chemistry entails forming a highly cross-linked polymeric resin around the target molecule such that the resin contains chemical sites that selectively recognize this molecule. Because a highly cross-linked material is obtained, flux of the target molecule through this material will be low. Hence, this is a situation where the ultrathin film composite membrane concept might be especially useful. We have used a photopolymerization method[5] to prepare ultrathin film composite membranes based on a polymer that has been imprinted on the bronchodilator theophylline.[17] The rate and selectivity of theophylline transport across this new type of ultrathin film composite membrane is described here.

Experimental Section

Materials. The theophylline-imprinted polymer prepared is similar to that described by Vlatakis et al.[17] It was

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photopolymerized[5] from a mixture of methacrylic acid (Aldrich, the molecular-recognition monomer), ethylene glycol dimethacrylate (Aldrich, the cross-linking monomer), and theophylline (Aldrich, the print or target molecule).[17] The polymerization inhibitor was removed from the monomers immediately prior to use by passing the monomers through an inhibitor-removal column (Aldrich 30,631-2). Unless otherwise noted, the polymerization solution consisted of a mixture that was 9:1 (w/w) ethylene glycol dimethacrylate:methacrylic acid that was saturated with theophylline. The saturation point for this solution is ca. 14 mg of theophylline per milliliter of solution. Caffeine (Aldrich), a molecule chemically very similar to theophylline, was used to probe the selectivity of the theophylline-imprinted polymers; caffeine differs only in the 7 position where the proton on theophylline is replaced with a methyl.

The theophylline-imprinted polymer was formed as an ultrathin skin (ca. 500 nm thick) across the surface of a microporous alumina support membrane (Whatman Anodisc 47, pore size = 20 nm).[5−7,18] This membrane contains 200 nm diameter pores throughout most of its thickness (55 μm); these pores branch into much smaller pores (ca. 20 nm diameter) at one face of the membrane. The polymer was formed across this 20 nm pore-diameter face.

Photopolymerization Method. The support membrane was placed, 20 nm face up, onto four sheets of filter paper (Whatman 4) that had been saturated with the polymerization solution. The polymerization solution filled the pores of the support membrane and ascended (capillary action) to the upper face of the membrane.[5] This assembly was placed on top of a Teflon stage mounted within a cylindrical PVC cup (diameter ca. 10 cm). The cup is equipped with a screw-cap lid that contains a quartz window.

The window was illuminated with UV light from a Spectroline Model ENF-240C UV lamp (235 nm). The source was positioned ca. 4 cm above the quartz window, and the angle between the incident bean and the window was 53°.[5] The bottom of the cup is attached to the shaft of an electrical motor so that the cup can be rotated during the 1 h photopolymerization period (rotation rate ca. 100 rpm). After photopolymerization, the film was immersed for 1 h in 9:1 (v/v) methanol/acetic acid and then in two portions of pure methanol for 1 h. This was done to remove the print molecule and any excess monomer.

Transport Measurements. The ultrathin film composite membrane to be studied was mounted between the two halves of a U-tube cell.[19] A 1.5 cm diameter O-ring held the membrane in place and defined the area of the membrane exposed to the feed and permeant half-cell solutions. The feed half-cell was filled with a solution of either theophylline, caffeine, or both (see below) dissolved in methanol. The permeant half was filled with pure methanol. The membrane was mounted such that the polymer film faced the feed solution. The feed and permeant solutions were stirred during the permeation measurements.

Two types of permeation experiments—single-molecule and two-molecule—were done. In the single-molecule experiments, the feed solution contained only theophylline or only caffeine, and the object was to measure the flux of that molecule across the composite membrane. This was accomplished by circulating the permeant solution through an HPLC UV detector (Waters 486, 10 mm path length). A dual piston HPLC pump (Cole-Parmer) was used to circulate the solution at a flow rate of 5 mL min^{-1}. Both theophylline and caffeine were detected at 272 nm, and the amount of each molecule transported was determined with reference to calibration curves obtained for each molecule. An automated data collection system based on an IBM PC was used.

The following experimental protocol was used for such single-molecule permeation experiments: The desired quantity

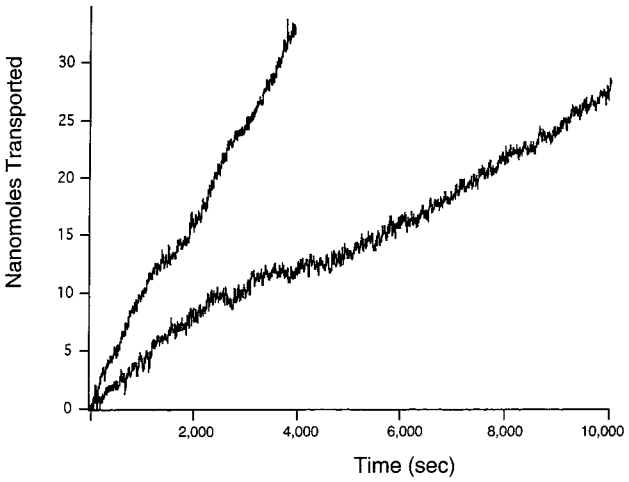

Figure 1. Typical transport curves for theophylline (upper) and caffeine (lower) transport across the ultrathin film composite membrane. These are the raw (unsmoothed) transport data. Concentration of theophylline and caffeine in the feed solution was 10^{-5} M.

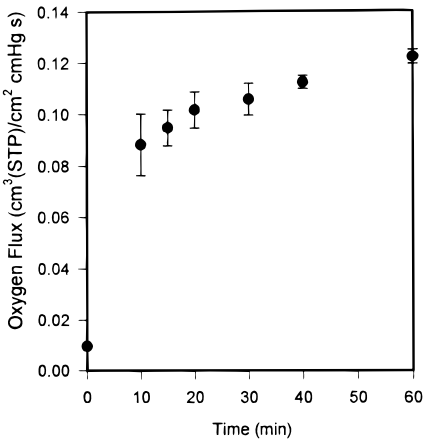

Figure 2. Oxygen flux across a theophylline-imprinted polymer. The polymer was initially saturated with theophylline. The *x*-axis is time of exposure to methanol which leaches the theophylline from the polymer film.

of pure methanol (depending on the experiment 10−100 mL) was added to the permeant half-cell, and the contents of this cell were circulated through the detector to establish a baseline response. The permeant solution (2×10^{-2} to 1×10^{-6} M theophylline in methanol) was then added to the feed half-cell. Permeation data were collected by monitoring the theophylline absorbance in the permeant half-cell as a function of time. These data were collected by the data acquisition system (one data point every 1.5 s) and converted to plots of moles transported vs time (Figure 2).

Such transport curves can show a nonlinear region at short times corresponding to non-steady-state diffusion across the polymer film.[20] A window of linear moles transported vs time response follows, and the flux (moles transported cm^{-2} h^{-1}) can be obtained from the slope. At long times, the rate of transport will ultimately decrease due to buildup of a significant concentration of the permeant molecule in the permeant solution. With the ultrathin films used here the region of nonlinear transport at short times was often not seen (e.g., Figure 1). The slope of the linear part of the transport curve was obtained via linear least-squares analysis after smoothing the raw transport data. Time intervals in excess of 1000 s were used for these least-squares analyses, and the correlation

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coefficients obtained ranged from 0.95 to 0.99. The exponential smoothing program provided with MicroSoft Excell was used to smooth the raw transport data.

Analogous experiments were done using a solution of caffeine in the feed half-cell. The corresponding caffeine transport data provided the caffeine flux across the theophylline-imprinted polymer. The selectivity coefficient for theophylline vs caffeine transport was obtained by ratioing the theophylline and caffeine fluxes. In analogy to the gas-transport selectivity coefficient obtained from such single-molecule-transport experiments,[5–10] this selectivity is given the symbol α. Transport data were also obtained for caffeine-imprinted polymers and for polymers made in the absence of any print molecule.

To confirm that the selectivity coefficient obtained from the single-molecule-transport experiment accurately reflects the selectivity that would be observed when both molecules are present in solution together, a two-molecule-transport experiment was also done. In this case, the feed solution contained 10^{-5} M theophylline and 10^{-5} M caffeine. Again, the permeant was initially pure methanol. Permeation was allowed to occur until steady-state transport was achieved. The permeant solution was then sampled and the concentrations of theophylline and caffeine were determined via HPLC. The ratio of these concentrations provided the two-molecule selectivity coefficient. Ideally, the selectivity coefficients from the single-molecule and two-molecule experiments should be the same.

Other Measurements. As per our previous work, film thickness was determined using electron microscopy.[5–7] Films of ca. 500 nm thickness (1 h photopolymerization period) were used for all of these studies. Finally, a series of gas (O_2) permeation experiments were conducted on the theophylline-imprinted polymer. The gas-transport cell used is similar to that described in ref 21. It consists of an upper half-cell (which was maintained at a pressure of 2 psig with pure O_2) and a lower half-cell at ambient pressure. The composite membrane separated the two half-cells. The outlet of the lower half-cell was fed into a series of soap-bubble flow meters to measure the O_2 flux through the composite membrane. The flux is reported here in units of cm^3(STP) cm^{-2} (cm Hg)$^{-1}$ s^{-1}.

Results and Discussion

Molecularly-Imprinted Polymers. Polymers of this type have been used as stationary-phase materials to make highly selective liquid chromatography columns, with special emphasis on chiral separations.[22] In addition, this approach has been used to imprint polymers on transition-state analogues to make enzyme mimics.[23] Imprinted polymers have also been used as substitutes for antibodies in competitive binding assays akin to radioimmunoassay.[17] There have also been recent reports of using molecularly-imprinted polymers in sensors.[24,25]

There have been two very recent reports of using the molecular-imprinting approach to make selectively-permeable membranes,[26,27] the main objective of this paper. The first entailed the use of a resin bearing a tetrapeptide derivative as the molecular-recognition site for optical resolution of amino acids.[26] The second, which is more related to the work done here, entailed the use of a methacrylic acid−ethylene glycol dimethacrylate copolymer (similar to the one used here) that had been imprinted on 9-ethyladenine.[27] The rates of transport of adenine and other nucleic acid bases across this molecular-imprinted polymer were investigated. Because the polymer prepared in this study[27] was chemically similar to the one used here (albeit imprinted on a different molecule), this prior work provides for an interesting comparison with our work. In particular, because free-standing films were used that were much thicker than the films prepared here, the fluxes observed[27] were significantly lower than the fluxes obtained here (see below).

Table 1. Fluxes[a] and Transport Selectivity Coefficients (α) Obtained for Polymer Films Imprinted on Theophylline, Caffeine, and for a Film Synthesized in the Absence of Any Print Molecule

print molecule used	theophylline flux[a] (mol cm^{-2} h^{-1})	caffeine flux[a] (mol cm^{-2} h^{-1})	α
theophylline	1.7×10^{-8}	6.5×10^{-9}	2.6[b]
none	7.2×10^{-9}	9.8×10^{-9}	0.73[b]
caffeine	5.9×10^{-9}	1.8×10^{-8}	3.0[c]

[a] Fluxes obtained for a feed concentration of 1×10^{-5} M. [b] Selectivity for theophylline over caffeine. [c] Because this film was imprinted on caffeine, this is selectivity for caffeine over theophylline.

Rate and Selectivity of Theophylline Transport. Figure 1 compares rates of transport of theophylline and caffeine through a typical theophylline-imprinted membrane. The single-molecule-transport experiment was used. It is important to point out that in prior studies of transport of water through a similar composite membrane, we showed that because the alumina support is so highly porous, the net flux across the composite is limited by transport in the polymer film.[13] This is certainly true for the large molecules and highly cross-linked resins investigated here. Fluxes and selectivity coefficients obtained from plots such as those shown in Figure 1 are presented in Table 1.

Table 1 shows that the polymer that had been imprinted on theophylline selectively transports theophylline, and that the polymer that had been imprinted on caffeine selectively transports caffeine. In addition, a polymer synthesized in the absence of either print molecule shows much lower selectivity but has a small preference for caffeine transport. The data in Table 1 were obtained using feed solutions that were 10^{-5} M in theophylline or caffeine. As will be discussed below, higher selectivities can be obtained at lower feed-solution concentrations; this observation is in agreement with the relevant theory.[28]

The ultrathin film composite membrane approach was used here in order to obtain higher permeant fluxes than would be possible with thick, free-standing membranes. A previous report which dealt with thick, free-standing membranes prepared from the same monomers makes for an interesting comparison.[27] As would be expected,[5] the ultrathin film composite membranes investigated here showed dramatically higher fluxes—10^{-10} mol cm^{-2} h^{-1} (Table 1 in ref 27) vs 10^{-8} mol cm^{-2} h^{-1} (for the imprinted polymers in Table 1, below). These data clearly demonstrate the flux advantage of the ultrathin film composite membrane concept. (Other

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Table 2. Effect of Feed Solution Concentration on the Theophylline vs Caffeine Selectivity Coefficient

concentration of theophylline or caffeine in the feed solution (M)	theophylline flux (mol s^{-1} cm^{-2})	selectivity coefficient, α
2×10^{-3}	3.82×10^{-10}	1.4
2×10^{-4}	5.34×10^{-11}	1.8
4×10^{-5}	2.22×10^{-11}	2.5
1×10^{-5}	7.1×10^{-12}	2.6
1×10^{-6}	1.20×10^{-11}	5.0

factors which affect the magnitude of the flux are the size of the molecule being transported and the concentration of this molecule in the feed solution. While the molecule in the previous work was somewhat larger than the molecule used here, higher feed solution concentrations were also used.[27] In addition, the membranes prepared here are more highly cross-linked.)

Molecularly-imprinted polymers have sites that selectively bind the print molecule.[14−17] As a result, from a transport point of view, these polymers should resemble facilitated transport membranes—specifically, facilitated transport membranes with fixed[28] as opposed to mobile[29] carriers. One of the features of the facilitated transport process is that maximum transport selectivity is observed when the concentration of the permeant molecule in the feed solution is very low, and selectivity decreases at higher feed concentrations.[28,29] To probe this issue, we investigated the effect of feed concentration on the theophylline vs caffeine selectivity coefficient.

Table 2 shows selectivity coefficients obtained for various concentrations of theophylline in the feed solution. These α values were obtained using the single-molecule method, and the concentration of caffeine used in each case was the same as the concentration of theophylline used. In agreement with the predictions of the facilitated transport model, α increases with decreasing concentration of the print molecule in the feed solution.[28] The value of $\alpha = 5.0$ reported in Table 2 is the highest transport selectivity coefficient obtained for a molecularly-imprinted polymer membrane to date.

In research on membranes for industrial gas separations it is common to use the single-molecule-transport experiments to evaluate selectivity coefficients for a new membrane material.[8−10] However, it is also advisable to do two-molecule-transport experiments,[30] since in real applications the target molecule will be present in the feed with at least one other molecule. In most cases the single-molecule and two-molecule assessment of selectivity yield the same results. To see if this is the case for the polymers studied here, an HPLC method was used to evaluate the transport selectivity when the feed solution was 10^{-5} M in both theophylline and caffeine. A selectivity coefficient of $\alpha = 2.1$ was obtained. This is very similar to the selectivity coefficient obtained from the single-molecule transport experiment (Table 1) at this concentration of theophylline and caffeine in the feed solution.

Gas-Permeation Experiments. The polymer films prepared here are highly cross-linked resins and, as such, are inherently porous. This point is proven by the high rates of gas transport through these films (see below). This inherent porosity is undesirable because these pores are nonselective transport pathways through the film. Caffeine, for example, uses this nonselective transport pathway (i.e., the inherent porosity of the film) to traverse the film. If this nonselective transport pathway could be closed off, higher transport selectivities would be obtained.

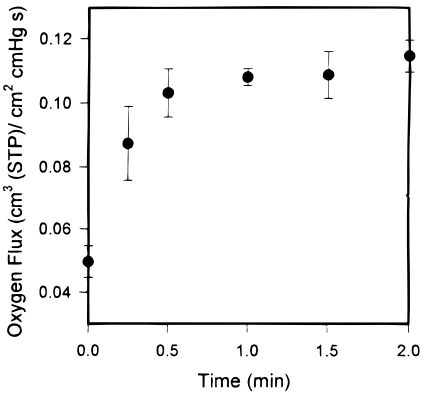

Figure 3. Oxygen flux across a theophylline-imprinted polymer. The polymer was initially saturated with caffeine. The *x*-axis is time of exposure to methanol which leaches the caffeine from the polymer film.

To explore this issue further, we conducted gas-permeation experiments on the theophylline-imprinted polymers. A theophylline-imprinted polymer was first soaked for 1 h in 9:1 (v/v) methanol−acetic acid to remove the print molecule and unreacted monomer. The print molecule was then reintroduced by soaking the membrane in theophylline-saturated methanol for 24 h. The flux of O_2 across the theophylline-loaded polymer was then measured. The membrane was then reimmersed into pure methanol to leach a fraction of the incorporated theophylline from the polymer, and the O_2 flux was remeasured. This process of immersion in methanol to remove a portion of the incorporated theophylline followed by remeasurement of the O_2 flux was repeated until all of the theophylline had been leached from the polymer.

An analogous set of experiments were done on a theophylline-imprinted polymer that was loaded with caffeine. A theophylline-imprinted polymer was soaked in 9:1 (v/v) methanol−acetic acid and then immersed for 24 h in caffeine-saturated methanol. The flux of O_2 across the caffeine-loaded polymer was then measured. The membrane was then reimmersed into pure methanol to leach a fraction of the incorporated caffeine from the polymer, and the O_2 flux was remeasured. This process was repeated until all of the caffeine had been leached from the polymer.

The results for these two sets of experiments are shown in Figures 2 and 3 as plots of O_2 flux vs time of exposure to the leaching methanol. Note first that the magnitude of the O_2 flux through the theophylline-saturated polymer (time = 0 point, Figure 2) is significantly lower than the O_2 flux through the caffeine-saturated polymer (time = 0 point, Figure 3). In addition, the time required to leach the molecule is significantly less for the caffeine-saturated polymer than for the theophylline-saturated polymer. However, in

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both cases, the polymer ultimately reaches a flux of ca. 0.12 cm^3(STP) cm^{-2} (cm Hg)$^{-1}$ s^{-1} when all of the caffeine or theophylline had been removed (long time data points in Figures 2 and 3).

These data can be explained as follows: First, it is important to reiterate that both of these experiments were done on theophylline-imprinted polymers. The O_2 flux is higher in the caffeine-saturated polymer because, while caffeine can occupy the nonselective pores in the polymer (inherent porosity of the polymer, see above), it cannot occupy the theophylline-selective sites. As a result the theophylline-selective sites (and pores that are too small for either of these molecules) are open for O_2 transport. (That O_2 is transported through the theophylline-selective sites is not surprising given the very small size of the O_2 molecule.) When the polymer is theophylline-saturated, both the nonselective pore system and the theophylline-selective sites are blocked with theophylline. Now O_2 transport is possible only through the pores that are too small for either of these molecules. As a result, the O_2 flux through the theophylline-saturated polymer is significantly smaller.

This explanation is supported by the fact that the rate at which theophylline is leached from the polymer is significantly lower than the rate at which caffeine is leached (compare time axes in Figures 2 and 3). The slower rate of removal of theophylline cannot be related to molecular size because theophylline is the smaller of these two molecules. Rather, theophylline removal is slower because this process entails breaking of the chemical interactions (hydrogen bonding[17]) that hold the theophylline within the selective sites. These gas-permeation studies support the idea that there are nonselective pores and theophylline-selective sites within the membrane and that competing molecules (e.g., caffeine) can be transported via the nonselective pores. In addition, these studies show that there are even smaller pores that can transport small molecules such as O_2.

It is also important to point out that the rate of gas-transport through these films is extremely high (Figures 2 and 3). As indicated above, these high gas fluxes support the conclusion that these polymers are inherently porous. There is an alternative possibility—there are pinholes or defects in the films. This, however, is disproven by the various permeation data obtained here. For example, the key result from Figures 2 and 3 is that the *molecules* theophylline and caffeine can dramatically change the rate at which gas is transported through these films. As discussed in detail above, the simplest way to think about this is that these molecules are corks, and they are plugging up the pores and selective sites in the film. If, in contrast, there were pinholes in the films, molecules would not be able to plug these much larger defects, and it would be impossible for theophylline and caffeine to dramatically change the rate at which gas is transported through these films.

In addition, the key result of this paper is that the imprinted films can be selective to the molecule on which the film is imprinted. If there were pinholes in the film, transport would be dominated by these pinholes. Again, because such pinholes would be much larger than molecular dimensions, the pinholes would show no selectivity. The fact that molecule-selective transport is seen clearly indicates that there are no large pinholes in these films.

Conclusions

These results show that the molecularly-imprinted polymer concept can be used, in conjunction with a photopolymerization method, to prepare a new type of ultrathin film composite membrane for chemical separations. While good selectivity can be observed for the print molecule (theophylline) relative to a chemically very similar competing molecule (caffeine), higher selectivities are always desirable. This should be possible if a method for closing down the nonselective pores within the polymer can be developed.

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