



Separation of Olefin/Paraffin Mixtures with Carrier Facilitated Membranes

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TABLE OF CONTENTS

| | |
|---|----|
| EXECUTIVE SUMMARY | 4 |
| 1. INTRODUCTION | 6 |
| 2. TECHNICAL BACKGROUND..... | 9 |
| 3. EXPERIMENTAL PROCEDURES..... | 12 |
| 3.1 Preparation of the Polymer Electrolyte Composite Membranes..... | 12 |
| 3.2 Membrane Stamp Permeation Measurements | 14 |
| 4. INITIAL PERMEATION AND SORPTION PROPERTIES OF SILVER SALT FACILITATED TRANSPORT MEMBRANES..... | 15 |
| 4.1 Effect of AgBF ₄ Content on the Initial Pure and Mixed-Gas Properties of Pebax [®] 2533+AgBF ₄ Membranes | 15 |
| 4.2 Effect of Multi-Component Feed Mixtures and Pressure on the Initial Permeation Properties of Pebax [®] 2533+AgBF ₄ Membranes..... | 20 |
| 4.3 The Impact of Salt Addition on Non-Facilitated Gas Permeances and Selectivities of Pebax [®] 2533 Composite Membranes | 22 |
| 4.4 Olefin and Paraffin Sorption in Pebax [®] 2533+AgBF ₄ Membranes..... | 23 |
| 5. TIME-DEPENDENT PERMEATION IN SILVER SALT FACILITATED TRANSPORT MEMBRANES | 25 |
| 5.1 Background and Initial Findings..... | 25 |
| 5.2 High Silver Salt Content Facilitated Transport Membranes are Not Stable Over Time with Ideal Olefin/Paraffin Gas Mixtures | 29 |
| 5.3 Understanding the Mechanism of Performance Decline in Silver Salt Facilitated Transport Membranes – Olefin Conditioning..... | 32 |
| 5.4 Investigating the Reversibility of Olefin Conditioning | 36 |
| 5.5 FTIR Analysis of Olefin Conditioning | 40 |
| 5.6 Effect of Temperature, Polymer Plasticizers and Humidified Feed | 41 |
| 5.7 Sorption Hysteresis | 47 |
| 5.8 Summary of Time-Dependent Membrane Studies | 49 |
| 6. CARRIER POISONING AND REGENERATION OF SILVER SALT FACILITATED TRANSPORT MEMBRANES..... | 49 |
| 6.1 Carrier Poisoning Studies | 49 |
| 6.2 Stabilization and In-situ Regeneration of Reduced Silver Salt Membranes..... | 54 |
| 7. NEW OLEFIN CARRIERS..... | 59 |
| 7.1 Permeation Properties of Membranes Containing Alternate Olefin Carrier Salts..... | 59 |
| 7.2 Permeation Properties of Membranes Containing Mixed Carrier Salts..... | 60 |
| 7.3 Development of Non-Silver Salt Olefin Carriers..... | 64 |
| 8. OLEFIN/PARAFFIN SEPARATION APPLICATIONS | 71 |
| 8.1 Introduction..... | 71 |
| 8.2 Olefin Metathesis..... | 72 |
| 9. CONCLUSIONS..... | 74 |

EXECUTIVE SUMMARY

This document describes the results of a DOE-funded joint effort of Membrane Technology and Research Inc. (MTR), SRI International (SRI), and ABB Lummus (ABB) to develop facilitated transport membranes for olefin/paraffin separations. In the United States, ethylene and propylene are produced in larger quantities than any other organic chemicals. Currently, olefins and paraffins are separated by distillation—an extremely energy-intensive process because of the low relative volatilities of olefins and paraffins. A new type of carrier facilitated membrane discovered by MTR offers potential energy savings of 48 trillion Btu per year by the year 2020 if this membrane technology could be successfully commercialized. As a step toward development of these membranes, a detailed analysis of membrane time-dependent performance, including performance after exposure to carrier poisoning species, was conducted during this project.

We discovered that silver salt-based facilitated transport membranes are not stable even in the presence of ideal olefin/paraffin mixtures. This decline in membrane performance appears to be caused by a previously unrecognized phenomenon that we have named olefin conditioning. As the name implies, this mechanism of performance degradation becomes operative once a membrane starts permeating olefins. Unfortunately, the very species targeted for separation by the carrier membranes (olefins) are a source of membrane instability.

This project is the first study to identify olefin conditioning as a significant factor impacting the performance of facilitated olefin transport membranes. To date, we have not identified an effective strategy to mitigate the impact of olefin conditioning, other than running at low temperatures or with low olefin feed pressures. In our opinion, this issue must be addressed before further development of facilitated olefin transport membranes can proceed.

In addition to olefin conditioning, traditional carrier poisoning challenges must also be overcome. Light, hydrogen, hydrogen sulfide, and acetylene exposure adversely affect membrane performance through unwanted reaction with silver ions. Harsh poisoning tests with these species showed useful membrane lifetimes of only one week. These tests demonstrate a need to improve the stability of the olefin complexing agent to develop membranes with lifetimes satisfactory for commercial application.

A successful effort to improve membrane coating solution stability resulted in the finding that membrane performance loss could be reversed for all poisoning cases except hydrogen sulfide exposure. A novel in-situ regeneration treatment restored aged and poisoned membranes to nearly their initial performance values. This discovery offers the potential to extend membrane lifetime through cyclic regeneration. We also found that certain mixed carriers exhibited greater stability in reducing environments than that exhibited by silver salt alone. These results offer promise that solutions to deal with carrier poisoning are possible.

The main achievement of this program was the progress made in gaining a more complete understanding of the membrane stability challenges faced in the use of facilitated olefin transport membranes. Our systematic study of facilitated olefin transport uncovered the full extent of the stability challenge, including the first known identification of olefin conditioning and its impact on membrane development.

We believe that significant additional fundamental research is required before facilitated olefin transport membranes are ready for industrial implementation. The best-case scenario for further development of this technology would be identification of a novel carrier that is intrinsically more stable than silver ions. If the stability problems could be largely circumvented by development of a new carrier, it would provide a clear breakthrough toward finally recognizing the potential of facilitated olefin transport.

1. INTRODUCTION

Olefins are the most important building blocks of the petrochemical industry. In the United States, ethylene and propylene are produced in larger quantities than any other organic chemical – approximately 48 and 28 billion pounds annually, respectively. Most olefins are produced by steam cracking of ethane, propane, naphtha, or gas oil. Production is highly energy intensive. Current distillation processes for the separation of ethylene/ethane and propylene/propane mixtures—which account for most of the energy consumption and much of the capital cost of the steam cracker—consume an estimated 120 trillion Btu of energy per year in the United States. The difficulty of the olefin/paraffin separation step stems from the low relative volatilities of the components. As a result, very large distillation towers with 120-180 trays and high reflux ratios are required. Even small improvements in these separations could result in significant energy and cost savings to the petrochemical industry.^[1-3]

In light of the importance of olefin/paraffin separations, and because of the costliness of distillation, alternative technologies have been and continue to be the focus of industry study. Two recent reviews by Eldridge^[2, 3] describe the current status of research. Reactive absorption, one of the more promising new techniques, uses silver or copper salts to extract the olefin from bulk gas in an absorber/stripper process.^[4] Union Carbide and BP/Stone and Webster have taken this type of process to the pilot plant stage. Other processes that have been evaluated include extractive distillation and molecular sieves.^[5] Despite this work, however, a viable alternative to conventional distillation has yet to be developed.

Membranes, an energy efficient, environmentally friendly technology, are potentially useful for olefin/paraffin separations. Although polymeric membranes have been used successfully in several gas separation applications, including nitrogen production from air and hydrogen removal from refinery streams, the selectivities and gas fluxes of such membranes are inadequate for separating olefins from saturated hydrocarbons. Under industrial operating conditions, the best polymeric membranes offer olefin/paraffin selectivities of four to five. To replace or supplement distillation for the separation of olefins and paraffins in steam crackers or propane dehydrogenation plants, membranes with selectivities of 10 or more are necessary.

Facilitated transport membranes have long attracted research interest because of their potential to perform separations more efficiently than simple, passive membranes. In a facilitated transport process, passive diffusion down a concentration gradient is aided by the presence of a carrier agent that selectively and reversibly binds with a compound targeted for separation, enhancing its movement across a barrier. The complexation reaction of the carrier with the facilitated species creates another transport route in addition to the typical solution-diffusion mechanism that occurs in dense passive membranes. This second transport avenue is not available to non-facilitated or inert species that are unable to interact with the carrier. Consequently, facilitated transport membranes can exhibit selectivities well beyond the bounds that govern typical passive membranes. For example, mixed-gas ethylene/ethane selectivities of more than 50 have been demonstrated.^[6, 7]

The spectacular separation performance of facilitated transport membranes has generated considerable interest from academic and industrial groups. Over the past 40 years, hundreds of

papers have been published describing membranes for facilitated transport of various gases. A pioneering paper in this area was published by Scholander in 1960.^[8] This study reported facilitated oxygen transport in supported liquid membranes containing hemoglobin as the carrier agent. Scholander found an eight-fold increase in oxygen flux for membranes containing hemoglobin solution compared to those containing water only.^[8] A few years later, Ward and Robb reported facilitated carbon dioxide transport across immobilized liquid films containing an aqueous bicarbonate carrier solution.^[9] These membranes exhibited a selectivity of 4,100 for carbon dioxide over oxygen. Like Scholander's membrane, the carrier solution Ward and Robb used was immobilized or supported within the pores of a microporous membrane. This same concept was extended to facilitated olefin transport membranes by Steigelmann and Hughes at Standard Oil, who used an aqueous silver (I) ion carrier contained within the pores of a cellulose acetate film or fiber.^[10, 11] These authors continued working on their facilitated olefin transport membranes for over a decade, and a serious effort was made to commercialize the technology.^[12]

The primary drawback to these supported liquid membranes is that over time the aqueous carrier solution will evaporate or otherwise be pushed out of the membrane pores.^[13] When this happens, gases can pass non-selectively through the open pores. To improve stability and allow reasonable lifetimes, the membranes have to be made relatively thick, which has the undesirable effect of lowering transmembrane gas flux. Other means of improving the stability of supported liquid facilitated transport membranes have been explored, including adding dense sealing layers,^[14] an absorbent liquid sweep,^[12] or less volatile carrier solvents.^[15] Nevertheless, the inherent instability of supported liquid membranes is a serious deficiency that limits their commercial potential.

In 1980, LeBlanc and coworkers^[16] published an important paper describing facilitated olefin transport in a dense ion-exchange membrane saturated with water. Silver was used as the counter ion in a sulfonated poly(dimethylphenylene oxide) membrane. An advantage of this membrane configuration is that the carrier species cannot be easily forced out of the membrane because it is held in place within the polymer by electrostatic forces. In the following years, a number of groups studied this type of facilitated transport membrane.^[17-20] Although their stability is better than the supported liquid membrane configuration, the ion-exchange membranes require humidification to achieve facilitated transport. Without water, the silver cation is held too tightly by the polymer exchange site (frequently SO_3^-), and is unable to interact with olefins. Moreover, the ion-exchange polymers used in these membranes tend to be expensive.

Ho overcame some of this cost hurdle by showing that relatively cheap hydrophilic polymers, such as polyvinyl alcohol, containing silver salts could facilitate olefin transport when water swollen.^[21, 22] Around this same time, Peinemann reported high olefin/paraffin selectivities for humidified membranes with a selective layer composed of a simple physical blend of Nafion[®] and AgBF_4 .^[23] Soon afterwards, Pinnau and Toy showed that hydrophilic polymers with functional groups capable of solvating silver ions, such as polyethers, could facilitate olefin transport even without humidification.^[6, 7] Kang and co-workers examined facilitated olefin transport in these dry solid polymer electrolyte membranes in detail.^[24, 25] Recently, they have shown that even hydrophobic polymers, such as polydimethylsiloxane, containing dispersed silver salts can exhibit facilitated olefin transport.^[26]

Despite the progress outlined above, a number of daunting challenges remain before facilitated olefin transport membranes can be used in industry. The most well-known of these problems is the lack of carrier stability. In addition to complexing with olefins, known carriers also tend to react with other species causing undesirable carrier deactivation or poisoning over time. For example, the silver (I) ion – the most commonly-used carrier for facilitated olefin transport – can be reduced to inactive silver metal by exposure to light or reducing gases such as hydrogen.^[27] Silver ions can also react with contaminants such as hydrogen sulfide or acetylene to form non-facilitating, and in the case of silver acetylide, potentially dangerous, compounds.^[4] This carrier poisoning problem is often ignored or only briefly alluded to in the multitude of facilitated transport membrane papers published each year.

The few detailed descriptions of olefin carrier poisoning are mostly found in industrial studies of absorption systems. The idea of using silver (I) or other metal ions that can complex with olefins to separate these species from mixtures dates to the early 20th century.^[28-30] In 1951, Dewar explained the metal-olefin π -bonding mechanism responsible for these complexes. Olefin separation processes using aqueous silver salts as the absorbing solution in a packed column were developed by Farbwerke Hoechst^[27] in the 1950s and 1960s and Union Carbide^[4] in the 1970s and 1980s. At both companies, the issue of carrier poisoning was addressed. To mitigate the reduction of silver ions caused by reducing gases, hydrogen peroxide was added to the absorbing solution in both company's processes.^[27, 31] Keller et al. at Union Carbide discovered a method of managing silver acetylide formation through oxidation with silver permanganate.^[31] Keller suggested that the only solution to silver ion poisoning by sulfur compounds was to use pretreatment to reduce these species to very low concentrations.^[4] Although thorough engineering solutions were worked out and large demonstrations of the technology conducted, neither the Hoechst nor Union Carbide process caught on commercially, presumably due to stability difficulties and cost.

The most detailed discussion of carrier poisoning in a facilitated olefin transport membrane process comes from the work of Hughes et al. at Standard Oil.^[12] This group also used hydrogen peroxide to stabilize silver ions contained in their supported liquid membrane.^[32] The technology was field tested on the vent stream of a polypropylene plant using commercial-scale hollow fiber modules impregnated with silver nitrate (AgNO_3) solution. Even though a liquid hexane sweep was used to mitigate solvent leak from the fibers, membrane deactivation due to water loss was shown to adversely affect long-term performance. Lack of tolerance to poisons such as H_2S and acetylenes was also acknowledged as a process shortcoming.^[12] Later, Davis et al. at British Petroleum tried a similar supported liquid membrane contactor approach using a recirculating AgNO_3 solution.^[33] This process also failed to achieve commercial success due to cost and carrier stability problems.

A few groups have explored different olefin complexing agents in the hope of identifying a more stable carrier for facilitated transport membranes. The most commonly studied carriers other than silver are copper salts. Copper (I) ions form π -bond complexes with olefins in the same manner that silver does. Unfortunately, copper carriers also suffer from stability problems.^[3] Alternate carriers that function via a different complexing mechanism have been examined as well. In a patent assigned to the University of Colorado, DuBois and coworkers describe molybdenum sulfide dimers that reversibly complex olefins and are unaffected by H_2S .^[34]

Unfortunately, these materials are difficult to prepare and bind tightly with alkynes. Wilson et al. report reversible olefin complexation for a palladium-containing cubane compound.^[35] This material is stable in the presence of hydrogen and acetylenes, but degrades upon exposure to H₂S or oxygen.

Membrane Technology and Research, Inc. (MTR) has continued to investigate the solid polymer electrolyte facilitated transport membranes first described by Pinnau and Toy.^[6, 7] These composite membranes, consisting of a thin selective layer of silver salt dissolved in polyethers and coated on a microporous support, can give useful permeances and selectivities without humidification. However, as with previous silver salt membranes, they are subject to limited membrane lifetimes because of carrier poisoning.

In this report, we describe our efforts to understand carrier poisoning and other membrane stability issues as a first step in the scale-up and development of these facilitated transport membranes for commercial use. A novel regeneration process capable of restoring the initial properties of reduced facilitated transport membranes will be discussed. This discovery offers the potential to periodically regenerate aged or poisoned membranes in a manner analogous to backflushing of fouled filtration membranes. This encouraging finding is tempered by the discovery of a previously unrecognized aging mechanism not related to carrier poisoning. The causes of this time-dependent behavior, which is a serious barrier to further development of these membranes, will be addressed in Section 5 of this report.

2. TECHNICAL BACKGROUND

The reversible reaction between transition metal ions and olefins has been known for more than a century.^[36] Metal salts, such as those of silver, form electron donor/acceptor complexes with olefins through interaction of olefin π -orbitals with σ - and π -orbitals of the metal. Because they react reversibly with olefins and their cost is relatively low, silver and copper salts have received the most attention as potential olefin/paraffin separating agents.^[3]

Previous work at MTR has identified silver tetrafluoroborate (AgBF₄) as an effective olefin complexing agent when dispersed in a polymer electrolyte. The mechanism by which facilitated olefin separation takes place in a membrane is illustrated in Figure 1 for an ethylene/ethane (C₂H₄/C₂H₆) mixture. On the high-pressure side of the membrane, both ethylene and ethane are sorbed into the membrane material. Because ethylene forms a complex with the silver-ion carrier, its solubility in the membrane is significantly higher than that of ethane. Desorption of ethylene on the low-pressure side of the membrane leads to dissociation of the ethylene/silver complex. Because ethane cannot form a complex with silver, it cannot access this facilitated transport mechanism. At the same time that ethylene is transported selectively by silver complexation, both ethylene and ethane are permeating by ordinary solution-diffusion. This regular molecular permeation is relatively slow in comparison to that resulting from silver/olefin complexation. As a result, membrane olefin/paraffin selectivities are very high.

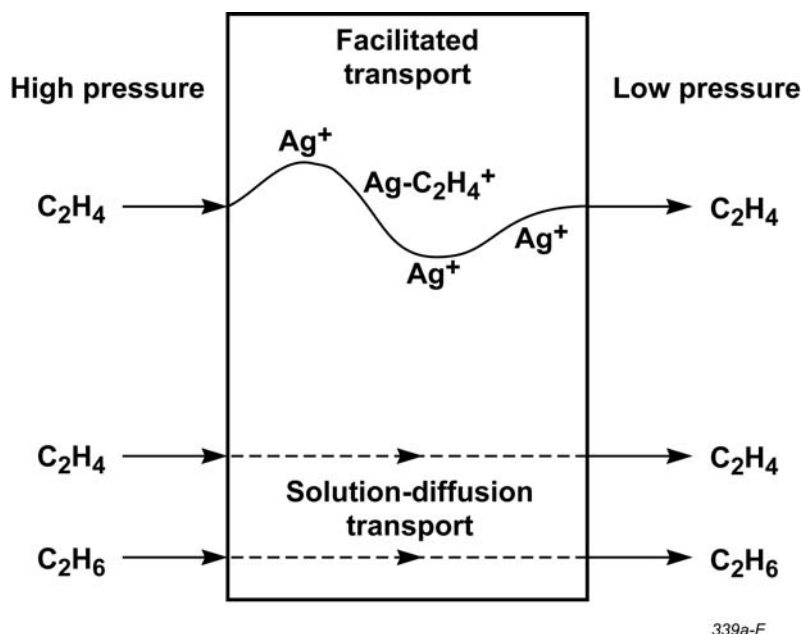


Figure 1. Schematic representation of a facilitated transport membrane containing silver ions that react reversibly with olefins (ethylene, in this case).

While silver ions are known to form complexes with olefins, the exact mechanism by which the ions transport olefin molecules across a dense membrane has been the subject of debate. Previous findings suggest that the olefin/silver complex is relatively immobile in the membrane.^[6, 37, 38] Upon sorbing into the membrane, olefin molecules are believed to hop from silver ion to silver ion, thereby traversing the film. The strongest evidence for this mechanism comes from silver salt loading studies in which a percolation threshold is observed. Below a critical loading, the space between silver ions is apparently too great for olefin molecules to hop to a neighboring site, and no facilitated olefin transport occurs.

This result is illustrated in Figure 2, which shows the mixed-gas ethylene/ethane selectivity of a polyether-polyamide block copolymer (Pebax[®] 2533) membrane that contains various amounts of AgBF₄. As the silver concentration in the polymer increases from 0 to 30 vol%, the ethylene/ethane selectivity is close to 1 and nearly constant. At silver loadings of greater than 30 vol%, the olefin/paraffin selectivity increases dramatically. This happens to be the point at which geometric percolation is reached for a simple dispersion of spheres within a medium. One can imagine that a situation similar to that shown in the inset of Figure 2 is occurring. Below percolation (<30 vol%), silver particles are separated by spaces filled with polymer. Permeating olefin molecules complex with the silver ions, but then must diffuse through the polymer matrix to reach the next silver particle. The diffusion step is relatively slow. In contrast, above percolation (>30 vol%), the silver particles are in close communication, so olefin molecules can hop from one silver ion to the next. This pathway is apparently much faster than diffusion through the polymer phase, and consequently, olefin/paraffin selectivities are high above the percolation threshold. For this reason, high loadings (typically around 80 wt% or 40 vol% of silver salt) are used in our solid polymer electrolyte membranes.

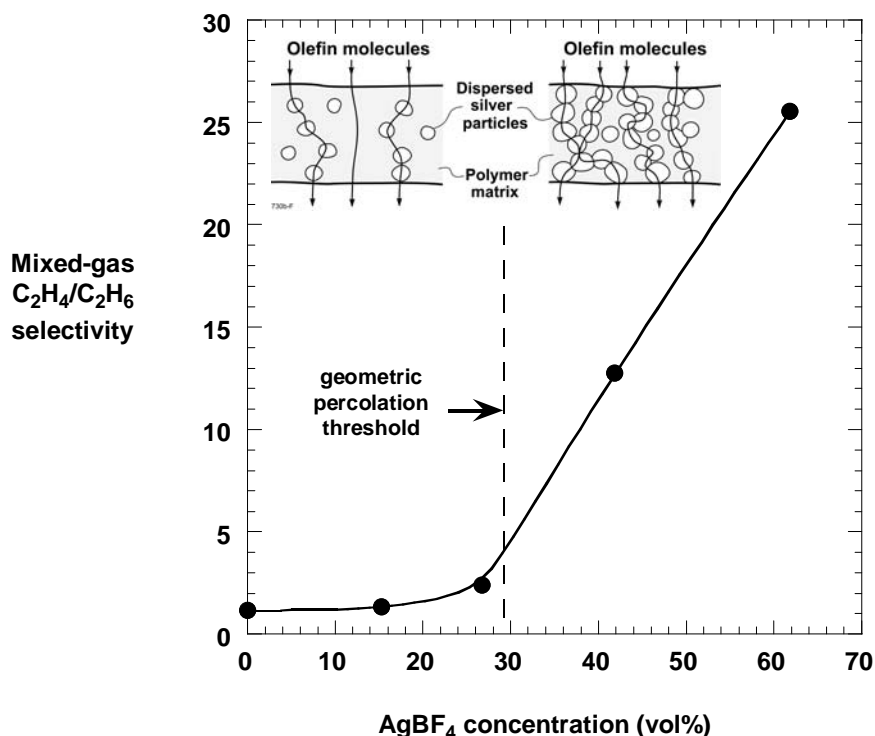
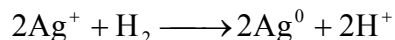


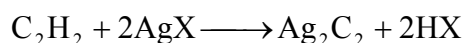
Figure 2. Mixed-gas ethylene/ethane selectivity in Pebax[®] 2533 as a function of AgBF₄ content. Feed: 70 mol% ethylene/30 mol% ethane; Pressure: 50 psig; Temperature: 22°C.

The fact that membrane permeation properties appear to depend on the distribution of silver ions within the matrix is important. As will be shown in Section 5, time-dependent changes in membrane structure can significantly impact membrane performance.

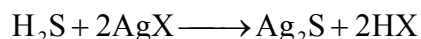
Another way that membrane performance can be affected over time is through the presence of carrier poisoning species. In addition to interacting with olefins, silver ions react with hydrogen, acetylenes, hydrogen sulfide and other sulfur species.^[3] These side reactions can deactivate the silver carrier such that it is no longer able to complex olefins. As a result, membrane olefin/paraffin selectivity is progressively lost with exposure time. The main side reactions that are believed to occur are shown below; X is the anionic component of the silver salt (typically, BF₄⁻).



Hydrogen reduction



Silver acetylide formation



Silver sulfide formation

In addition, silver salts can be reduced by light:

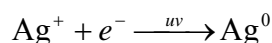


Photo-reduction

Despite the general understanding that these undesirable reactions can occur, there is very little quantitative information available on the impact of carrier poisons on membrane performance. This type of knowledge is important to gauge membrane lifetimes. In this report, we describe the effect of light and carrier poisons on facilitated transport membrane performance. Methods of mitigating the effect of these contaminants are also discussed.

3. EXPERIMENTAL PROCEDURES

3.1 Preparation of the Polymer Electrolyte Composite Membranes

The membranes used in this project were composite structures typically consisting of a thin selective polymer-electrolyte/silver-salt layer sandwiched between a microporous support layer and a protective top coat. A schematic drawing and an electron micrograph of a solid polymer electrolyte facilitated transport membrane are shown in Figure 3. Mechanical strength is provided by the poly(vinylidene fluoride) (PVDF) microporous support membrane. This support is coated with a thin ($\sim 2\ \mu\text{m}$ thick) selective layer composed of a polymer electrolyte (often Pebax[®] 2533, a polyether-polyamide block copolymer composed of 80 wt% tetramethylene oxide and 20 wt% nylon 12, and available from Arkema, Inc.) doped with a silver salt (AgBF_4). Finally, an extremely thin protective coating is applied on top of the selective Pebax[®] 2533+ AgBF_4 layer to seal defects and protect the membrane from damage during handling.

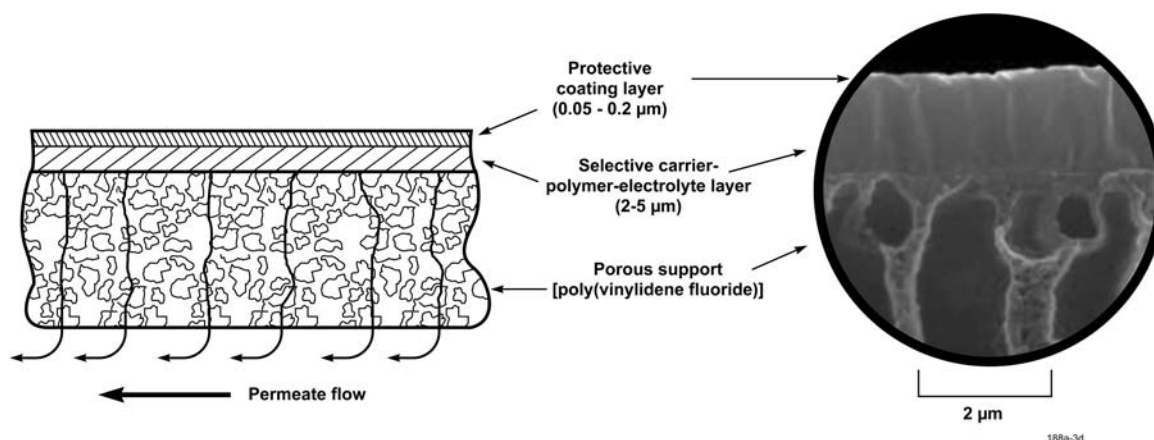


Figure 3. Schematic drawing and electron micrograph of a solid-state facilitated transport composite membrane.

As shown in the electron micrograph, the inert PVDF support is quite porous and imparts mechanical strength without providing significant resistance to mass transport. The matrix polymer generally used for the selective layer, Pebax[®] 2533, was selected in a previous project because it coated easily and appeared to yield the highest steady-state olefin permeances of the various polyether-based materials examined. Other polymers examined have included poly(ethylene oxide) (PEO), poly(vinyl pyrrolidone) (PVP), and poly(1-trimethylsilyl-1-propyne) (PTMSP). Previously, we discovered that the Pebax[®] 2533+ AgBF_4 selective layer is extremely hygroscopic causing the surface of these membranes to be very tacky. This surface tackiness makes it difficult to handle Pebax[®] 2533+ AgBF_4 membranes. To change the surface

properties, a hydrophobic protective layer was added to the composite membrane. This top layer successfully altered the surface properties, allowing the membranes to be handled and rolled into modules.

The microporous PVDF support was prepared with the casting machine shown in Figure 4. The casting solution, which contains the polymer, a water-miscible solvent, and an additive, is doctored onto a moving belt of polyester fabric. The belt is then collected on a take-up roll, after which the membrane is washed overnight to remove any remaining solvent and, finally, dried in an oven to form the support film.

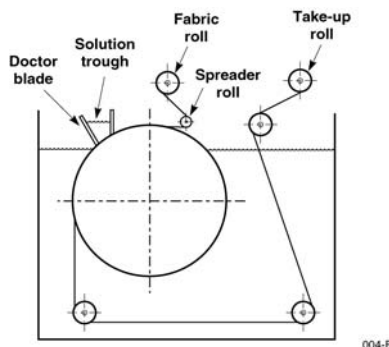


Figure 4. Schematic diagram of the MTR casting machine.

The PVDF support layer was then coated with a solution of the polyelectrolyte and silver salt. Acetonitrile and aliphatic alcohols are solvents for both Pebax[®] 2533 and AgBF₄. Hence, thin-film polymer electrolyte composite membranes were easily formed using a conventional dip-coating process with the equipment shown schematically in Figure 5. The support membrane passes from the feed roll through the dip-coating station, through a drying oven, and is finally wound up on a product roll.

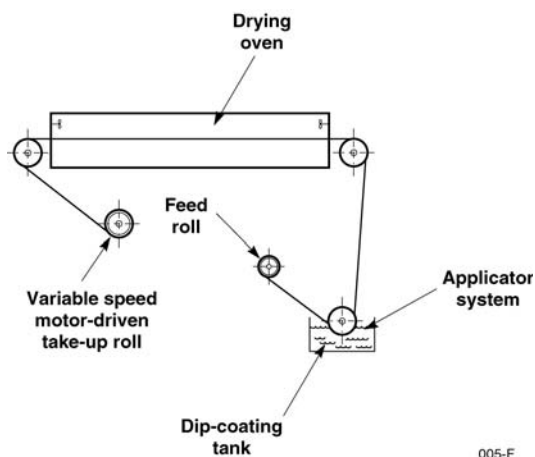


Figure 5. Schematic diagram of MTR's thin-film coating machine.

Membrane thickness can be varied by adjusting the concentration of the coating solution and the coating conditions. Normally, the thickness of the selective layer on a composite membrane is

determined by comparing the flux of a composite membrane stamp with that of a homogeneous film of known thickness. Because of the complex nature of the polymer electrolyte facilitated transport membrane, it is somewhat difficult to determine thickness in this manner. Instead, we used electron micrograph images, such as that shown in Figure 3, to estimate the thickness of the selective layer. The selective layer coated from a 2 wt% Pebax[®] 2533+AgBF₄ in ethanol solution was ~2 μm thick.

3.2 Membrane Stamp Permeation Measurements

Figure 6 shows the system used to test Pebax[®] 2533+AgBF₄ composite membrane stamps (area: 12.6 cm²) with gas mixtures. Each stamp was tested with a 50/50 ethylene/ethane mixture at a feed pressure of 50 psig and a permeate pressure of 0 psig at 23°C unless otherwise noted. The compositions of the feed, residue and permeate gases were analyzed with an on-line gas chromatograph equipped with a thermal conductivity detector (TCD). Typically, the system is operated at 1% stage cut (where stage cut equals the permeate flow rate divided by the feed flow rate), so that the compositions of the feed and residue streams are essentially equivalent.

Because the permeation properties of silver salt facilitated transport membranes have been found to depend on membrane preparation history, the method of measurement, and time, it is important to compare results for stamps under similar conditions with similar histories. After coating, each sample was dried in an oven at 50°C for one hour. The sample was then placed in the test cell and operated at 1% stage cut for 30 minutes before a measurement was taken. The value obtained at this time was taken as the initial or time zero reading.

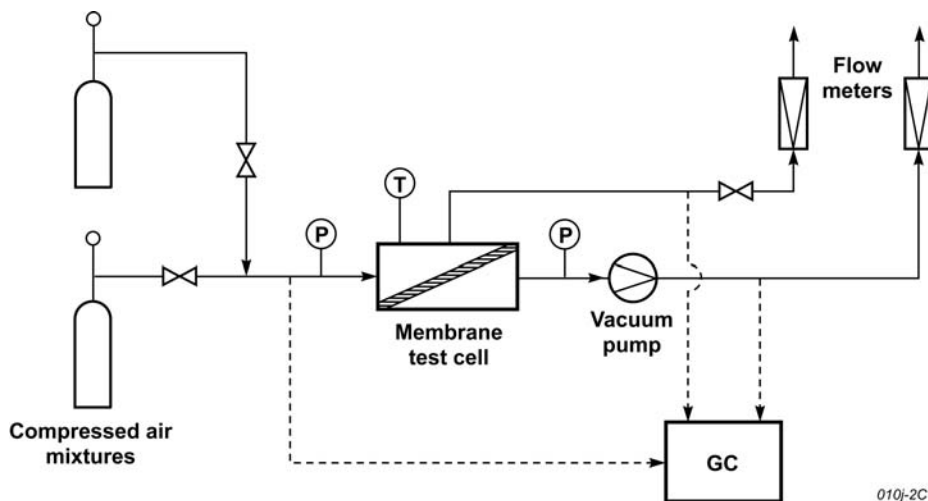


Figure 6. Flow diagram of the mixed-gas permeation test system.

Early in this program, we realized that it would be necessary to test a large number of membrane stamps for long periods of time in aging experiments. Consequently, a custom re-circulating, multi-cell permeation test system was built for this project. This system is described in Section 5.

4. INITIAL PERMEATION AND SORPTION PROPERTIES OF SILVER SALT FACILITATED TRANSPORT MEMBRANES

4.1 Effect of AgBF₄ Content on the Initial Pure and Mixed-Gas Properties of Pebax[®] 2533+AgBF₄ Membranes

Previous work at MTR has shown that the addition of AgBF₄ (silver tetrafluoroborate) to Pebax[®] 2533 (a block copolymer of nylon 12 and tetramethylene oxide) dramatically increases olefin/paraffin selectivities in membranes fabricated from these materials. For example, membranes made from Pebax[®] 2533 without AgBF₄ have virtually no selectivity for ethylene over ethane. In contrast, pure-gas ethylene/ethane selectivities of >100 and mixed-gas C₂ selectivities of >30 are commonly observed in Pebax[®] membranes containing 80 wt% AgBF₄. The high selectivity of Pebax[®]+AgBF₄ membranes results from the fact that AgBF₄ addition reduces paraffin permeance and, at high enough loadings, increases olefin permeance through membranes. These transport effects are caused by the presence of dissolved Ag⁺ ions in the membrane that selectively and reversibly complex olefin molecules. In doing so, the Ag⁺ ions enhance olefin transport rates, while increasing the cohesive energy density of the matrix and reducing the permeance of non-facilitated molecules (paraffins and other 'inert' species). Despite this understanding, at the inception of this project there was very little quantitative information on the effect of AgBF₄ content on the transport rates of common gases through facilitated transport membranes. Consequently, our first efforts were directed at developing a basic set of performance data to provide this information.

Figure 7 presents the effect of AgBF₄ content in Pebax[®] 2533 composite membranes on the pure-gas permeances of hydrogen (H₂), oxygen (O₂), nitrogen (N₂), methane (CH₄), and carbon dioxide (CO₂). These data are also summarized in Table 1. As expected, the data confirm that increasing amounts of AgBF₄ reduce the permeances for all of these non-facilitated gases. The largest decrease in permeance with increasing AgBF₄ content occurs for methane, the largest molecule in this group. This result indicates that AgBF₄ increases the size-sieving nature of Pebax[®] 2533, which is consistent with the idea that Ag⁺ ions increase the cohesive energy density of the matrix. It is believed that Ag⁺ ions can form weak complexes with polar ether groups in the polymer backbone. These complexes function as transient cross-links that restrict polymer chain mobility. Consequently, the diffusion coefficients of permeating molecules are reduced, with larger species being affected to a greater extent, leading to a more size-selective membrane.

Table 1. Effect of AgBF₄ Content on Pure-Gas Permeances of Inert Gases in Pebax[®] 2533 Membranes

| AgBF ₄ Content (wt%) | Pure-Gas Permeances (gpu) | | | | |
|---------------------------------|---------------------------|----------------|----------------|-----------------|-----------------|
| | H ₂ | N ₂ | O ₂ | CH ₄ | CO ₂ |
| 0 | 12 | 1.4 | 4.2 | 7.5 | 5.0 |
| 20 | 3.9 | 0.3 | 0.9 | 0.6 | 1.8 |
| 40 | 4.0 | 0.3 | 0.7 | 0.3 | 1.1 |
| 67 | 2.0 | 0.1 | 0.3 | 0.1 | — |
| 80 | 2.0 | 0.04 | 0.08 | 0.02 | 0.4 |

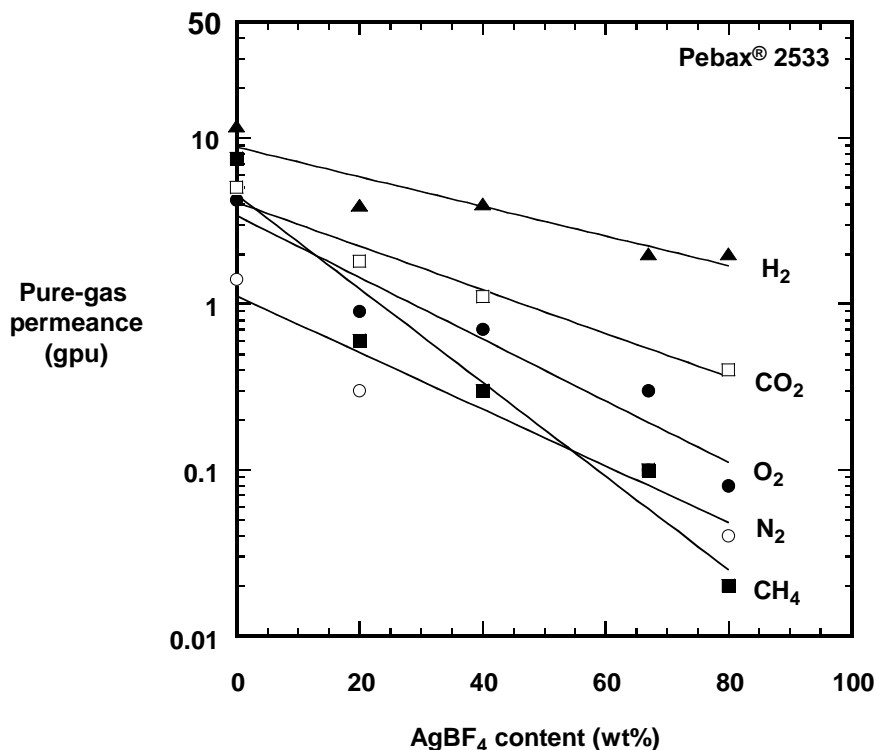


Figure 7. Pure-gas permeances in Pebax[®] 2533+AgBF₄ composite membranes as a function of AgBF₄ content in the dried selective layer. All measurements were taken at room temperature with 100 psig feed pressure and 0 psig permeate pressure. All coating solutions contained a small amount (<1 wt%) of H₂O₂/HBF₄ stabilizer.

Consistent with this interpretation, the permeances of the larger paraffins, ethane and propane, decrease at an even faster rate than that of methane as AgBF₄ content increases, as demonstrated in Figure 8. For example, propane (C₃H₈) permeance decreases by two orders of magnitude as AgBF₄ content increases from 0 to 40 wt% in Pebax[®] 2533, and is too low to be measured at higher silver salt concentrations. Also shown in Figure 8 is the effect of AgBF₄ content on ethylene and propylene (C₃H₆) pure-gas permeances. Like the non-facilitated gases, at low silver loadings the permeances of the olefins decrease. However, at higher silver loadings, this trend reverses, and thereafter olefin permeance increases substantially with increasing silver salt content. The increase in olefin permeance is due to the reversible reaction of olefins with silver ions. This facilitated transport mechanism represents an additional permeation route accessible to olefins but not to paraffins or other species that cannot complex with silver ions. The impact of AgBF₄ content on ethylene and propylene permeance can be explained in terms of the competing effects of increased matrix energy density (which reduces permeance) and facilitated transport (which increases permeance). Above a percolation threshold amount of AgBF₄, transport by complexing with silver ions dominates – perhaps reflecting the need for a minimum density of Ag⁺ ions in the membrane to allow site-to-site hopping of olefin molecules. Interestingly, the threshold appears to occur at different silver loadings for different olefin molecules.

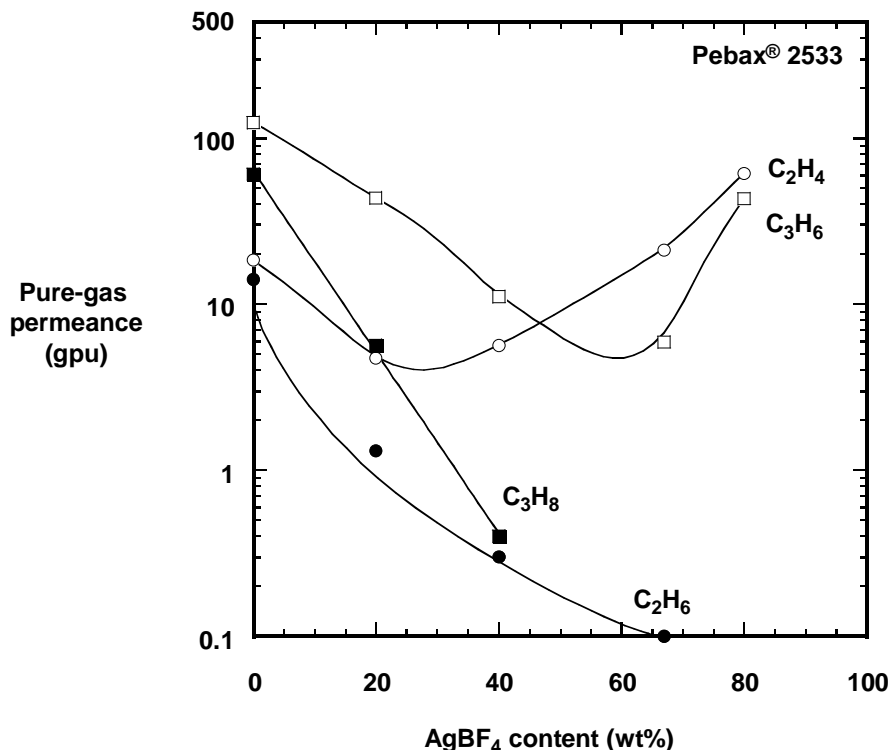


Figure 8. Pure-gas olefin and paraffin permeances in Pebax[®] 2533+AgBF₄ composite membranes as a function of AgBF₄ content in the dried selective layer. All measurements were taken at room temperature with 50 psig feed pressure and 0 psig permeate pressure. All coating solutions contained a small amount (<1 wt%) of H₂O₂/HBF₄ stabilizer.

Figure 9 compares the effect of AgBF₄ loading on the pure- and mixed-gas permeances of ethane and ethylene. For the facilitated gas, ethylene, the permeation behavior in pure- and mixed-gas experiments is very similar. In both cases, there is a percolation threshold around 30 wt% AgBF₄, beyond which permeances increase significantly with increasing silver salt content. For the non-facilitated gas, ethane, there is more difference between the pure and mixed-gas results. In both cases, ethane permeance decreases monotonically with increasing AgBF₄ loading; however, the pure-gas permeance decreases significantly more than the mixed-gas permeance. For instance, at AgBF₄ loadings of greater than 60 wt%, pure-gas ethane permeance is more than an order of magnitude lower than mixed-gas ethane permeance.

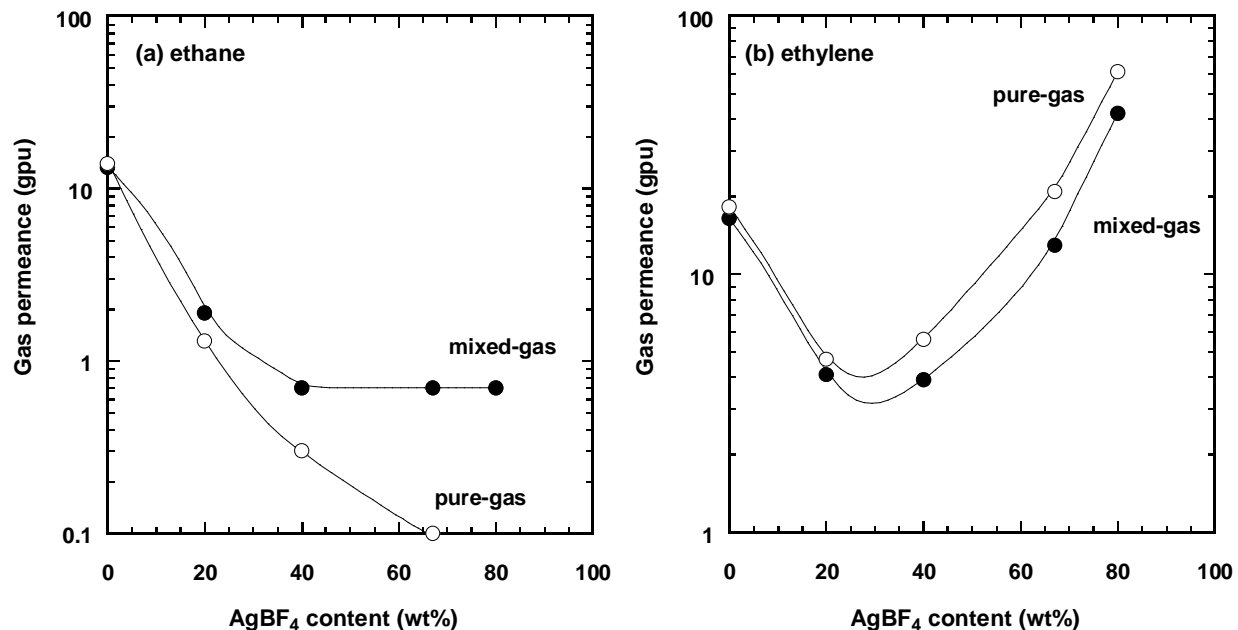


Figure 9. Pure- and mixed-gas (a) ethane and (b) ethylene permeances in Pebax[®] 2533+ AgBF₄ composite membranes as a function of AgBF₄ content in the dried selective layer. Pure-gas data collected at a feed pressure of 50 psig and 0 psig permeate pressure. Mixed-gas data for a 65/35 C₂H₄/C₂H₆ mixture operating at 50 psig feed, 0 psig permeate and <1% stagecut.

The higher ethane permeance in mixture experiments is caused by swelling of the polymer matrix resulting from extensive sorption of ethylene. This behavior is often seen in facilitated membrane systems, and results in lower mixed-gas olefin/paraffin selectivities as compared to ideal values (calculated from pure-gas experiments). Figure 10 illustrates this point, showing that mixed-gas ethylene/ethane selectivities are lower than the corresponding pure-gas selectivities for all AgBF₄ loadings, and this difference increases with increasing silver salt concentration.

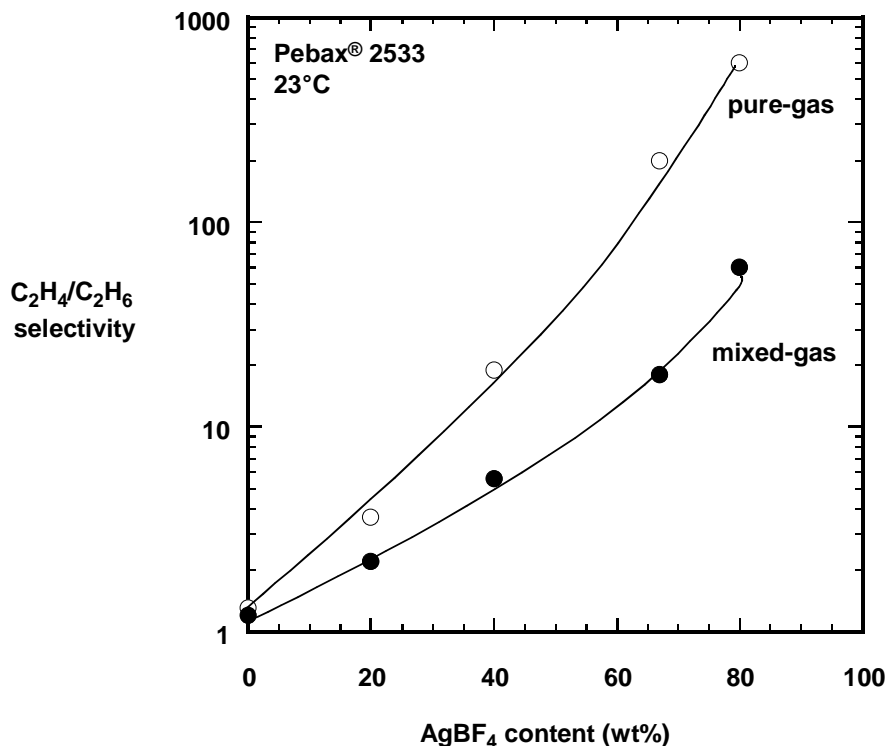


Figure 10. Pure- and mixed-gas ethylene/ethane selectivities in Pebax[®] 2533+AgBF₄ composite membranes as a function of AgBF₄ content in the dried selective layer. Pure-gas data were collected at a feed pressure of 50 psig and 0 psig permeate pressure. Mixed-gas data are for a 65/35 C₂H₄/C₂H₆ mixture operating at 50 psig feed, 0 psig permeate and <1% stagecut.

The Figure 10 results, showing an increase in mixed-gas ethylene/ethane selectivities with increasing AgBF₄ content, even at low silver loadings, differ from our previous results which showed an increase in selectivity only at high silver salt loadings. A comparison of our new data obtained in this project (data set R) with older results (data set A) from a previous NSF project is shown in Figure 11.

The reasons for the performance differences are related to membrane treatment history and measurement time. Olefin permeation rates and olefin/paraffin selectivities in silver salt membranes are time dependent. In general, olefin permeances and olefin/paraffin selectivities decrease over time. This behavior is related to a number of factors including changes in the amount of solvent or atmospheric water present in the membranes, reduction of silver carrier ions, and olefin-induced structural changes that occur in the membranes over time. These issues will be discussed in more detail in Section 5. Although the treatment history and measurement time for our previous results shown in Figure 11 (data set A) are unknown, the lower selectivities are consistent with aged membranes.

To compare membrane properties throughout this report, unless otherwise stated, olefin permeances and olefin/paraffin selectivities represent initial or as-prepared values (measured

after drying freshly-coated membranes for 1 hour at 50°C, then exposing the membranes to the standard feed mixture for 30 minutes at <1% stagecut). Time-dependent permeation properties will be clearly identified as such.

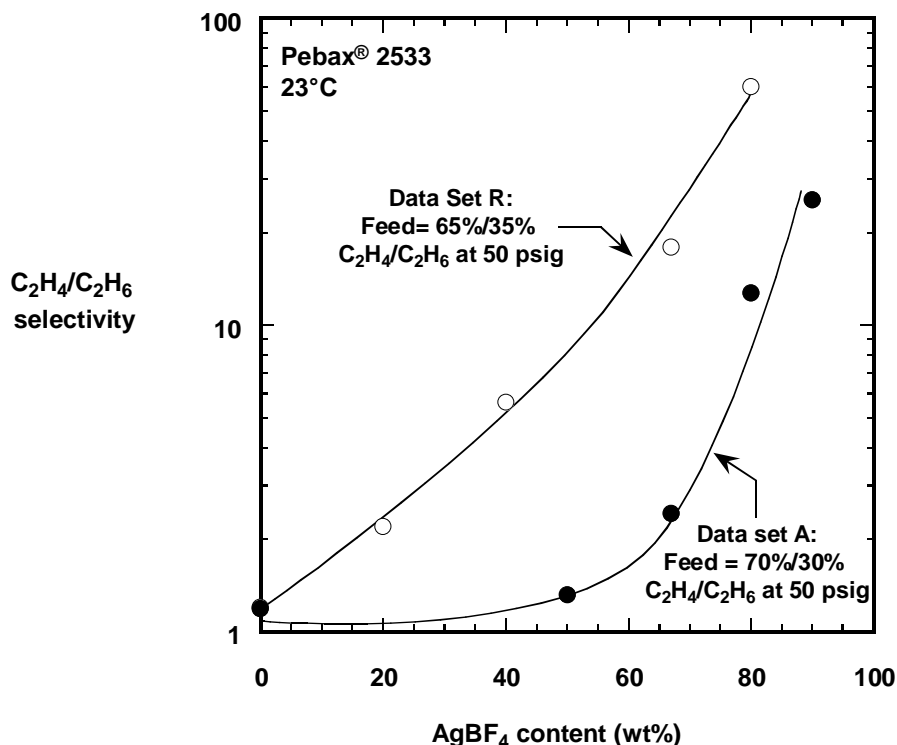


Figure 11. Comparison of data sets for mixed-gas ethylene/ethane selectivities in Pebax[®] 2533+AgBF₄ composite membranes as a function of AgBF₄ content. All experiments were conducted at 0 psig permeate and <1% stagecut. Data set R measurements were taken after 1 hour oven drying followed by 30 minutes of mixed-gas permeation. Sample preparation history and measurement time are unknown for data set A.

4.2 Effect of Multi-Component Feed Mixtures and Pressure on the Initial Permeation Properties of Pebax[®] 2533+AgBF₄ Membranes

Pebax[®] 2533 composite membranes containing 80 wt% AgBF₄ were evaluated with binary and four-component gas mixtures at different feed pressures. Figure 12 illustrates the impact of feed pressure on binary mixed-gas ethylene/ethane permeances and selectivity. Often, the selectivity of facilitated transport membranes will decrease with increasing feed pressure because the carrier species becomes saturated. This appears to be the case for our Pebax[®] 2533+80 wt% AgBF₄ membranes. As feed pressure is increased, ethylene permeance decreases linearly, but ethane permeance is roughly constant. As a result, ethylene/ethane selectivity also drops linearly, as seen in Figure 12.

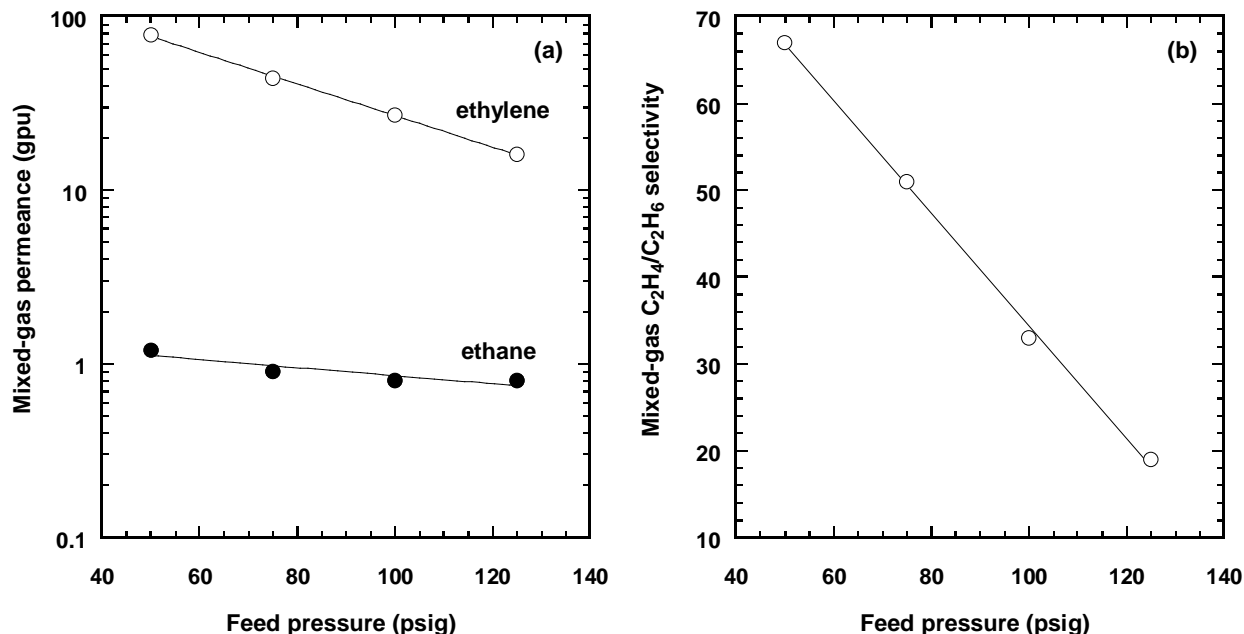


Figure 12. Mixed-gas ethane/ethylene (a) permeances and (b) selectivities in Pebax[®] 2533+80 wt% AgBF₄ composite membranes as a function of feed pressure. All experiments conducted at 0 psig permeate, room temperature, and <1% stagecut with a 65/35 C₂H₄/C₂H₆ mixture.

Although carrier saturation effects are observed, Pebax[®] 2533+80 wt% AgBF₄ membranes still yield high selectivities at industrially relevant pressures. For example, a selectivity of about 30 is obtained for an ethylene/ethane feed mixture at 100 psig. This differentiates these membranes from other facilitated membrane systems where high selectivities are observed only at low, even sub-atmospheric pressures.

Figure 13 presents the effect of feed pressure on the permeances and selectivities of Pebax[®] 2533+80 wt% AgBF₄ membranes for a four-component mixture comprised of carbon dioxide, methane, ethane, and ethylene. The mixed-gas permeances of these species follow the order: C₂H₄ > CO₂ > CH₄ > C₂H₆. As expected, the facilitated gas—ethylene—is the most permeable species, followed by the other gases in the order of increasing molecular size. In comparing the data in Figures 7 and 13, it is evident that the mixed-gas permeances of the non-facilitated gases (CO₂, CH₄, and C₂H₆) are roughly an order of magnitude higher than their pure-gas permeances. This result is consistent with the idea that sorption of ethylene during co-permeation swells the membrane, allowing non-facilitated gases to permeate faster. Also shown in Figure 13 is the effect of feed pressure on ethylene/ethane selectivity. Similar to the data for a binary mixture (Figure 12), mixed-gas ethylene/ethane selectivity decreases with increasing feed pressure for the four-component mixture. The ethylene/ethane selectivities observed for the four-component mixture are significantly lower than those observed in the binary case. The reasons for this difference are not known.

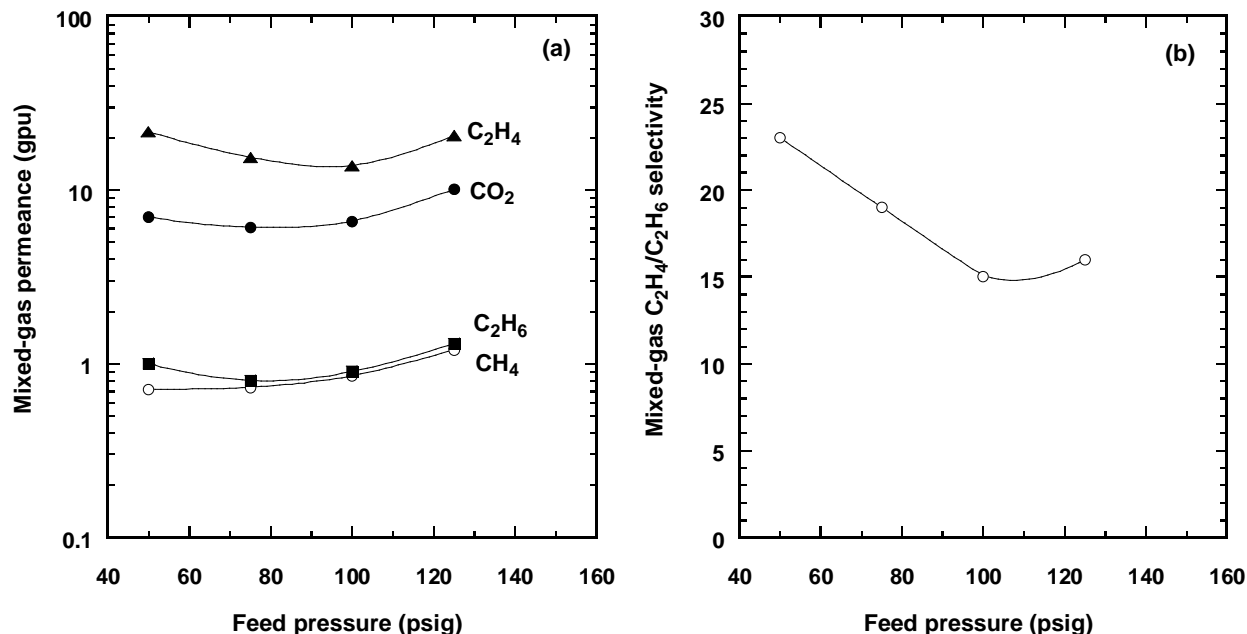


Figure 13. Four-component mixed-gas permeances and ethylene/ethane selectivities in Pebax[®] 2533+80 wt% AgBF₄ composite membranes as a function of feed pressure. All experiments were conducted at 0 psig permeate, room temperature, and <1% stagecut with a feed mixture composed of 33 mol% ethane / 32% ethylene / 25% methane / 10% carbon dioxide.

4.3 The Impact of Salt Addition on Non-Facilitated Gas Permeances and Selectivities of Pebax[®] 2533 Composite Membranes

To further examine the effect of salt addition on membrane properties, additional Pebax[®] 2533 composite membranes containing salts were prepared and tested with non-facilitated gases. Pure-gas O₂, N₂, CH₄, and CO₂ permeances and selectivities for Pebax[®] 2533 membranes containing AgBF₄, AgNO₃, and the lithium salts LiNO₃ and LiCl are summarized in Table 2. Compared to an unfilled Pebax[®] 2533 membrane, all of the salts except AgNO₃ reduced gas permeances. The extent of this permeance reduction varied depending on the salt. For example, at 30 wt% salt loading, AgBF₄ reduces CO₂ permeance by 67%, LiNO₃ reduces the permeance by only 30% and AgNO₃ appears to slightly increase permeance. These results are likely related to the relative extent to which the salts are disassociated in Pebax[®] 2533. The large BF₄⁻ anion is rather weakly held to Ag⁺ and thus most, if not all, of the silver ions are free to interact with the polymer matrix and increase the cohesive energy density of the matrix. AgNO₃, on the other hand, forms a much tighter bond and is known to be only partially disassociated even in dilute aqueous solution. Consequently, its silver ions are not as free to interact with ether groups in the polymer as those present in AgBF₄. LiNO₃ has a lower dissociation energy than AgNO₃, but higher than that of AgBF₄ and thus has an intermediate effect on permeance.

In addition to reducing gas permeances, incorporating salts into Pebax[®] 2533 membranes generally increases size selectivity. For example, the CO₂/CH₄ and O₂/N₂ selectivities of Pebax[®] 2533 membranes containing 30 wt% LiNO₃ are 15 and 3.5, respectively, compared to 9.2 and 2.7

for the Pebax[®] membrane without salt. This result is consistent with the well-known trade-off relationship between membrane permeance and ability of the matrix to discriminate between molecules based on size differences. As salt is added to the membrane, the polymer cohesive energy density increases, which in turn reduces diffusion coefficients and increases diffusion selectivity. Consequently, the selectivity of the membrane for smaller molecules (O₂ and CO₂) over larger molecules (N₂ and CH₄) increases with salt content.

Table 2. Effect of Salt Addition on Permeances and Selectivities of Pebax[®] 2533 Composite Membranes

| Membrane type | Pure-gas Permeances | | | | Pure-gas Selectivity | |
|---|---------------------|----------------|-----------------|-----------------|--------------------------------|----------------------------------|
| | N ₂ | O ₂ | CH ₄ | CO ₂ | O ₂ /N ₂ | CO ₂ /CH ₄ |
| Pebax [®] 2533 / PVDF | 1.6 | 4.4 | 5.4 | 50 | 2.7 | 9.2 |
| Pebax [®] 2533 + 20 wt% LiNO ₃ / PVDF | 0.85 | 2.6 | 2.8 | 28 | 3.1 | 9.6 |
| Pebax [®] 2533 + 30 wt % LiNO ₃ / PVDF | 0.77 | 2.6 | 2.4 | 35 | 3.5 | 15 |
| Pebax [®] 2533 + 30 wt% LiCl / PVDF | 0.75 | 2.2 | 2.2 | 27 | 2.9 | 13 |
| Pebax [®] 2533 + 30 wt% AgNO ₃ / PVDF | 2.2 | 6.1 | 7.5 | 57 | 2.8 | 7.6 |
| Pebax [®] 2533 + 30 wt% AgBF ₄ / PVDF | - | - | 1.7 | 17 | - | 10 |
| Pebax [®] 2533 + 80 wt% AgBF ₄ / PVDF | - | - | 1.0 | 7.0 | - | 7.0 |

4.4 Olefin and Paraffin Sorption in Pebax[®] 2533+AgBF₄ Membranes

Figure 14 presents ethylene and ethane sorption isotherms in Pebax[®] 2533 films containing varying amounts of AgBF₄. As expected, the addition of AgBF₄ dramatically increases the amount of ethylene sorbed by Pebax[®] 2533. For example at 10 atm, Pebax[®] 2533 containing 70 wt% AgBF₄ sorbs about 20 times as much ethylene as pure Pebax[®] 2533 (200 vs 10 cm³(STP)/cm³ polymer). This increase in ethylene sorption capacity is due to complexation of the olefin by dispersed silver ions. Figure 14(b) shows that ethane solubility is depressed by the addition of AgBF₄. For this non-interacting gas, the dominant effect of AgBF₄ addition is to increase the polymer cohesive energy density. The resulting decrease in ethane sorption is an example of the “salting-out” phenomenon. Interestingly, these sorption results suggest that even small amounts of AgBF₄ should yield membranes with much higher ethylene/ethane selectivities than pure Pebax[®] 2533. The fact that this often does not happen (see Figure 2 for example) suggests that ethylene may be held rather tightly by silver ions (yielding very low apparent ethylene diffusion coefficients). We will return to this issue in section 5.

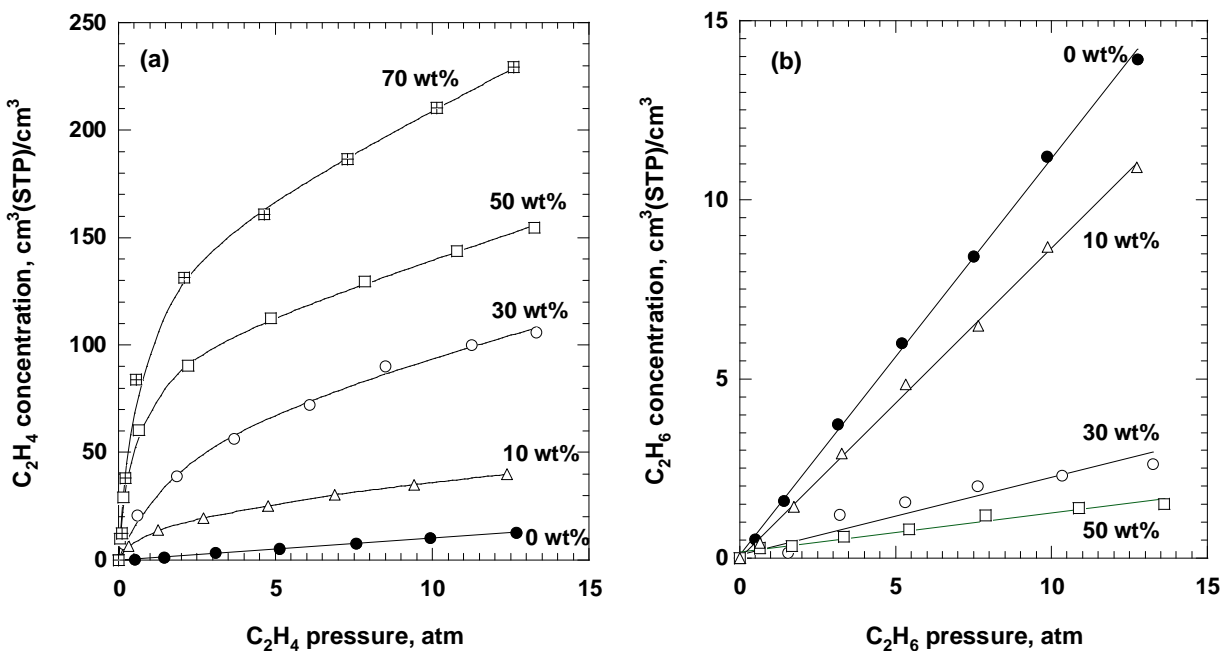


Figure 14. (a) Ethylene and (b) ethane sorption isotherms in Pebax® 2533 films containing varying amounts of AgBF₄ at 25°C.

The amount of ethylene sorbed by Pebax® 2533 membranes containing large amounts of silver salt is extremely high. Figure 15(a) illustrates this fact by comparing ethylene sorption in Pebax® 2533 containing 70 wt% AgBF₄ with that in poly(1-trimethylsilyl-1-propyne) (PTMSP). PTMSP is a high-free-volume glassy material with the highest sorption capacity of all known polymers. Nevertheless, Pebax® 2533+70 wt% AgBF₄ sorbs two to three times more ethylene than PTMSP. Another way to view ethylene sorption in silver salt membranes is shown in Figure 15(b). Here, ethylene sorption is expressed as the volume percent of liquid ethylene in the polymer/salt blend. At ethylene pressures typically encountered on the feed side of a Pebax® 2533+AgBF₄ composite membrane, the amount of ethylene in the selective layer exceeds 25 vol%. In this situation, the polyether/silver ion blend is practically swimming in a sea of ethylene. This highly plasticized environment suggests that some mobility of polymer and ionic species within the membrane is likely. Such mobility has implication for long-term membrane stability especially under pressure cycling.

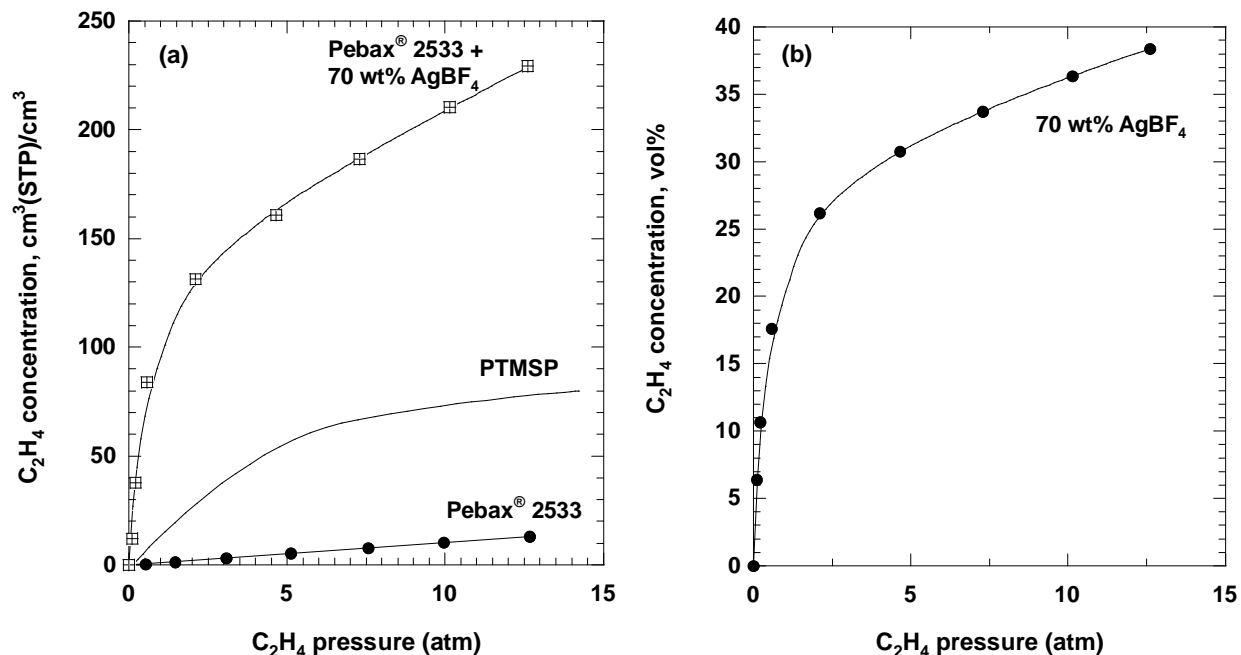


Figure 15. (a) Ethylene sorption isotherms in Pebax® 2533, Pebax® 2533 containing 70 wt% $AgBF_4$, and high free volume glassy PTMSP at 25°C. (b) Ethylene sorption in Pebax® 2533 containing 70 wt% $AgBF_4$ expressed as volume percent of sorbed liquid ethylene.

5. TIME-DEPENDENT PERMEATION IN SILVER SALT FACILITATED TRANSPORT MEMBRANES

5.1 Background and Initial Findings

The long-term instability of facilitated transport membranes has previously been recognized as the key obstacle preventing commercial use of this technology. At the inception of this project, the general belief was that deactivation of the silver ion carriers by reducing gases (H_2 , H_2S , C_2H_2) was the primary cause of membrane instability. The effect of these carrier poisons, and a novel solution to mitigate their impact, are discussed in Section 6. In this section, previously undocumented time-dependent membrane behavior not related to carrier poisoning is discussed.

Early in this program, we recognized that examining performance changes over long time frames in an efficient manner required a re-circulating, multi-cell permeation system. Figure 16 shows a picture of the system built for this purpose. After calibrating the new system, the first topic of investigation was the effect of time and $AgBF_4$ content on membrane selectivity with an ideal ethylene/ethane mixture (no carrier poisons). Previously, two data sets were shown (Figure 11) describing the impact of $AgBF_4$ concentration on membrane selectivity that were seemingly contradictory. One set of data (labeled set A) appeared to show a silver concentration percolation threshold, below which the membranes had essentially no olefin/paraffin selectivity. The second data set (labeled set R) showed a monotonic increase in olefin/paraffin selectivity as $AgBF_4$ concentration increased. It was suggested that this difference might be related to

differences in membrane preparation or the measurement time. Both sets of data in Figure 11 were measured in a single-pass experiment where the feed gas is drawn directly from a gas cylinder. The data set R results were collected after permeating gas at 1% stage cut for 30 min, while the measurement time for set A was unknown.



Figure 16. Re-circulating, multi-cell membrane test system.

Figure 17 presents mixed-gas selectivity data for membranes containing different AgBF_4 concentrations, measured over a period of five days on the re-circulating permeation system. The initial data, collected a few hours after startup, appear very similar to data set R in Figure 11. Over a period of several days, as the system runs continuously, mixed-gas selectivities decrease, especially at AgBF_4 contents below 60 wt%. After four days, the effect of silver content on mixed-gas ethylene/ethane selectivity is very similar to that observed for data set A. For example, the sample containing 40 wt% AgBF_4 , which originally had an ethylene/ethane selectivity of 14, has a selectivity of 1.2 after four days of continuous operation. This is consistent with the values measured in data set A. The membranes containing 80 wt% AgBF_4 appear to be less affected by this reduction in selectivity over time. However, even at this high silver concentration, performance does deteriorate over the course of the experiment.

The reasons for this performance decrease over time with an ideal gas mixture are discussed in the remainder of this section. Initially, a number of possible explanations were proposed, including

- the presence of residual solvent or atmospheric water in the freshly-coated membranes,
- morphological changes in the polymer-salt blend upon olefin exposure, or
- slow carrier salt recrystallization during operation.

All of these mechanisms may play some role, although as will be shown, the evidence points largely toward olefin-induced morphological changes in the polymer-salt blend. This phenomenon not only results in a decrease in olefin/paraffin selectivity over time (even at 80 wt% AgBF_4), but perhaps more importantly, it also causes a significant decrease in olefin permeance, as discussed below.

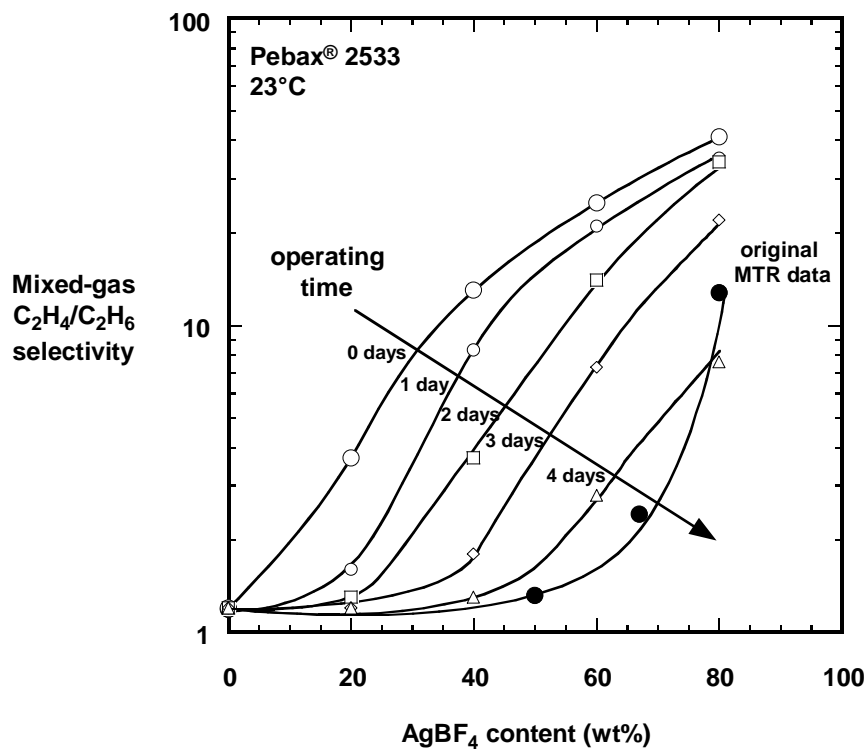


Figure 17. Effect of operating time and AgBF_4 content on the mixed-gas ethylene/ethane selectivity of Pebax® 2533 composite membranes.

Figure 18 presents the effect of operating time on ethylene permeance for membranes containing various levels of AgBF_4 . Two different types of time-dependent behavior are evident:

- the 0 and 20 wt% AgBF_4 samples exhibit stable ethylene permeances, and
- the higher silver salt content samples demonstrate decreasing permeances over time.

The initial (time zero) impact of silver salt on ethylene permeance can be rationalized as the interplay between two competing effects. The addition of an ionic salt species increases the cohesive energy density of the polymer matrix, which decreases diffusion coefficients. Increased cohesive energy density is the dominant effect as AgBF_4 content is increased from 0 to 20 wt%, and consequently, ethylene permeance decreases. At higher silver salt contents, increased

cohesive energy density (which reduces permeance) is offset by the increased carrier density that allows site-to-site hopping of olefin molecules (which increases ethylene permeance). As a result, the initial ethylene permeance exhibits the following trend with silver salt content:

$$80 \text{ wt}\% > 60 \text{ wt}\% > 40 \text{ wt}\% \approx 0 \text{ wt}\% > 20 \text{ wt}\%.$$

Over time, the ethylene permeances of the high silver salt content samples (40, 60, and 80 wt %) decrease substantially. It is this decrease in ethylene permeance that is the primary cause of the selectivity decline illustrated in Figure 17. It is interesting to note that after four days of operation, while the ethylene permeance has decreased in the 40, 60, and 80 wt% AgBF₄ samples, their permeance relative to each other is nearly unchanged (i.e., 80 wt% > 60 wt% > 40 wt%). This result suggests the hopping mechanism of ethylene transport is still operative in the aged membranes because the highest carrier density sample (80 wt %), where ethylene hopping is easiest, retains the highest permeance throughout the test period.

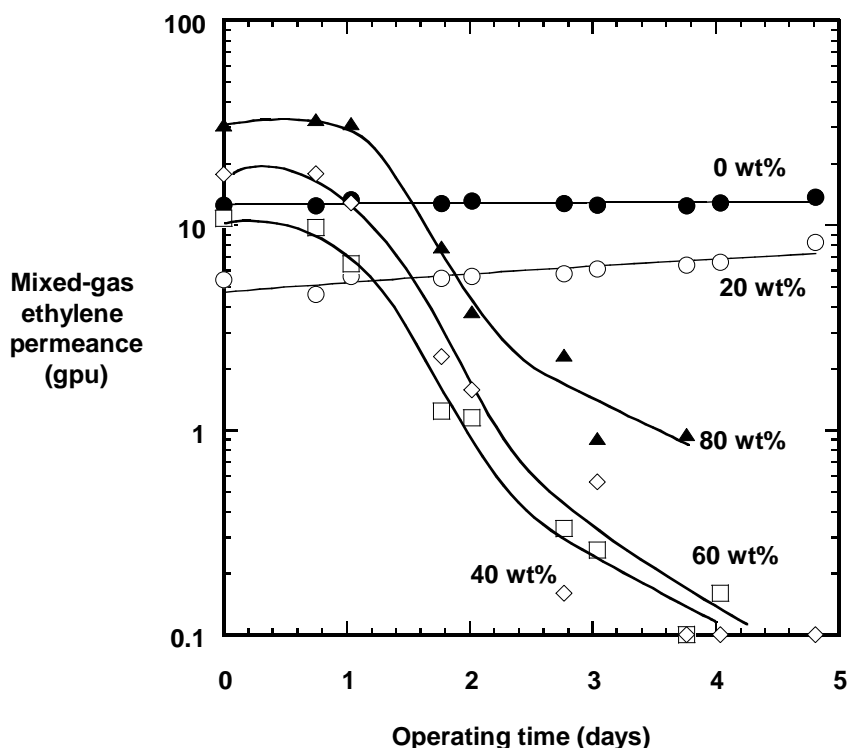


Figure 18. Mixed-gas ethylene permeance as a function of operating time for Pebax® 2533 membranes containing various concentrations of AgBF₄.

Figure 19 presents the effect of operating time on ethane permeance for membranes containing various amounts of AgBF₄. Ethane does not form a complex with silver ions, and consequently, the only impact of increasing silver salt content should be to increase membrane cohesive energy density, which reduces permeance. This is essentially the case, as the initial ethane permeance exhibits the following trend with silver salt content:

$$0 \text{ wt}\% > 20 \text{ wt}\% > 40 \text{ wt}\% \approx 60 \text{ wt}\% \approx 80 \text{ wt}\%.$$

Similar to the ethylene permeance results, ethane permeances in the 0 and 20 wt% AgBF_4 samples are relatively unchanged over the course of the experiment. However, the 40, 60, and 80 wt% AgBF_4 samples exhibit an ethane permeance decline over time, similar to that observed for ethylene. Because ethane cannot form complexes with silver ions, it is not able to access the carrier hopping transport mechanism. The fact that the permeance of the non-facilitated gas (ethane) decreases with time indicates that carrier deactivation is not the cause of the flux decline observed in Figures 18 and 19. Rather, there is something else that affects both the facilitated and non-facilitated species.

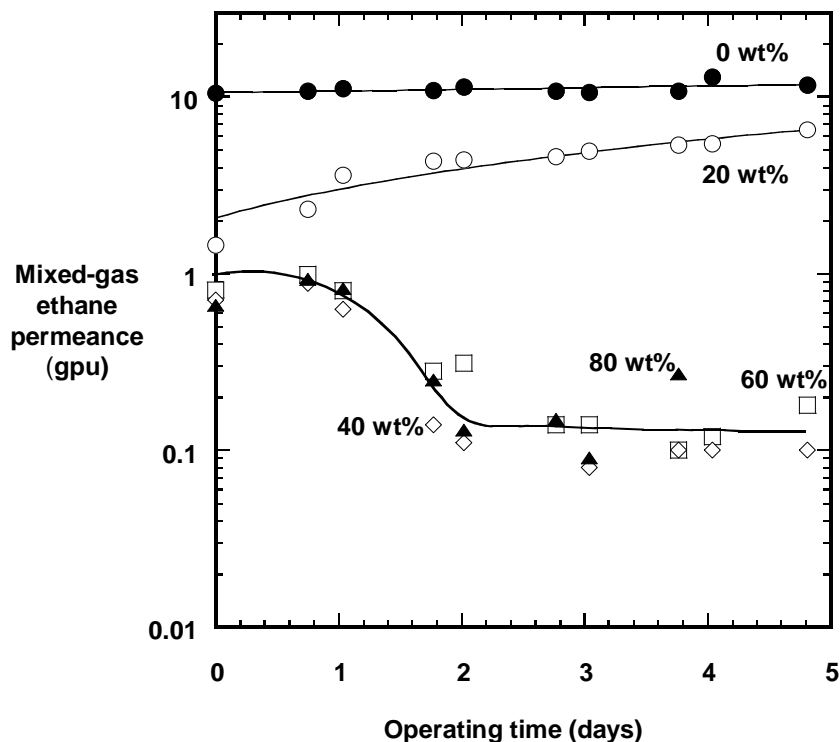


Figure 19. Mixed-gas ethane permeance as a function of operating time for Pebax[®] 2533 membrane containing various concentrations of AgBF_4 .

5.2 High Silver Salt Content Facilitated Transport Membranes are Not Stable Over Time with Ideal Olefin/Paraffin Gas Mixtures

In light of the findings shown in Figures 17-19, additional long-term permeation tests of the baseline membrane (Pebax[®] 2533+80 wt% AgBF_4) were conducted. Figure 20 presents time-dependent facilitated transport membrane results previously obtained at MTR. These data are compared with new results (Figure 21) collected in this program with our recirculating permeation system. Both sets of data are for 80 wt% AgBF_4 in Pebax[®] 2533 composite membranes using an ideal ethylene/ethane gas mixture. The results in Figure 20 show an initial permeance and selectivity decline over a period of two days followed by stable behavior thereafter. In contrast, the data of Figure 21 show a continuous decrease in permeance and selectivity over time. This result is surprising and contrary to previous results for AgBF_4 -based facilitated transport membranes reported here and in the literature.

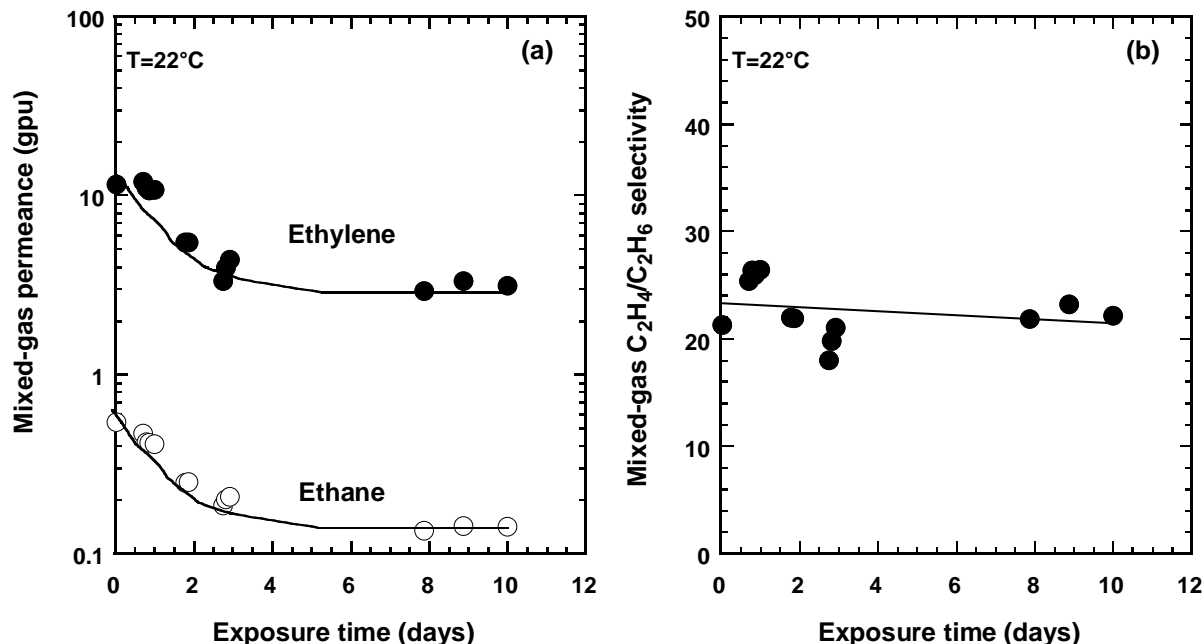


Figure 20. Mixed-gas (a) ethylene and ethane permeances and (b) ethylene/ethane selectivity for Pebax[®] 2533+80 wt% AgBF₄ membranes as a function of time. Measurements were conducted with a 70% ethylene / 30% ethane mixture at a feed pressure of 50 psig. Data were collected in a previous NSF project.

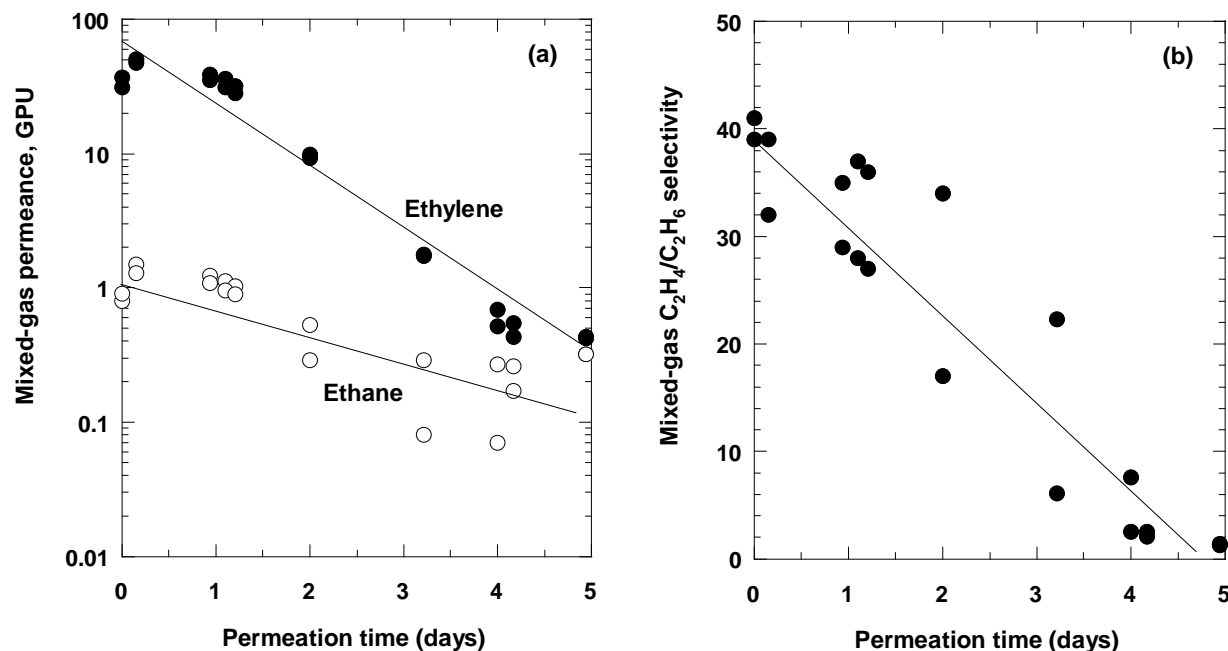


Figure 21. Mixed-gas (a) ethylene and ethane permeances and (b) ethylene/ethane selectivity for Pebax[®] 2533+80 wt% AgBF₄ membranes as a function of time. Measurements were conducted with a 50% ethylene / 50% ethane mixture at a feed pressure of 50 psig on the recirculating permeation test system.

The primary difference between the new and old results is the method of measurement. In all previous studies that we are aware of, mixed-gas permeance in silver salt facilitated transport membranes has been measured using cylinder gas to supply pressure to the feed side of the membrane. For these measurements, a high flow rate of gas must be passed across the feed side of the membrane to prevent depletion of the highly-permeable olefin in the mixture. Typically, the experiment is conducted at <1% stage cut, where >99% of the gas mixture fed to the membrane is vented out the residue side of the permeation cell. In the very few studies of long-term membrane performance, such as our data shown in Figure 20, the residue and permeate valves are typically closed between measurements to conserve the gas mixture. In contrast, for the recirculating permeation system, the residue and permeate gases are combined, compressed, and recirculated to the feed side of the membrane continuously. With this system, the residue and permeate gases can flow constantly without having to vent large amounts of the gas mixture.

The experimental difference in the new and old results obtained can be explained as follows: the x-axis of the data in Figure 20 is actually a measure of feed gas exposure time, while for Figure 21 the x-axis is truly permeation time. It appears that this difference is significant for long-term membrane performance, which will be important to successful industrial use of carrier facilitated membranes. For actual commercial operation, the membrane must run continuously for long permeation times.

To confirm our new results, we ran another long-term mixed-gas stamp test using a different permeation system where test gases are also compressed and recirculated continuously. These results, shown in Figure 22, are consistent with the data shown in Figure 21. The mixed-gas permeances of olefin and paraffin (propylene and propane, respectively) decrease continuously over time. Propylene permeance decreases faster, resulting in a steady decline in membrane selectivity. After six days, the permeances are simply too low to measure accurately.

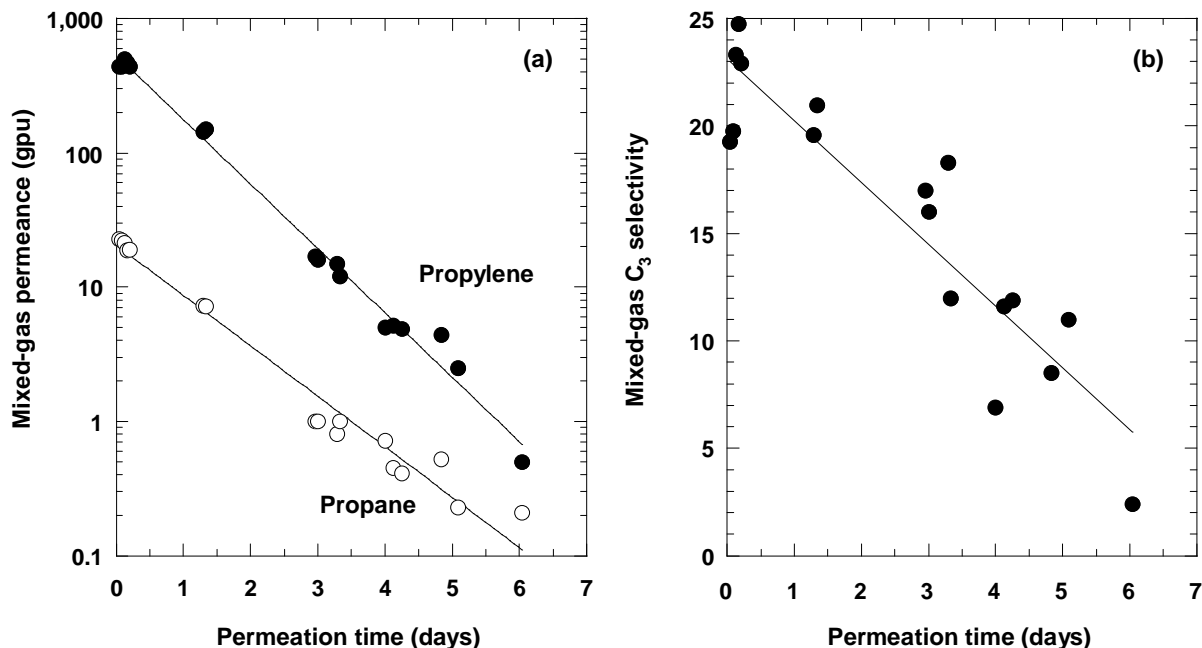


Figure 22. Mixed-gas (a) propylene and propane permeances and (b) propylene/propane selectivity for Pebax[®] 2533+80 wt% AgBF₄ membranes as a function of time. Measurements were conducted with a 50% propylene / 50% propane mixture at a feed pressure of 50 psig using recirculated gas on MTR's "beta" test system.

This new time-dependent membrane behavior when exposed to ideal olefin/paraffin mixtures was surprising and is a significant concern with regard to the viability of using these membranes industrially. To be a cost-competitive separation option, membrane modules must show commercial lifetimes of at least one year. We had anticipated the technical challenge of carrier deactivation by poisons such as hydrogen sulfide and acetylenes. This hurdle, and ways to alleviate its effects are discussed in Section 6. However, performance decline over time with ideal olefin/paraffin mixtures is a serious and separate issue that warranted further study.

5.3 Understanding the Mechanism of Performance Decline in Silver Salt Facilitated Transport Membranes – Olefin Conditioning

Figure 23 presents pure-gas helium permeance as a function of permeation time in silver salt membranes that utilize Pebax[®] 2533 or polyethylene oxide (PEO) as the matrix polymer. This test was conducted to determine whether the permeance of a non-facilitated gas (one that does not complex with Ag⁺ ions) through silver salt membranes is dependent on permeation time when the membrane is not exposed to an olefin. We chose helium as the non-facilitated gas because the pure-gas permeances of most other gases that do not complex with silver ions are too low to accurately measure in membranes containing high concentrations of AgBF₄. The data in Figure 23 show that helium permeance is completely stable in Pebax[®] 2533 and PEO membranes containing 80 wt% AgBF₄, as well as in a control Pebax[®] membrane that does not contain silver salt. This result is in contrast to mixed-gas permeance results for non-facilitated gases when an olefin is present in the mixture. For example, in Figure 21(a), ethane, a non-facilitated gas,

exhibits permeance decline over time when tested in a mixture with ethylene. A similar result is shown in Figure 22(a) for mixed-gas propane permeance. These findings suggest that the presence of an olefin, which can complex with silver ions, causes permeance decline in the membrane and that it alters the membrane in a way that impacts non-facilitated gas permeances.

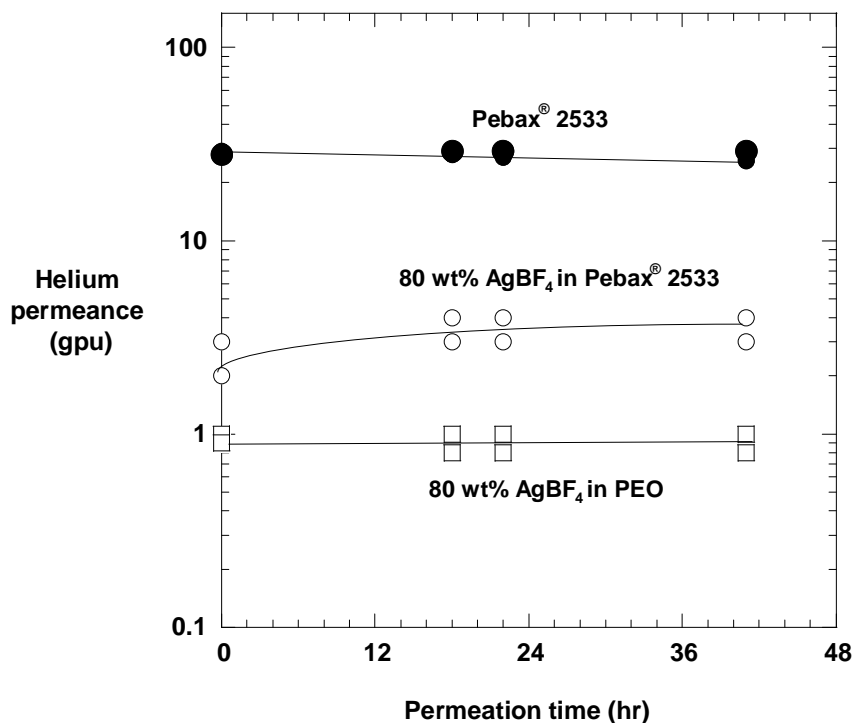


Figure 23. Pure-gas helium permeance as a function of permeation time in silver salt facilitated transport membranes based on Pebax® and polyethylene oxide (PEO).

After 40 hours of permeating helium, the feed gas for the membranes described in Figure 23 was switched to an ethylene/ethane mixture. Figure 24 shows the subsequent mixed-gas ethylene permeance of these membranes as a function of permeation time. The control Pebax® 2533 membrane that does not contain AgBF₄ exhibits stable ethylene permeance throughout the experiment. In contrast, the Pebax® and PEO membranes containing 80 wt% AgBF₄ show significant permeance decline, similar to that illustrated in Figure 21(a). These results indicate that regardless of the polymer matrix used (Pebax® or PEO), olefin-induced performance decline appears to be common for silver salt facilitated transport membranes. Although not shown, the permeance of the non-facilitated gas, ethane, also decreased continuously throughout these mixture experiments.

At the end of the mixed-gas experiment described in Figure 24, the feed gas was switched back to pure helium. Our goal in this experiment was to use helium as a probe molecule and see whether we could detect changes in the membrane structure after it was exposed to ethylene. For the control membrane that does not contain AgBF₄, the helium permeances before and after ethylene permeation were approximately equivalent. In contrast, the helium permeances for the membranes containing 80 wt% AgBF₄ were higher after ethylene permeation. For example, in a

Pebax[®] 2533+AgBF₄ membrane, helium permeance was 3 gpu before the ethylene mixed-gas test and 9 gpu after this experiment. This result confirms that membranes containing silver salt are altered by olefin permeation in a way that impacts gas permeances even after olefin molecules are removed from the membrane. Subsequent attempts to cycle these membranes to investigate the reversibility of the olefin conditioning effect were hindered by the formation of membrane defects. We will return to the issue of reversibility later in this section.

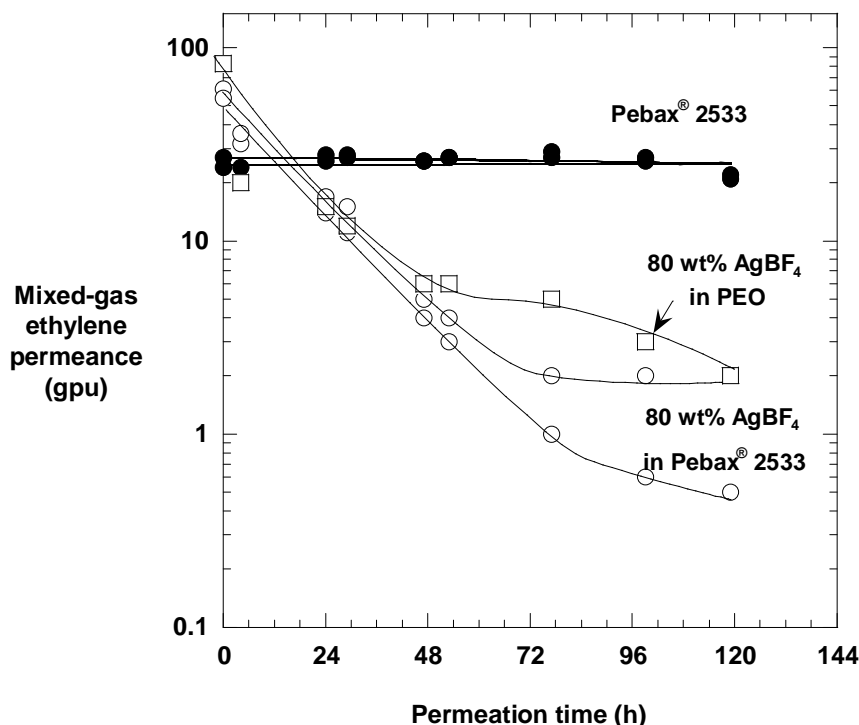


Figure 24. Mixed-gas ethylene permeance as a function of permeation time for two Pebax[®] 2533 membranes without AgBF₄, two Pebax[®] 2533 membranes containing 80 wt% AgBF₄, and a PEO membrane containing 80 wt% AgBF₄.

In the preceding discussion, it was shown that permeation of non-facilitated gases through Pebax[®]+AgBF₄ membranes is completely stable over long periods of time. However, as soon as the membrane begins permeating an olefin, the permeances of all species start to decline over time. This result suggests that the olefin-Ag⁺ ion complexation reaction causes time-dependent behavior. Because the permeances of non-facilitated gases are also affected when co-permeating with an olefin, it appears that the olefin-Ag⁺ ion interaction causes membrane structural changes that occur slowly over time.

Figure 25 presents mixed-gas ethylene permeance in Pebax[®] 2533+80 wt% AgBF₄ membranes as a function of permeation time for three different ethylene feed concentrations.

- When the feed gas is a 50/50 mixture of ethylene/ethane (yielding an ethylene partial pressure of 32.5 psia), the ethylene permeance decreases relatively rapidly. With this mixture, the ethylene permeance decreases by almost two orders of magnitude over 120 hours of permeation.

- When the ethylene concentration in the feed gas is only 15% (and the ethylene feed partial pressure is 9.8 psia), the rate of permeance decline is considerably slower. For example, over a similar period of 120 hours, the ethylene permeance decreases about one order of magnitude.
- Finally, if the ethylene concentration is reduced to 7% (an ethylene partial pressure of 4.5 psia), ethylene permeance is essentially stable during 280 hours of permeation.

These results are consistent with the idea that the olefin complexation reaction with Ag^+ ions is responsible for the time-dependent membrane performance. Previously, we have shown that membranes containing less than 40 wt% AgBF_4 exhibit stable permeation properties, although selectivities are low. Unfortunately, membranes with a high silver salt content, which is necessary for adequate olefin/paraffin selectivities, are not stable in the presence of olefins – the very species the membranes are being used to separate – unless the olefin feed concentration (or partial pressure) is low.

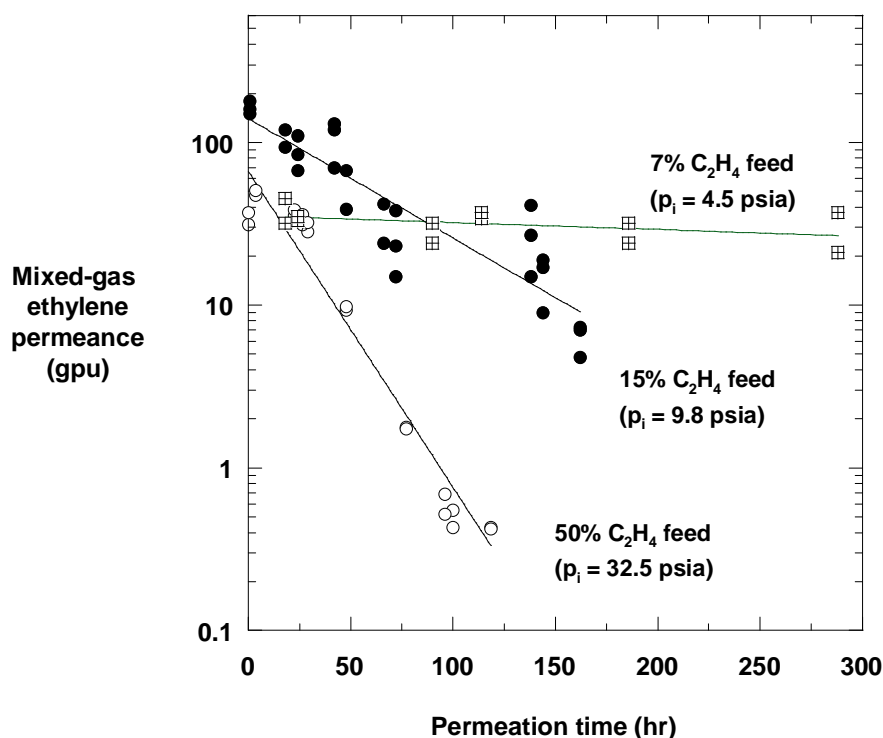


Figure 25. Mixed-gas ethylene permeance in Pebax[®] 2533 membranes containing 80 wt% AgBF_4 as a function of permeation time for three different feed mixtures. Tests were conducted at room temperature with 50 psig feed pressure and 0 psig permeate pressure.

Figure 26 shows the mixed-gas ethylene/ethane selectivities of Pebax[®] 2533+80 wt% AgBF_4 membranes for the same feed conditions described in Figure 25. There is considerable scatter in these data; nevertheless, the general trend appears to be similar to the ethylene permeance results. As the ethylene concentration (or partial pressure) in the feed mixture increases, the rate

of ethylene/ethane selectivity decline increases. Together, the data in Figures 25 and 26 provide further evidence for an “olefin conditioning” effect that is a cause of the decline in facilitated transport membrane performance. Because this conditioning is caused by olefins but affects the permeation of non-facilitated species, it suggests that the silver ion-olefin complexation reaction progressively alters the membrane structure. These changes are accelerated at higher olefin feed pressures or higher silver salt concentrations. Previously (Figure 15), it was shown that Pebax[®] 2533+AgBF₄ membranes sorb tremendous amounts of olefins. For example, at 50 psig ethylene uptake in these membranes is approximately 25 volume percent. One hypothesis is that once large amounts of olefin sorb, the highly swollen membrane allows redistribution of silver ions that result in the formation of ionic clusters (BF₄⁻ and Ag⁺). Such clusters would be a barrier to diffusion for all species, but might have a greater impact on olefins because redistribution of Ag⁺ could interrupt the proposed hopping mechanism of facilitated transport.

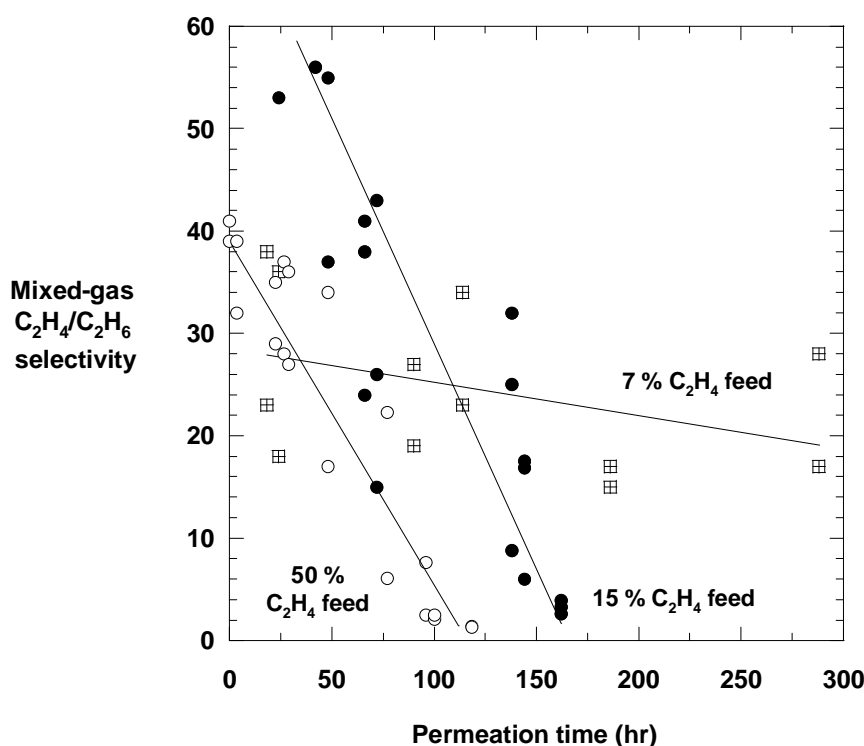


Figure 26. Mixed-gas ethylene/ethane selectivity of Pebax[®] 2533 membranes containing 80 wt% AgBF₄ as a function of permeation time for three different feed mixtures. Tests were conducted at room temperature with 50 psig feed pressure and 0 psig permeate pressure.

5.4 Investigating the Reversibility of Olefin Conditioning

To examine the reversibility of olefin-induced permeance decline, we conducted an experiment where the flow of feed gas is removed from the membrane for a period of time and then restarted. Figure 27 presents pure-gas ethylene permeance as a function of time for a standard Pebax[®] 2533+AgBF₄ membrane. For the first 2.3 hours, the stamp shows a typical decrease in ethylene permeance. After this period of time, the feed gas flow was turned off and the permeate

and residue valves closed. The pressure on the feed side was purged to atmospheric, so that the membrane was universally exposed to 14.7 psia of dry ethylene. The stamp was then held under this static condition for one hour. Thereafter, the feed flow was restarted, feed pressure set to 50 psig, valves opened, and permeation measurements resumed. After the one hour recovery time, membrane ethylene permeance increased four times and then began to decline again. The membrane did not recover completely to the initial permeance, but this may simply be related to the kinetics of the recovery process. This recovery phenomenon may be responsible for previous long-term results that appeared to show stable permeation behavior (see Figure 20, for example). When the feed flow was periodically turned off to conserve gas, it may have allowed the membrane permeance to recover in these tests. We believe that the limited long-term data available in the literature for facilitated olefin transport membranes may be tainted by this effect.

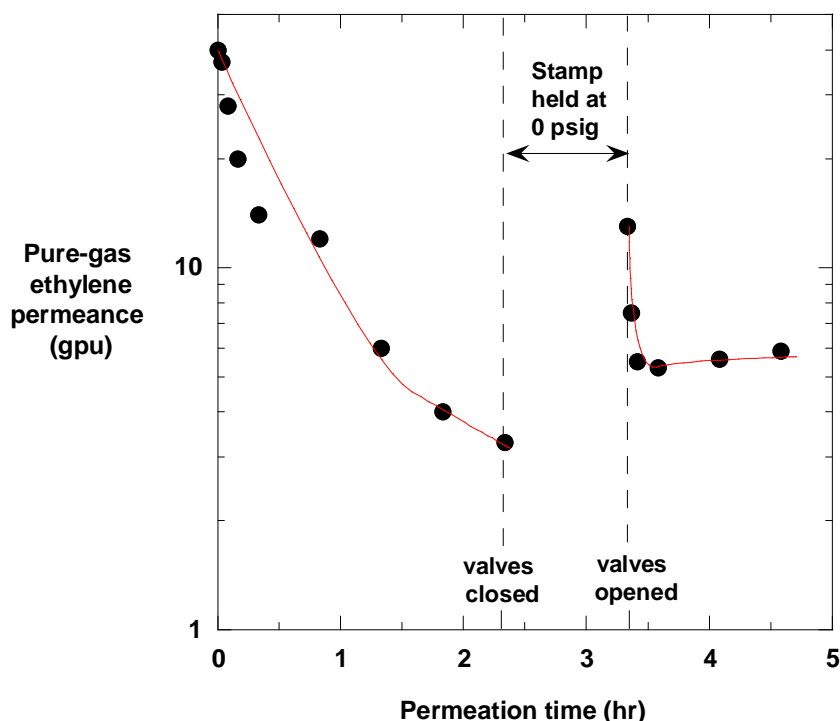


Figure 27. Pure-gas ethylene permeance as a function of permeation time for a standard Pebax[®] 2533+80 wt% AgBF₄ composite membrane. The feed pressure in this experiment was 50 psig and the permeate pressure was 0 psig.

A number of experiments were conducted where membrane samples were periodically evacuated or flows were reversed after olefin conditioning. Table 3 demonstrates the effect of a permeate-side vacuum on facilitated transport membrane performance. For this experiment, after nitrogen permeance was found to be very low (0.3 gpu), pure-gas ethylene permeance was monitored for 2 hours. During this time, ethylene permeance decreased from 46 to 2.6 gpu. At this point, nitrogen permeance was re-measured, the feed pressure was turned off, and a vacuum was applied to the permeate side of the membrane for 5 minutes. After vacuum treatment, nitrogen permeance was measured again and ethylene permeance was monitored over time. The data show that ethylene permeance increases and nitrogen permeance decreases after vacuum

treatment. This result suggests that the olefin conditioning effect is at least partially reversible. Nitrogen permeance probably decreases because the vacuum removes ethylene from the membrane, allowing it to recover from a highly swollen state. Ethylene permeance recovers after vacuum treatment presumably because silver ion-olefin clusters break up, allowing active silver ions to return to something close to their original distribution. We repeated this cycle of ethylene permeation and vacuum treatment five times, and in each case, ethylene permeance increased while nitrogen permeance decreased or remained constant after vacuum exposure. Finally, after 380 minutes (and six vacuum cycles), the nitrogen permeance increased significantly, indicating that the membrane had developed defects.

Table 3. Effect of Vacuum Treatment on Pebax[®]+80 wt% AgBF₄ Membrane Permeance

| Permeation Time (min) | Ethylene Permeance (gpu) | Nitrogen Permeance (gpu) |
|-------------------------------|--------------------------|--------------------------|
| 0 | 46 | 0.3 |
| 30 | 23 | - |
| 60 | 12 | - |
| 90 | 7.3 | - |
| 120 | 2.6 | 1.2 |
| Vacuum for 5 minutes | | |
| 140 | 12 | 0.9 |
| 170 | 2.9 | 1.8 |
| Vacuum cycle repeated 5 times | | |
| 380 | 21 | 33 |
| 410 | 4.2 | 30 |

To further investigate the reversibility of olefin conditioning, we tried periodically reversing the pressure gradient on the membrane and monitoring the effect on ethylene permeance. Table 4 summarizes the data obtained during this experiment.

Table 4. Effect of Reverse-Flow Treatment on Pebax®+80 wt% AgBF₄ Membrane Permeance

| Permeation Time (min) | Ethylene Permeance (gpu) | Nitrogen Permeance (gpu) |
|--|--------------------------|--------------------------|
| 0 | 25 | low |
| 30 | 21 | |
| 60 | 13 | |
| 90 | 8.6 | |
| Flow 5 psig of ethylene on the permeate face of the membrane for 5 minutes | | |
| 110 | 9.7 | |
| 125 | 11 | |
| Flow 5 psig of ethylene on the permeate face of the membrane overnight | | |
| 0 | 35 | 1.1 |
| Flow cycle 3 times | | |
| 255 | 5.1 | 20 |
| Add polymer coating | | |
| 330 | 48 | 0.7 |

Initially, the membrane permeated pure ethylene for 90 minutes until the permeance was less than 10 gpu. The feed side of the cell was then degassed to 0 psig and 5 psig of ethylene was applied to the permeate side of the membrane for 5 minutes. This short reverse-flow treatment seemed to have little impact on membrane properties, so it was repeated for a longer interval of time (overnight). After approximately 12 hours, when the flow was switched back to the normal configuration, the ethylene permeance had increased to a value even higher than the initial permeance. Apparently, reversing the olefin pressure gradient or simply reducing the olefin concentration in the membrane for a significant amount of time allows the membrane structure to revert back to a form that is more like that in the fresh, high-flux membrane.

Similarly to the vacuum exposure results, the membrane exhibited high nitrogen permeance after several cycles of reverse-flow treatment, indicating defects had formed. The formation of defects is probably caused by membrane expansion and contraction resulting from sorption and desorption of ethylene. As mentioned previously, at 50 psig, ethylene uptake in Pebax® 2533 membranes containing 80 wt% AgBF₄ is approximately 25 volume percent. This amount of sorption must cause significant polymer dilation. It is certainly reasonable that the pressure cycling described in Tables 3 and 4 could cause swelling and contraction that encourages membrane defect formation. As a final test to determine whether the bulk of the membrane was still functional, a thin coating of a highly-permeable polymer was applied to the membrane to seal defects. Subsequent testing showed that the membrane nearly returned to initial performance levels. This result demonstrates that in the absence of defects, the olefin conditioning effect is reversible.

5.5 FTIR Analysis of Olefin Conditioning

Previously, it has been shown that FTIR spectroscopy can be used to study the interactions of silver ions dispersed in a polymer matrix. We have employed this technique in an effort to understand the membrane changes that occur after olefin permeation. Figure 28 presents FTIR scans for PEO membranes containing 0, 40, and 80 wt% AgBF_4 . Both PEO and Pebax[®] 2533 contain ether linkages in the polymer backbone that are capable of interacting with silver ions. It is believed that these interactions allow silver ions to remain disassociated in the polymer matrix, and thus active for olefin complexation. The peak corresponding to ether linkages is evident for pure PEO at approximately 1100 cm^{-1} . When AgBF_4 is added to PEO, the ether peak broadens and shifts to lower wave numbers (shifts to the right in the figure). This result is consistent with previous data for silver salt facilitated transport membranes, and indicates that polymer C-O bonds are weakened due to the interaction of ether oxygens with Ag^+ ions.

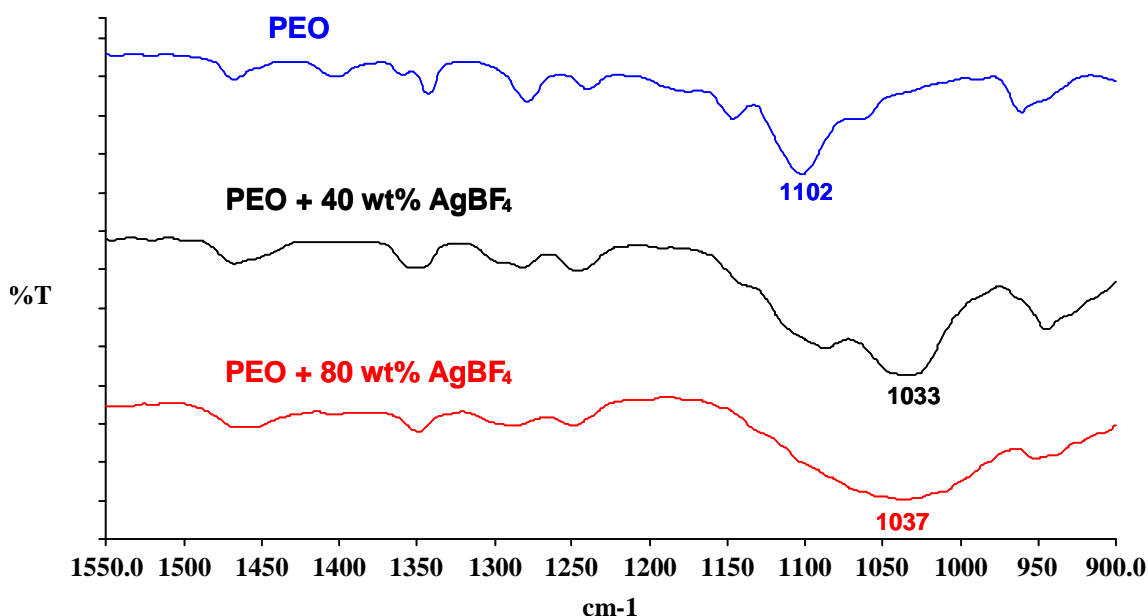


Figure 28. FTIR spectrographic scans of PEO membranes containing 0, 40, and 80 wt% AgBF_4 . %T = Relative percent transmission.

Figure 29 shows FTIR scans for three membranes containing 80 wt% AgBF_4 . One membrane is a fresh, as-cast sample, while the other two are aged membranes – one aged by exposure to the reducing gas hydrogen and the other aged by long-term ethylene permeation. The scans for the two aged membranes are very different. The hydrogen-exposed sample is black, indicating the presence of a large number of reduced Ag^0 particles. In contrast, the ethylene-exposed sample appears nearly white, similar to the fresh, as-cast sample. This visual difference is mirrored in the FTIR results of Figure 29. The hydrogen-aged sample does not show much of a peak in the $1000\text{--}1100\text{ cm}^{-1}$ range, indicating little interaction of Ag^+ ions with ether oxygens, and consistent with the notion that Ag^+ ions have been reduced to Ag^0 particles. In fact, the distinct absence of peaks in the entire range of the hydrogen-aged sample scan suggests that the large number of silver metal particles attenuate the FTIR signal altogether. In contrast, the ethylene permeation sample still shows a discernable ether linkage peak, indicating that at least some active Ag^+ ions

are present. This result adds to the evidence that two separate performance degradation mechanisms are operative in our facilitated transport membranes: in addition to the well-known carrier poisoning or reduction issue, the membranes show apparent olefin-induced performance loss that occurs even though active Ag^+ ions are present in the membrane.

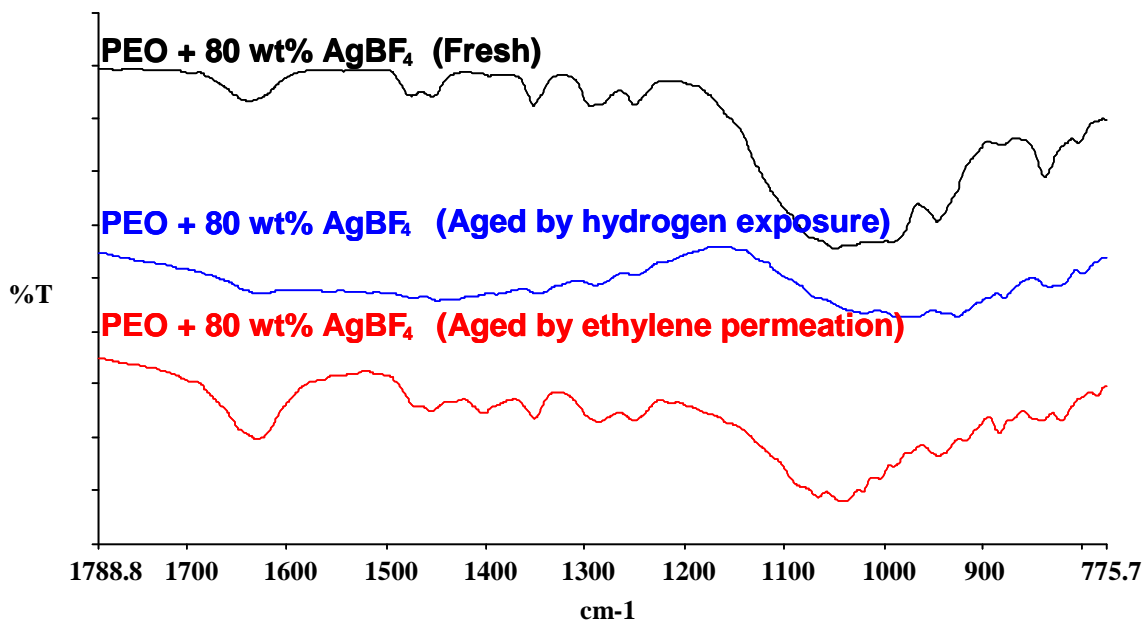


Figure 29. FTIR spectrographic scans of PEO membranes containing 80 wt% AgBF_4 that were freshly prepared, aged by hydrogen exposure, or aged by ethylene permeation. %T = Relative percent transmission.

5.6 Effect of Temperature, Polymer Plasticizers and Humidified Feed

Effect of Temperature

To further investigate the nature of olefin-induced performance decline in our membranes, we studied the effect of temperature on this phenomenon. Figure 30 presents normalized ethylene and ethane mixed-gas permeances in Pebax[®] 2533 containing 80 wt% AgBF_4 as a function of time and temperature. Based on the data in Figure 30(a), mixed-gas ethylene permeance decreases faster as temperature is increased. For example, after one hour of operation, ethylene permeance is reduced to 65% of its initial value at 5°C, while at 40°C the corresponding permeance is only 5% of the starting value. The impact of temperature on ethane permeance decline [Figure 30(b)] is less clear, predominately because the very low permeances (<2 gpu) for this non-facilitated gas make accurate measurements difficult. Nevertheless, certainly for ethylene and perhaps for ethane as well, permeance decline occurs faster at higher temperatures where the membrane matrix is more mobile. Later in the discussion in this section, we show that plasticizers, which increase matrix mobility, also accelerate permeance decline. These results are consistent with the notion that olefin-induced structural changes in the membrane, such as movement or clustering of silver ions, are responsible for the time-dependent membrane behavior.

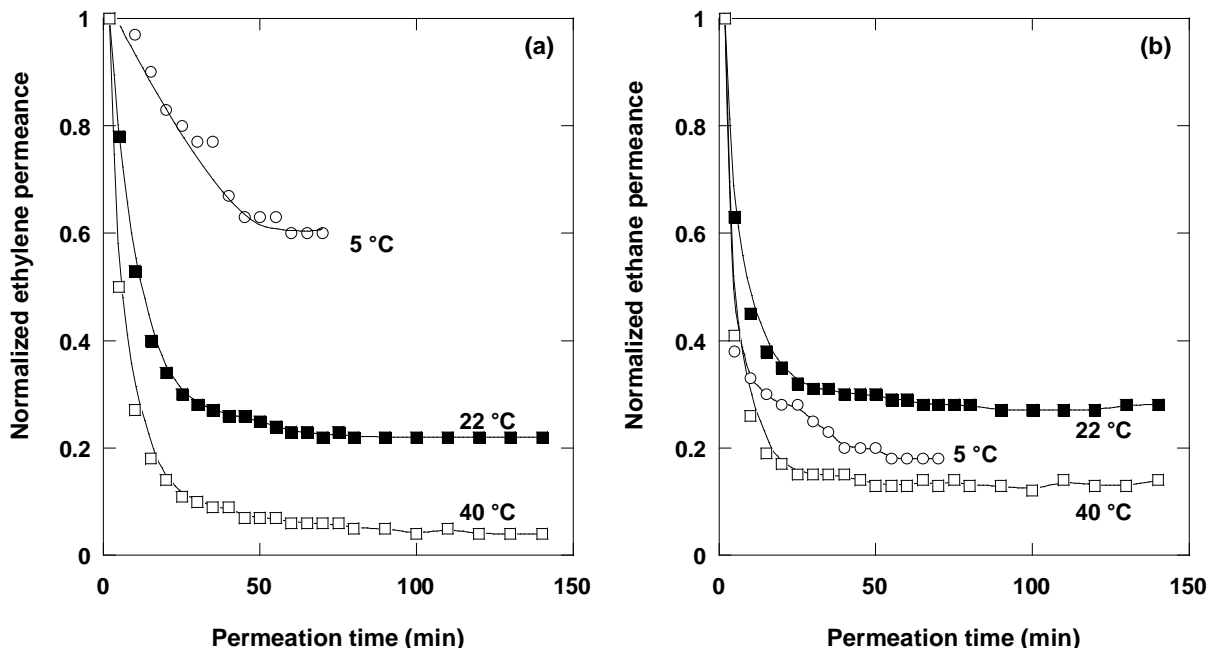


Figure 30. Normalized mixed-gas (a) ethylene and (b) ethane permeances of Pebax® 2533 membranes containing 80 wt% AgBF₄ as a function of time and temperature.

The data in Figure 30 indicate that lowering the system temperature is a way to slow the rate of ethylene permeance decline in facilitated transport membranes. Figure 31 shows that lower temperature also improves the stability of membrane mixed-gas selectivity. At 40°C, the ethylene/ethane selectivity is initially nearly 50, but decreases quite rapidly with increasing permeation time. At 5°C, the membrane behaves quite differently: selectivity starts off at only 20, but then actually increases over the course of the experiment. The selectivity increase occurs because ethane permeance decreases faster over time than that of ethylene. The reason for this behavior is not readily apparent; however, it clearly implies that there may be benefits to running the facilitated transport membranes at low temperature. This intriguing result warrants more long-term study.

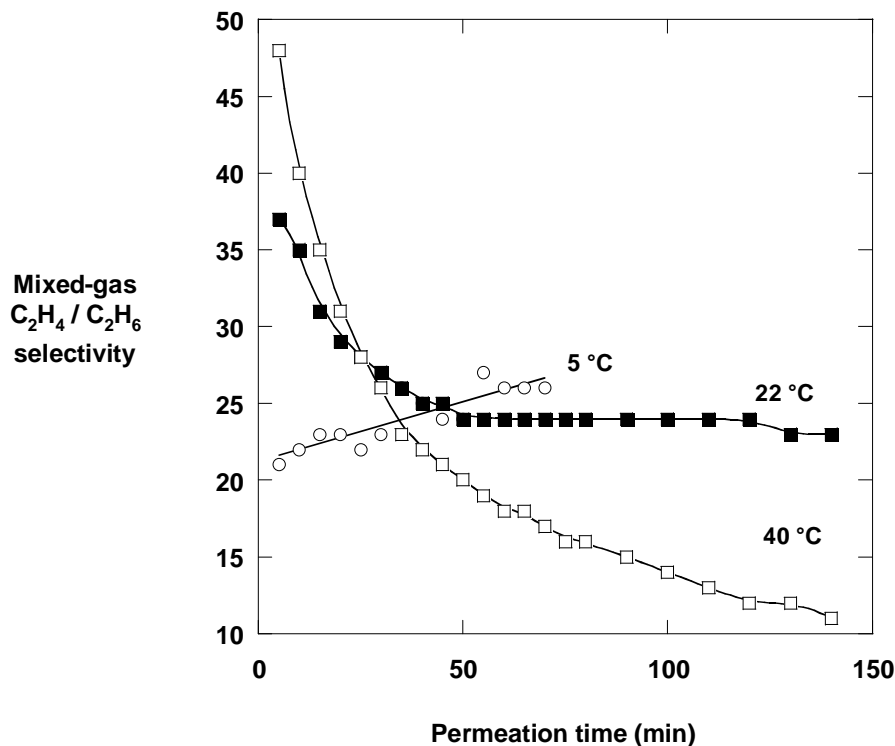


Figure 31. Mixed-gas ethylene/ethane selectivity of Pebax[®] 2533 membranes containing 80 wt% AgBF₄ as a function of time and temperature.

Effect of Polymer Plasticizers

One theory proposed to describe the olefin-induced permeance decline described in this section is that the silver carrier ions are mobile within the polymer matrix. When the membrane is exposed to an olefin, the polymer matrix becomes highly swollen as olefin sorbs into the membrane to react with silver ions. In this mobile environment, silver ions may cluster, as they are known to do in liquid solutions. These crystal-like clusters would represent low permeability regions, through which olefins and non-facilitated gases would have a difficult time passing. This type of structural rearrangement might also explain why facilitated transport membranes often become defective during long-term olefin permeation tests. Incompatibility between rigid crystal-like domains and polymeric regions could yield micron-scale interfacial regions where gases flow non-selectively.

To see whether these low-permeability regions could be broken up, we added a plasticizer to our baseline facilitated transport membrane. Polyethylene glycol (PEG) with a molecular weight of 200 is a non-volatile liquid that is compatible with Pebax[®] 2533 and silver salts. A number of early attempts failed to yield defect-free membranes; however, we eventually succeeded in fabricating membranes containing 80 wt% AgBF₄ in a matrix of 50% PEG and 50% Pebax[®] 2533. Figure 32 compares mixed-gas ethylene permeance as a function of time in this membrane, a baseline Pebax[®] 2533+80 wt% AgBF₄ membrane, and a control membrane without silver salt. Interestingly, ethylene permeance decreases faster over time in the Pebax[®] 2533+AgBF₄ membrane containing PEG, relative to the baseline membrane without plasticizer.

It appears that rather than enhancing membrane permeances, the PEG plasticizer accelerates structural changes in the membranes that cause permeance decline. This result is consistent with the temperature effect data, which shows that increased matrix mobility increases the rate of permeance decline.

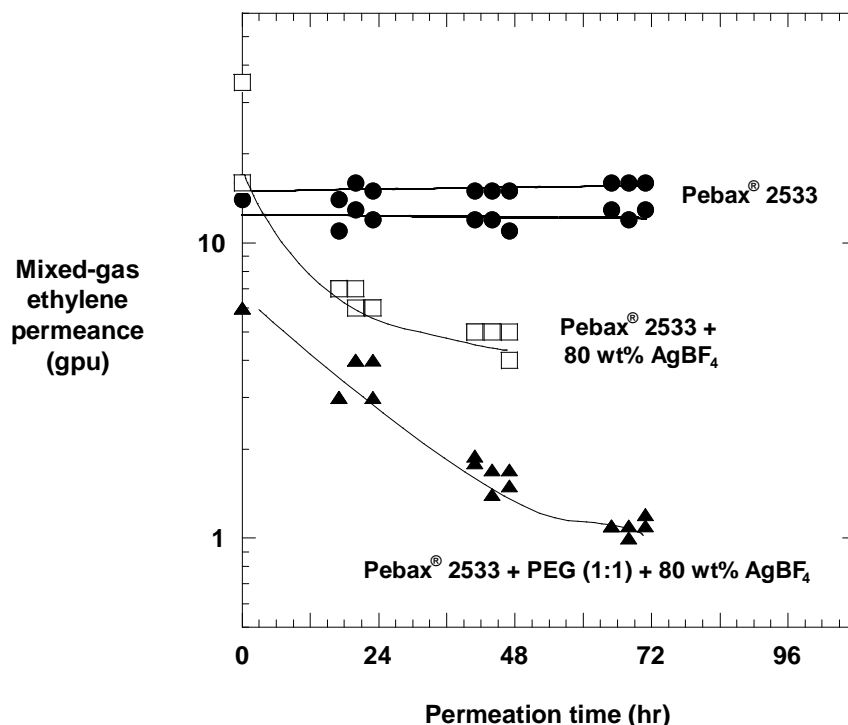


Figure 32. Mixed-gas ethylene permeance as a function of permeation time for plasticized and unplasticized Pebax® 2533 membranes.

Effect of Humidified Feed

In prior testing, we have shown that membranes containing less than 40 wt% AgBF₄ exhibit stable permeation properties, although selectivities are low. Water vapor is known to increase olefin permeation and selectivity in facilitated transport membranes that use silver salts. Consequently, experiments were conducted with a humidified feed gas to see whether water vapor would enhance the performance of membranes containing low amounts of silver salt. Figure 33 shows mixed-gas ethylene permeances as a function of permeation time for PEO membranes containing 20, 40, and 60 wt% AgBF₄ with a humidified feed. Gas chromatograph measurements showed that the feed mixture contained about 0.15 mol% water vapor, which amounts to an activity of approximately 0.3 at room temperature.

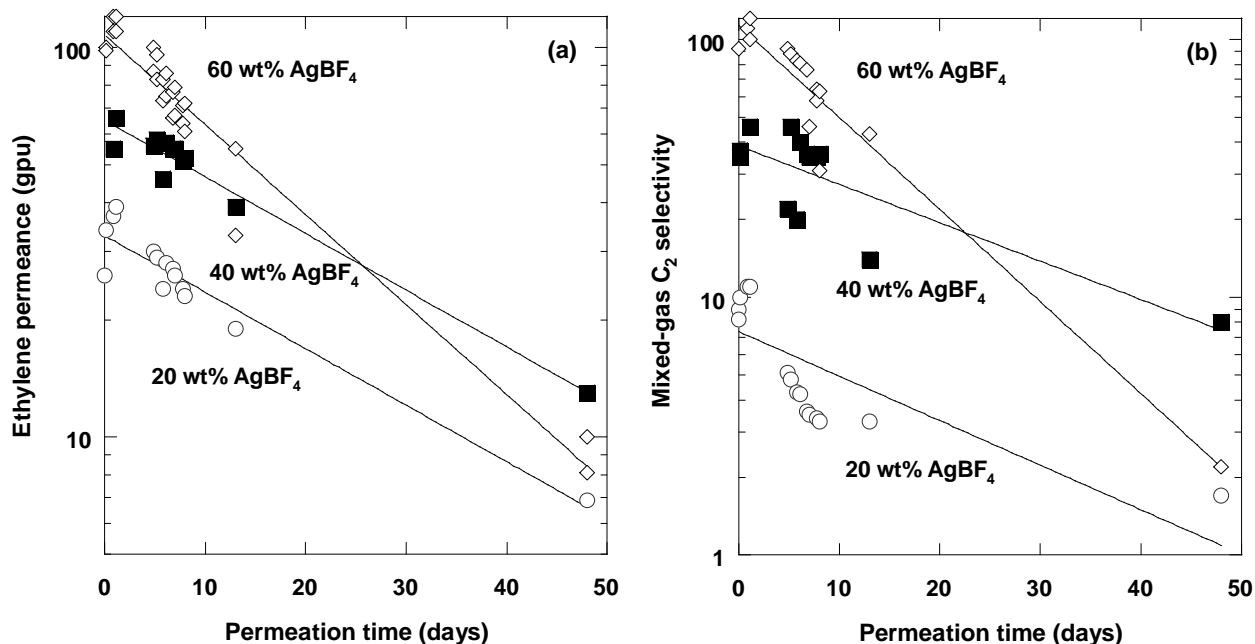


Figure 33. Mixed-gas (a) ethylene permeance and (b) ethylene/ethane selectivity for PEO composite membranes containing 20, 40, and 60 wt% AgBF_4 with a humidified feed gas. Water content of the feed gas was 0.15 mol% as determined by gas chromatography.

Initially, the ethylene permeances and selectivities of the membranes with a humidified feed were very high. For example, the initial mixed-gas ethylene/ethane selectivity for a membrane containing 20 wt% AgBF_4 was approximately 10, compared to a typical value of 1.5 for this same membrane with a dry feed. Despite the high initial performance, the membrane permeances and selectivities decreased continuously over time. After 10 days, the ethylene permeance and ethylene/ethane selectivity of the 20 wt% AgBF_4 membrane were less than half the initial values. Similar results were found for the other silver salt concentrations, with the 60 wt% AgBF_4 membrane showing the most rapid decline in performance. This result is consistent with the idea that higher amounts of silver salt cause more pronounced time-dependent permeation behavior, presumably due to membrane structural changes induced by the complexation reaction of the carrier with olefin molecules.

The time-dependent permeation behavior shown in Figure 33 for a humidified feed with membranes containing as little as 20 wt% AgBF_4 is different from results using a dry feed. For example, with a dry feed, a membrane containing 20 wt% AgBF_4 shows nearly constant ethylene permeances and ethylene/ethane selectivities of <10 gpu and 1.5, respectively (see Figure 18). These values are much less than the initial performance with a humidified feed. However, after 48 days, the performance of the humidified 20 wt% AgBF_4 membrane appears to be approaching that of the typical dry membrane permeance and selectivity. While water vapor definitely enhances the initial performance of membranes with low silver salt content, it does not solve the membrane stability issue. It appears that a membrane with useful olefin/paraffin selectivities is subject to olefin-induced performance decline, regardless of whether it is a dry membrane with >40 wt% AgBF_4 or a humidified membrane with lower silver salt content.

After completing the long-term study shown in Figure 33, sample membranes prepared at the beginning of the test and stored at ambient conditions during the experiment were examined. Figure 34 shows a picture of these stored membranes after 48 days, as well as the membranes run in the long-term, humidified feed test.

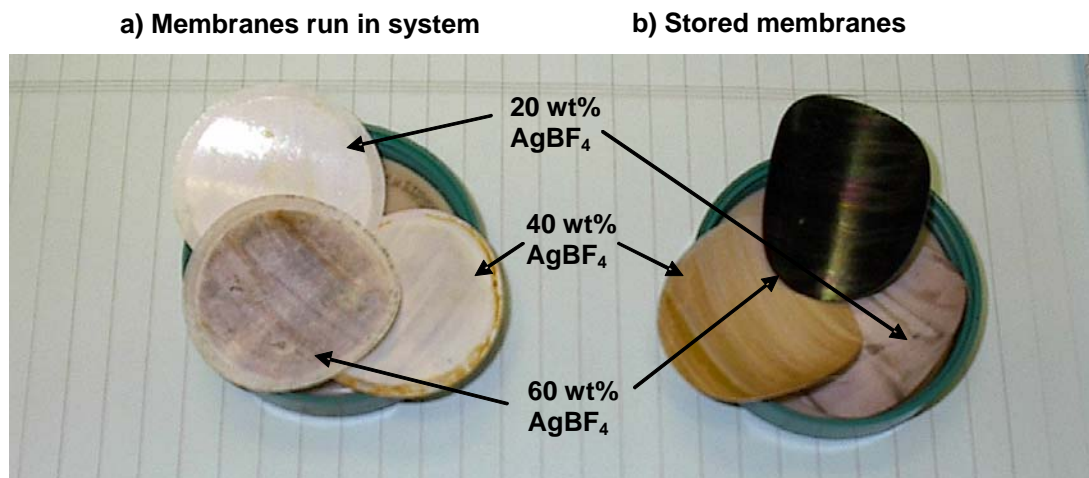


Figure 34. Photograph of (a) membranes run in the humidified feed permeation system and (b) stored membranes after 48 days.

Originally, all of the membranes were white; however, after 48 days, the stored membranes (b) have turned brown or black, indicating silver particle reduction. The color of the membranes follows their initial AgBF_4 concentration, with higher silver content yielding darker membranes. A similar trend with silver content is observed for the membranes run in the test system. Compared to the stored membranes, the test system samples (a) are much lighter in color, suggesting less silver reduction. This is consistent with the fact that the test system samples were shielded from light in the permeation cell, while the stored samples were exposed to ambient lighting (which is known to reduce silver ions).

After 48 days, the stored membranes were inserted into the re-circulating permeation system and tested with the humidified ethylene/ethane feed. The test results for these stored membranes, as well as the original and aged membranes, are summarized in Table 5. Interestingly, even though the stored membranes exhibit signs of greater silver reduction (see Figure 34), they show higher ethylene permeances and ethylene/ethane selectivities than the membranes that ran in the system for 48 days. In fact, the 20 and 40 wt% AgBF_4 membranes that were stored for 48 days show similar performance to fresh, as-cast membranes. This result again indicates that silver carrier reduction is not the only mechanism of performance decline. In fact, in this case, 48 days of olefin exposure has a significantly more negative impact on membrane performance than the same period of carrier reduction by light exposure.

Table 5. Properties of Aged PEO Membranes Containing 20 to 60 wt% AgBF₄: Comparison of Stored and Tested Samples after 48 Days.

| Membrane Type | AgBF ₄ Content wt % | Mixed-gas Permeance (gpu) | | Mixed-gas C ₂ Selectivity |
|--|-----------------------------------|-------------------------------|-------------------------------|---|
| | | C ₂ H ₄ | C ₂ H ₆ | |
| Fresh Membranes: Initial Properties | 20 | 19 | 2.1 | 9.0 |
| | 40 | 22 | 1.5 | 15 |
| | 60 | 79 | 0.8 | 99 |
| Aged Membranes: After 48 Days Of Testing | 20 | 6.9 | 4.1 | 1.7 |
| | 40 | 10 | 2.3 | 4.3 |
| | 60 | 9.1 | 4.5 | 2.0 |
| Stored Membranes: 48 Days Old | 20 | 26 | 2.5 | 10 |
| | 40 | 38 | 2.5 | 15 |
| | 60 | 43 | 2.3 | 19 |

5.7 Sorption Hysteresis

In an effort to better understand the fundamentals of the silver ion-olefin complexation reaction, we conducted sorption studies on our polymer + silver-salt selective layer material. Figure 35 presents some initial results in the form of an ethylene sorption/desorption isotherm for Pebax[®] 2533 containing 50 wt% AgBF₄. For this experiment, a film of Pebax[®] 2533 + AgBF₄ was cast from an ethanol solution and dried at ambient conditions. The sample was then inserted into a barometric sorption apparatus and exposed to vacuum for more than 24 hours. This drying protocol removes residual solvent, water and air gases from the sample. The dried sample was then exposed to progressively higher ethylene pressures and the equilibrium sorption uptake was measured at each pressure stage.

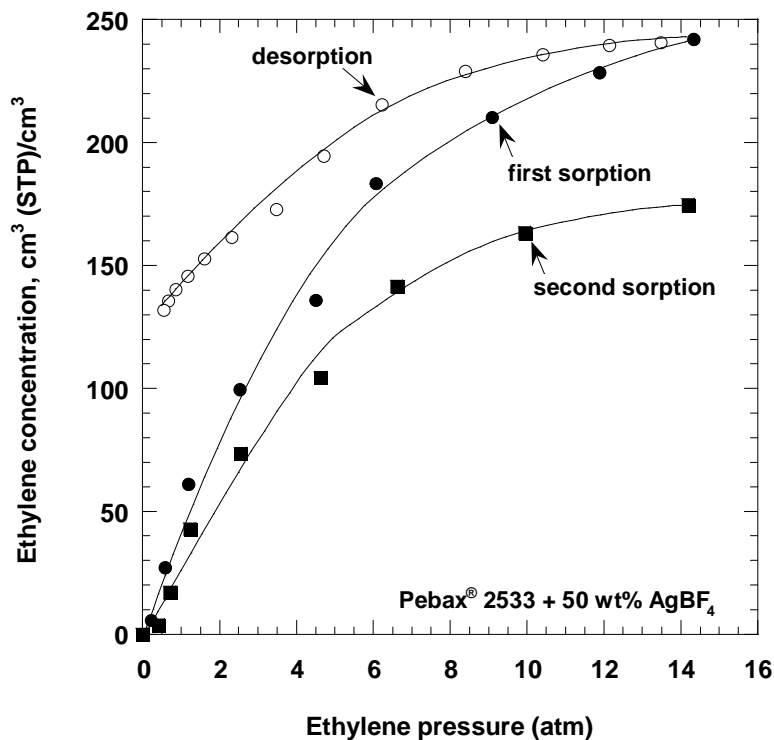


Figure 35. Ethylene sorption and desorption isotherms at 25°C in Pebax® 2533 containing 50 wt% AgBF₄.

- The curve labeled “first sorption” in Figure 3 represents the initial ethylene uptake upon first exposure of the polymer sample to the gas. The amount of ethylene sorption in the Pebax® 2533+50 wt% AgBF₄ sample is enormous. For example, at 10 atm this sample sorbs nearly 200 cm³(STP)/cm³ of ethylene, compared to only about 10 cm³(STP)/cm³ in pure Pebax® 2533. This 20-fold increase in ethylene sorption after adding AgBF₄ is clearly due to the presence of silver ions that complex with ethylene.
- Interestingly, it appears that this complexation reaction is not completely reversible. The open points labeled “desorption” in Figure 35 represent the amount of ethylene that remains in the sample as the ethylene pressure is lowered. Typically, gas sorption/desorption in polymer samples is completely reversible and the desorption isotherm falls on top of that measured for sorption. This is not the case for Pebax® 2533 containing 50 wt% AgBF₄, where hysteresis is clearly evident. As the gas pressure is lowered, the sample releases ethylene very slowly. For example, at 3 atm, the amount of ethylene sorbed in the sample during first sorption and desorption is roughly 110 and 170 cm³(STP)/cm³, respectively. This result suggests that after complexation occurs, silver ions in our polymer system hold onto ethylene molecules and do not disassociate as readily as was believed.

- After the final desorption point in Figure 35, there still appeared to be more than $130 \text{ cm}^3(\text{STP})/\text{cm}^3$ of ethylene sorbed in the Pebax 2533/AgBF₄ sample. The sample was then exposed to a vacuum overnight before beginning a second sorption isotherm. There is no way to tell from this experiment whether all of the sorbed ethylene was removed during the vacuum treatment. It is possible that some of the ethylene remained in the sample bound to silver ions.
- The second ethylene sorption isotherm (labeled “second sorption” in Figure 35) shows significantly lower ethylene uptake relative to the first isotherm. This suggests that some of the silver ions are not available to complex ethylene during the second sorption run. Apparently, some silver ions have become inactivated either because they are already bound to ethylene from the first run or through some other structural change. Future work will try to determine whether the polymer-silver system continues to change with repeated olefin cycling.

These sorption findings (i.e., hysteresis) are consistent with the time-dependent membrane properties described throughout this section. Clearly, olefin permeation in a silver salt facilitated transport membrane is not a simple idealized case of olefin molecules moving through an inert matrix, reversibly complexing with fixed carrier ions. Rather, it appears that olefin complexation by silver ions may be only partially reversible over short timescales (i.e., the desorption step is relatively slow) and sorption swells the matrix, creating a mobile environment that allows significant membrane structural changes over time.

5.8 Summary of Time-Dependent Membrane Studies

We have isolated a new mechanism of performance decline in silver salt facilitated transport membranes that is different from conventional carrier reduction or poisoning phenomena associated with facilitated transport membranes employing silver salts. Conventional carrier poisoning results in a loss of active silver ions in the membrane. This mechanism causes membranes to turn black, yields an attenuated and unshifted FTIR peak, and increases non-facilitated gas permeances. In contrast, the olefin-induced performance decline we have identified in this work lowers non-facilitated gas permeance in mixtures with olefins and does not result in FTIR signal or membrane color changes. It appears that regardless of the polymer matrix or type of silver salt used, gas permeance begins to decrease once the membrane has been exposed to an olefin. This effect is accelerated at higher temperatures and in the presence of water or polymeric plasticizers, suggesting a structural change to the membrane resulting from the silver ion-olefin complexation reaction. The mechanism of olefin-induced permeance decline warrants further investigation.

6. CARRIER POISONING AND REGENERATION OF SILVER SALT FACILITATED TRANSPORT MEMBRANES

6.1 Carrier Poisoning Studies

Previous work by others on facilitated transport membranes rarely mentions the impact of carrier poisoning on membrane performance. In fact, to our knowledge, there is no published

information quantitatively describing the effect of poisoning species on the separation performance of facilitated olefin transport membranes. As mentioned earlier, the principal species believed to interact with silver ions, and which might be expected to be present in industrial gas streams, are hydrogen, hydrogen sulfide, and acetylene. Consequently, we have investigated the effect of exposure to these compounds over time on membrane performance. We have also examined the effect of light on membrane separation performance because silver salts are known to be light sensitive.

Figure 36 presents the mixed-gas fluxes and ethylene/ethane selectivity of Pebax[®] 2533+80 wt% AgBF₄ facilitated transport membranes as a function of aging time in ambient light. It is well known that silver ions are gradually reduced to silver metal upon exposure to light.^[39] In fact, this is the principle behind chemical-based photography. The greater the exposure to light, the more silver ions are reduced to silver metal nanoparticles, which appear dark in color. Over the course of 34 days, the exposed facilitated transport membrane progressively turned darker until it was completely black at the end of the experiment. Correspondingly, the mixed-gas selectivity of the membrane decreased from 34 to 1.1 as the silver carrier ions became deactivated. From the flux data, it is evident that the ethane/ethylene selectivity loss was largely due to increased ethane flux over time. If one examines the effect of silver ion content on gas fluxes from Figure 2 (Section 2), the observed aging effects can be explained as traveling from right to left on this plot. In other words, as light reduces silver from ion form to metal, we are moving from high Ag⁺ content (the right side of Figure 2) to low Ag⁺ content (the left side of Figure 2). In doing so, ethane flux should increase monotonically (as it does in Figure 36), while ethylene flux should decrease initially and then increase slightly (as it does in Figure 36).

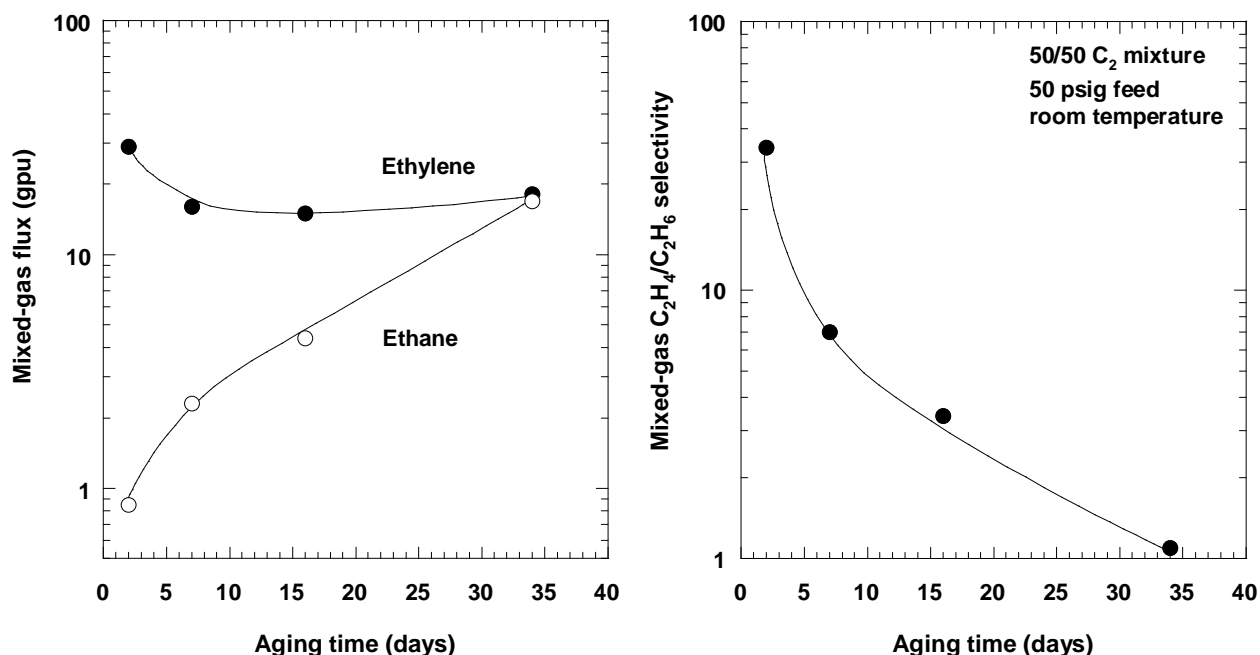
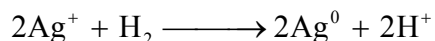


Figure 36. Mixed-gas ethylene and ethane fluxes and ethylene/ethane selectivity as a function of aging time in ambient light for a Pebax[®] 2533+80 wt% AgBF₄ facilitated transport membrane.

The detrimental impact of light on our facilitated transport membranes is not considered a serious operational problem due to the fact that the membrane is not exposed to light once it is fabricated into modules. However, the effect of various chemical species on membrane performance is a concern. Figure 37 presents mixed-gas ethylene and ethane permeance and selectivity for Pebax[®] 2533+AgBF₄ membranes that were exposed to hydrogen between measurements. In these tests, the membrane continuously permeated pure hydrogen at 20 psig feed and 0 psig permeate pressure except for periodic interruptions where mixed-gas ethylene and ethane fluxes were measured. Hydrogen is a reducing gas and is believed to react with silver ions in the following way:



The data in Figure 37(b) show that ethylene/ethane selectivity decreases rather rapidly after three days, and after a week is only slightly greater than one. Figure 37(a) indicates this loss of selectivity is primarily due to increasing ethane (non-facilitated gas) permeance. Such behavior is consistent with a decrease in the ionic character of the membrane over time. This transport result is supported by a visual inspection of the membranes. The membranes, which are initially white, turn black after hydrogen exposure, indicating that silver ions have been reduced to silver particles (Figure 38).

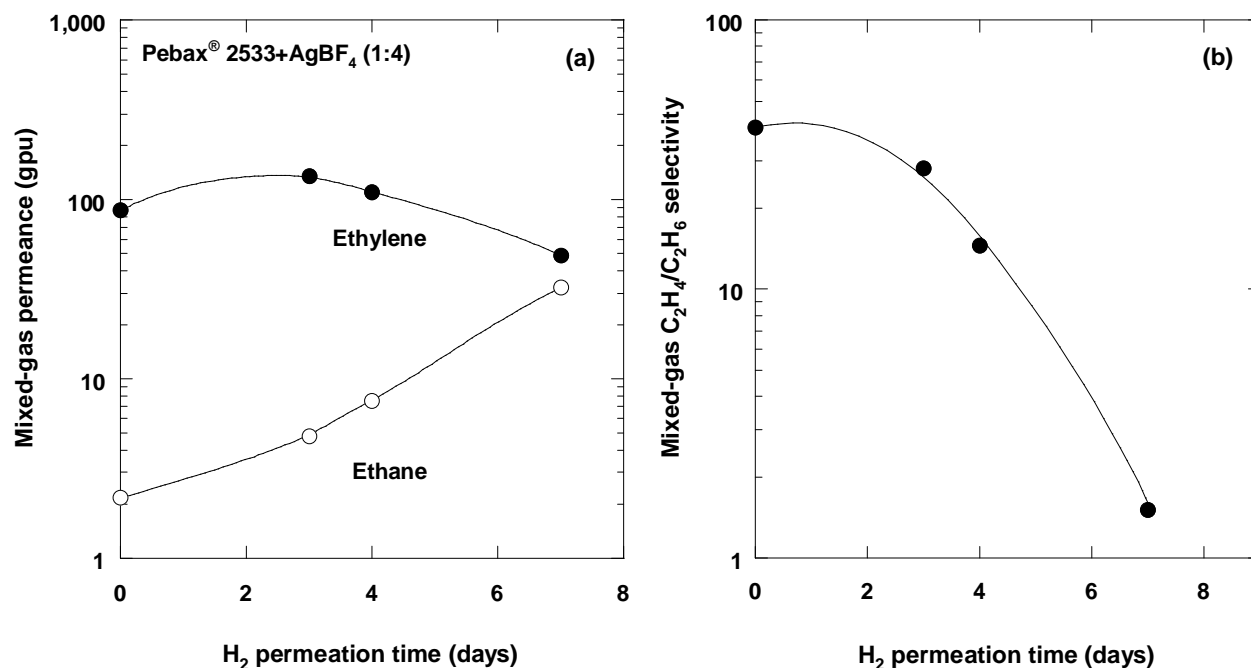


Figure 37. Mixed-gas ethylene and ethane (a) permeance and (b) selectivity as a function of hydrogen exposure time for Pebax[®] 2533+AgBF₄ composite membranes.

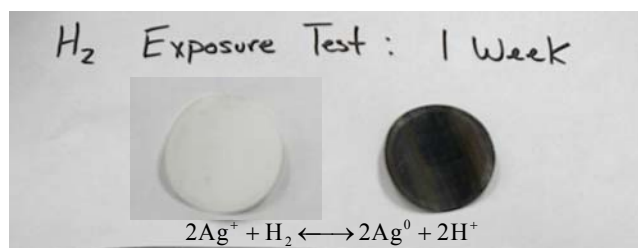
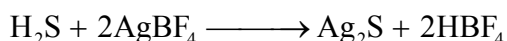


Figure 38. Picture of a Pebax[®] 2533+AgBF₄ composite membrane stamp before (white) and after (black) hydrogen permeation.

This hydrogen exposure experiment is a particularly harsh test because the membrane permeates pure hydrogen continuously between mixed-gas ethylene/ethane measurements. In the actual applications where the membrane would be used, such as at the bottom of a C₂ splitter or on metathesis C₄ purge streams, the concentration of hydrogen is in the ppm range according to our ABB Lummus colleagues. Additionally, in a mixture with olefins, silver ions may be more resistant to hydrogen reduction because they are complexed with olefin molecules. Nevertheless, it is clear that hydrogen does reduce impregnated silver ions in our facilitated transport membranes, thereby degrading performance over time.

Figure 39 presents the effect of hydrogen sulfide exposure on mixed-gas Pebax[®] 2533+AgBF₄ membrane performance. During this experiment, the membrane continuously permeated 10 ppm of H₂S in ethylene between ethylene/ethane measurements. Similar to the results with hydrogen poisoning (Figure 37), membrane mixed-gas ethylene/ethane selectivity decreases dramatically over one week. In contrast to the hydrogen results, for H₂S exposure, the permeance of both ethylene and ethane decrease over time. This result may reflect the formation of impermeable silver sulfide crystals in the membrane. It is believed that H₂S reacts with silver ions by the following mechanism:



At the end of the hydrogen sulfide exposure experiment, the membrane was reddish-brown in color (see Figure 40). Previously, we calculated that for a 10 ppm H₂S feed, if every hydrogen sulfide molecule participated in the silver sulfide formation reaction, all of the silver ions in the membrane would be converted to Ag₂S in roughly five days. Based on the data in Figure 39, this estimate appears reasonably accurate, given that after seven days there is very little facilitation of ethylene. Like the hydrogen exposure experiment, this hydrogen sulfide study is a particularly harsh test of membrane durability.

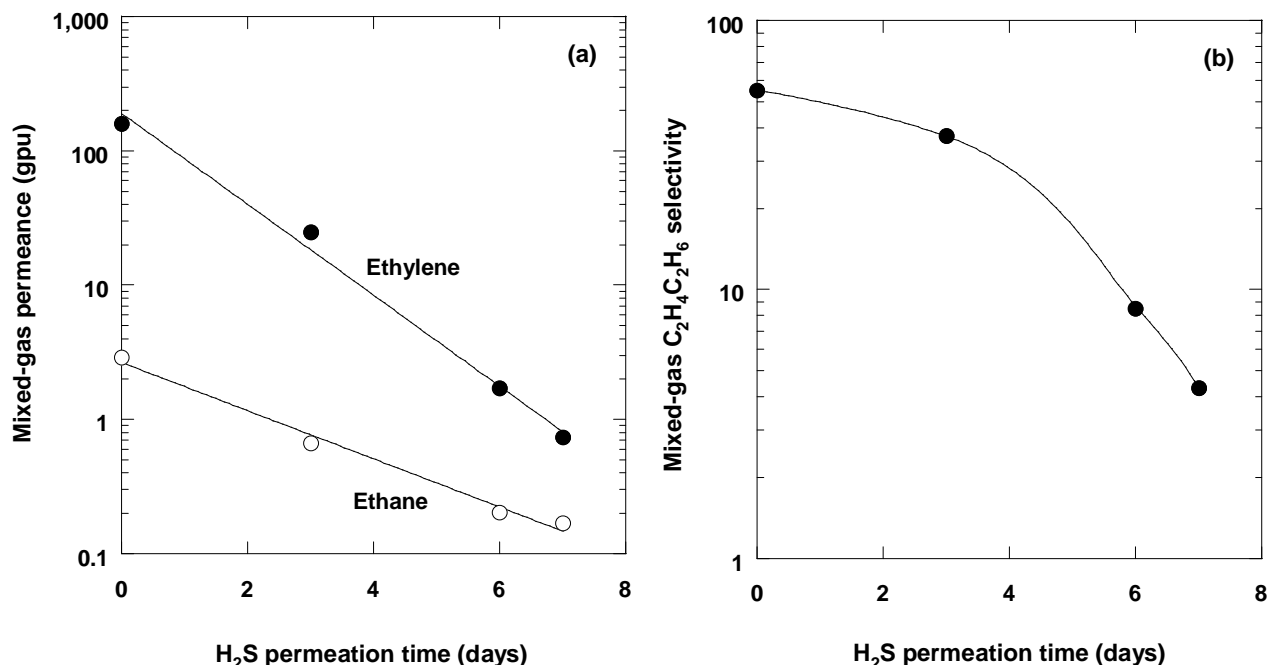


Figure 39. Mixed-gas ethylene and ethane (a) permeance and (b) selectivity as a function of hydrogen sulfide permeation time for Pebax[®] 2533+80 wt% $AgBF_4$ membranes. The membrane samples continuously permeated 10 ppm H_2S in ethylene between mixture permeation measurements.

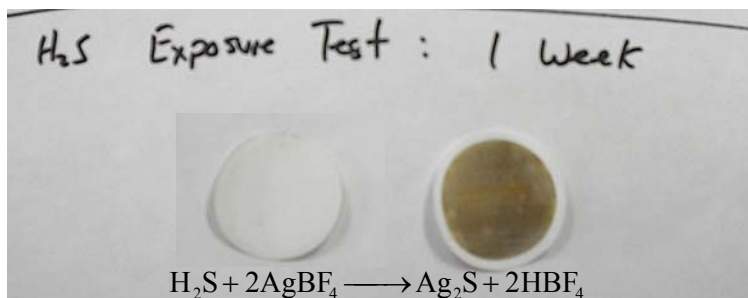


Figure 40. Picture of a Pebax[®] 2533+80 wt% $AgBF_4$ composite membrane stamp before (white) and after (brown) hydrogen sulfide permeation.

Effective sulfur clean-up technologies routinely reduce H_2S levels in gas streams to <1 ppm. Based on discussions with ABB Lummus, sulfur species in the applications where our membranes would be used (bottoms of C_2 splitter, metathesis C_4 purge) are typically less than 0.1 ppm. This is two orders of magnitude lower than the amount tested in Figure 39. We did not have time to quantify the effect of lower H_2S concentrations on membrane performance in this program. It is reasonable to expect that lower contaminant concentrations would result in longer membrane lifetimes.

Pebax[®] 2533+80 wt% $AgBF_4$ facilitated transport membrane was also tested with a feed gas containing 10 ppm of acetylene (C_2H_2) in ethylene at 20 psig. Similarly to results presented for

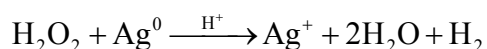
the other poisoning species, membrane selectivity decreased significantly after acetylene exposure. For instance, after five days of permeating acetylene, the mixed-gas ethylene/ethane selectivity of a membrane stamp was reduced from 32 to 4.7. At the end of the five days, the stamp was removed from the test cell and examined. In contrast to a control which appeared to be in the as-cast condition, the acetylene-exposed sample had turned dark brown. As in the case of results obtained for light and hydrogen exposure, the loss in selectivity for the acetylene-exposed membrane resulted primarily from an increase in ethane flux. This is in contrast to the hydrogen sulfide exposure tests where both ethylene and ethane fluxes decreased tremendously. As will be shown in the following section, this difference in exposure impact on transport properties also manifests itself as a difference in the reversibility of the poisoning reactions. While it seems that carrier deactivation induced by light, hydrogen and acetylene can be reversed under simple regeneration conditions, the effect of hydrogen sulfide on the silver carrier appears to be irreversible.

6.2 Stabilization and In-situ Regeneration of Reduced Silver Salt Membranes

A key technical challenge identified at the start of this project was to improve the lifetime of our facilitated transport membranes in the presence of process stream components or conditions that may deactivate the olefin carrier species. The work in the previous section has shown that active, olefin-complexing Ag^+ ions can be deactivated by reduction to silver metal (Ag^0), caused by exposure to light or reducing chemical species such as hydrogen, and by reaction with hydrogen sulfide (H_2S) or acetylene (C_2H_2) to yield non-complexing silver compounds (Ag_2S or Ag_2C_2). Once Ag^+ ions have been reduced, they are no longer active olefin carriers and membrane performance deteriorates.

During the course of these studies, we discovered that almost all aged and some poisoned Pebax[®] 2533+ AgBF_4 membranes can be regenerated by exposure to an oxidizing vapor or liquid treatment. This discovery offers the possibility that membrane lifetime could be enhanced by a periodic, in-situ regeneration treatment, much like ultra- or microfiltration membranes are regularly backflushed to manage fouling.

The finding that facilitated olefin transport membranes can be regenerated evolved from an effort to stabilize our Pebax[®] 2533+ AgBF_4 coating solutions. Without the addition of a stabilizing agent, coating solutions turn black within a few hours, indicating that silver ions are being reduced to silver metal particles. After a week, such reduction leads to large silver deposits on the container walls. This ‘plate-out’ occurs more rapidly if the solution is exposed to light, but proceeds even in a dark environment, suggesting that the polymer, solvent, and/or container walls contribute to silver reduction. Based on patent literature from the 1970s,^[32] we added small amounts of hydrogen peroxide (H_2O_2) and hydrogen borofluoride (HBF_4) to our coating solution to prevent silver ion reduction. This strategy proved very effective, as $\text{H}_2\text{O}_2/\text{HBF}_4$ additions of less than 0.5 wt% completely stabilized the coating solutions. It is believed that the strong oxidizing agent, H_2O_2 , can react in an acidic environment with silver metal to yield silver ions in the following manner:





Hydrogen peroxide is known to be quite unstable at pH levels greater than 5, and testing confirmed that without the addition of an acid, the stabilizing effect of H_2O_2 on the coating solution is rather short-lived. An initial screening suggested that HBF_4 in approximately a 1:1 ratio with H_2O_2 was most effective at stabilizing the coating solution and restoring aged membrane properties.

Figure 41 illustrates the impact of $\text{H}_2\text{O}_2/\text{HBF}_4$ stabilizer added to Pebax[®] 2533+ AgBF_4 coating solutions. The coating solutions in the containers were more than nine months old at the time of this picture. The solution without stabilizer is black and membranes prepared from it are brown. In contrast, the stabilized solution is tan and membranes prepared from it appear white (actually the selective layer is transparent and the white appearance comes from the microporous support membrane). Table 6 presents the transport properties of membranes prepared with and without stabilizer in the solution. The permeances and selectivities of the membrane stamps are similar. This result suggests that despite the dark color of the unstabilized solution and membranes, there are still enough active silver ions in these membranes to enable olefin facilitation. Thus, although the $\text{H}_2\text{O}_2/\text{HBF}_4$ stabilizer prevents coating solution plate-out, membranes with good initial properties can be coated from aged solutions with or without the stabilizer.



Figure 41. Comparison of Pebax[®] 2533+80 wt% AgBF_4 coating solutions prepared with and without $\text{H}_2\text{O}_2/\text{HBF}_4$ stabilizer. Both solutions are >9 months old. The container on the right contains 0.5 wt% $\text{H}_2\text{O}_2/\text{HBF}_4$. In the foreground are composite membranes as they appear immediately after coating PVDF support with the respective solution.



Table 6. Comparison of Pebax[®] 2533+80 wt% AgBF₄ Membranes Prepared from Aged Solutions With and Without H₂O₂/HBF₄ Stabilizer

| Membrane Description | Membrane Appearance | Mixed-Gas Permeance (gpu) | | Mixed-Gas C ₂ H ₄ /C ₂ H ₆ Selectivity |
|--|---|-------------------------------|-------------------------------|--|
| | | C ₂ H ₄ | C ₂ H ₆ | |
| Membrane prepared from old solution <i>without</i> H ₂ O ₂ /HBF ₄ |  | 79 | 2.4 | 33 |
| | | 66 | 1.7 | 39 |
| Membrane prepared from old solution <i>with</i> H ₂ O ₂ /HBF ₄ |  | 49 | 1.4 | 35 |
| | | 54 | 1.3 | 41 |

The coating solution with stabilizer contained 0.5 wt% H₂O₂ aqueous solution (35 wt% in H₂O) and 0.5 wt% HBF₄ aqueous solution (50 wt% in H₂O). Both coating solutions were >9 months old at the time membranes were prepared and tested. Test conditions: feed pressure = 50 psig, T = 23°C. Mixture composition: 65% C₂H₄, 35% C₂H₆.

The situation is different for aged membranes coated from these two solutions. Table 7 presents the transport properties and appearance of Pebax[®] 2533+AgBF₄ membranes coated from solutions with and without stabilizer and then aged for at least 9 months. After coating, the membranes were stored in a sealed plastic bag. The membranes without H₂O₂/HBF₄ stabilizer have undergone significant silver reduction, as evidenced by their black color. Their transport properties reflect this fact; the mixed-gas ethylene/ethane selectivities are less than four. In contrast, aged membranes prepared from coating solution containing the H₂O₂/HBF₄ stabilizer are white and show mixed-gas ethylene/ethane selectivities of about 40, very close to the initial values. Apparently, the presence of an oxidizing stabilizer in the coating solution allows for stable storage of Pebax[®] 2533+AgBF₄ membranes in a closed environment (plastic bag). The beneficial effect is minimized if the membranes are stored in the open atmosphere (membrane is noticeably stabilized for only 1-3 days). Presumably, the volatile stabilizer components evaporate over time (these compounds are relatively low boiling liquids - T_b = 150°C and 130°C for H₂O₂ and HBF₄, respectively).



Table 7. Comparison of Aged Pebax[®] 2533+80 wt% AgBF₄ Membranes Prepared from Solutions With and Without H₂O₂/HBF₄ Stabilizer

| Membrane Description | Membrane Appearance | Mixed-Gas Permeance (gpu) | | Mixed-Gas C ₂ H ₄ /C ₂ H ₆ Selectivity |
|---|---|-------------------------------|-------------------------------|--|
| | | C ₂ H ₄ | C ₂ H ₆ | |
| Nine month old membrane: <i>Without</i> H ₂ O ₂ /HBF ₄ |  | 16 | 6.2 | 2.5 |
| | | 13 | 3.7 | 3.7 |
| Nine month old membrane: <i>With</i> H ₂ O ₂ /HBF ₄ |  | 29 | 0.8 | 39 |
| | | 22 | 0.5 | 44 |

The coating solution with stabilizer contained 0.5 wt% H₂O₂ aqueous solution (35 wt%) and 0.5 wt% HBF₄ aqueous solution (50 wt%). Membranes were stored in a sealed plastic bag for roughly 9 months prior to testing. Test conditions: feed pressure = 50 psig, T = 23°C. Mixture composition: 65% C₂H₄, 35% C₂H₆.

In addition to stabilizing the coating solution and stored membranes, $\text{H}_2\text{O}_2/\text{HBF}_4$ mixtures can restore the properties of aged or poisoned Pebax[®] 2533+AgBF₄ membranes. Table 8 presents the transport properties and appearance of aged membranes (the same 9-month-old samples without stabilizer from Table 7) before and after exposure to $\text{H}_2\text{O}_2/\text{HBF}_4$ vapors. The membrane color has changed from black to white and mixed-gas ethylene/ethane selectivities have increased from less than 4 to about 20. This result is the first documentation of *in-situ* regeneration of a facilitated olefin transport membrane.

Table 8. Regeneration of Aged Membrane Using $\text{H}_2\text{O}_2/\text{HBF}_4$ Vapors

| Membrane Description | Membrane Appearance | Mixed-Gas Permeances (gpu) | | Mixed-Gas $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ Selectivity |
|---|--|----------------------------|------------------------|---|
| | | C_2H_4 | C_2H_6 | |
| Old membrane aged nine months |  | 16 | 6.2 | 2.5 |
| | | 13 | 3.7 | 3.7 |
| Old membrane after regeneration with $\text{H}_2\text{O}_2/\text{HBF}_4$ vapors |  | 59 | 3.0 | 20 |
| | | 40 | 2.5 | 16 |

Membrane was stored in a plastic bag for roughly 9 months prior to testing. Test conditions: feed pressure = 50 psig, $T = 23^\circ\text{C}$. Mixture composition: 65% C_2H_4 , 35% C_2H_6 . Regeneration conditions: Aged membrane sample was placed in a sealed container that held a 50/50 mixture by weight of H_2O_2 aqueous solution (35 wt%) and HBF_4 aqueous solution (50 wt%). The membrane was in contact with the vapor pressure of this mixture at room temperature for ~16 hours.

From the aforementioned results, it is evident that peroxide/acid treatment can restore the transport properties of photo-reduced membranes. However, the utility of this discovery is significantly enhanced if the treatment can be shown to rejuvenate membranes deactivated by the chemical poisoning species discussed in Section 6.1. Subsequent testing showed that facilitated transport membranes deactivated by hydrogen and acetylene can be regenerated by peroxide/acid treatment, while those poisoned by hydrogen sulfide cannot be restored. As an example, Figure 42 presents results for membrane stamps deactivated by hydrogen poisoning. As for light-exposed membrane samples, treatment of a hydrogen-reduced stamp with $\text{H}_2\text{O}_2/\text{HBF}_4$ vapors results in a dramatic color change from black to white, and more importantly, a restoration of high mixed-gas ethylene/ethane selectivity. Interestingly, the time required to restore the hydrogen-reduced sample using $\text{H}_2\text{O}_2/\text{HBF}_4$ vapors (~60 h) is considerably longer than that required to regenerate light-reduced membranes (~10 h). The reason for this difference is unknown, although it may be related to differences in the extent to which silver ions are reduced throughout the bulk of the membrane.

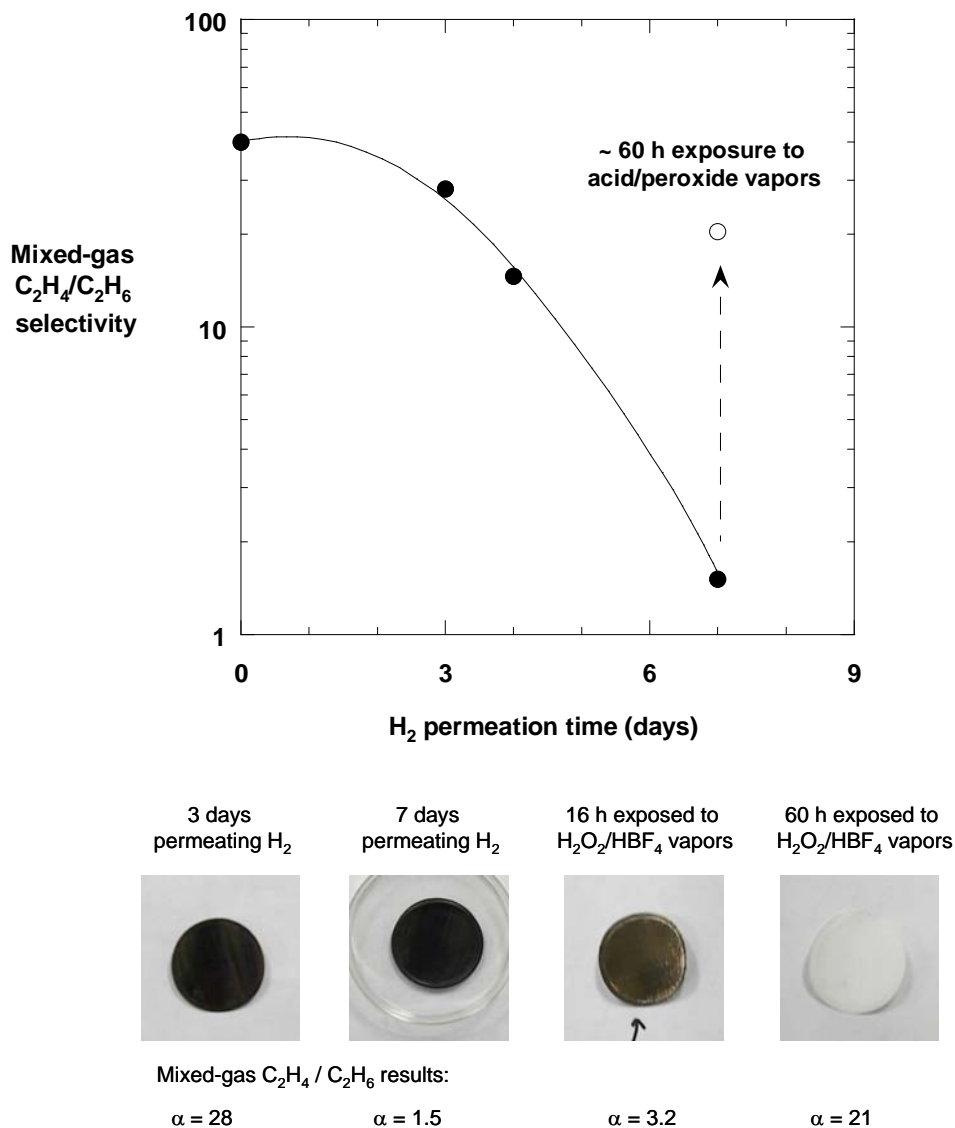


Figure 42. Deactivation of a Pebax[®] 2533+80 wt% AgBF₄ composite membrane stamp by hydrogen reduction and regeneration of the same stamp by H₂O₂/HBF₄ vapor treatment.

Peroxide/acid treatment was also effective at regenerating membrane samples deactivated by acetylene exposure. For example, after five days of permeating 10 ppm acetylene, a membrane stamp exhibited a mixed-gas ethylene flux of 29 gpu and an ethane flux of 6.3 gpu, yielding a selectivity of 4.7. This same stamp, after 1 min immersion in a 50/50 H₂O₂/HBF₄ bath, demonstrated a mixed-gas selectivity of 22 based on an ethylene flux of 35 gpu and an ethane flux of 1.6 gpu. In contrast, neither liquid nor vapor H₂O₂/HBF₄ treatment produced any change in the appearance or transport behavior of samples deactivated by hydrogen sulfide, even after prolonged immersion periods (>1 week). At least with regard to the examined chemistry, the reaction of hydrogen sulfide with Ag⁺ appears to be irreversible.

Despite the inability to restore sulfur-poisoned facilitated olefin transport membranes with $\text{H}_2\text{O}_2/\text{HBF}_4$ vapors, the regeneration method shows promise as a means of prolonging membrane lifetime. One might imagine a process whereby partially deactivated facilitated transport modules could be periodically taken offline and regenerated by a peroxide/acid vapor stream. In this manner, the regeneration process, in combination with sulfur removal upstream of the membranes, could be a route to industrial use of facilitated olefin transport membranes. Because of the need to protect species-sensitive catalysts, there are refinery olefin/paraffin streams that are relatively clean, containing only small amounts of sulfur species. For example, based on discussions with ABB Lummus, several applications where facilitated transport membranes could be used (bottoms of C_2 splitter, metathesis C_4 purge) typically contain less than 0.1 ppm sulfur. Unfortunately, the olefin-conditioning stability problems described in Section 5 will also need to be resolved before commercial use of carrier-facilitated membranes in olefin-related applications can advance any further.

7. NEW OLEFIN CARRIERS

7.1 Permeation Properties of Membranes Containing Alternate Olefin Carrier Salts

Previous studies at MTR have shown that AgBF_4 is an effective carrier for facilitated olefin transport membranes, whereas various other silver salts, such as AgNO_3 , are not. It is believed that small anions like NO_3^- bind tightly with Ag^+ , preventing the silver cation from complexing olefins. In contrast, large, bulky BF_4^- anions are more easily disassociated, allowing silver ions to interact with olefin molecules. As part of an effort to identify additional effective (and perhaps more stable) carriers, a number of different salts possessing large anions were tested for their ability to facilitate olefin transport in membranes. The results of mixed-gas ethylene/ethane tests for Pebax[®] 2533 membranes containing 80 wt% of eight different salts are shown in Table 9. The copper and cobalt salts tested were either insoluble in the Pebax[®] coating solution or showed no selectivity enhancement compared to a pure Pebax[®] 2533 membrane (mixture ethylene/ethane selectivity of less than 2). The silver salts showed better performance. Two silver salts, AgPF_6 and AgSbF_6 , exhibited mixed-gas ethylene/ethane selectivities of greater than 10. However, these selectivities are still lower than AgBF_4 ($\text{C}_2\text{H}_4/\text{C}_2\text{H}_6 \sim 30$) and more importantly, ethylene permeances in membranes containing 80 wt% AgPF_6 or AgSbF_6 are approximately an order of magnitude lower than those in AgBF_4 -containing membranes. For these reasons, from a transport standpoint, none of the salts tested are competitive with AgBF_4 .

Table 9. Mixed-gas Transport Properties of Pebax[®] 2533 Membranes Containing 80 wt% of Various Carrier Salts

| Carrier Salt | Mixed-gas Permeance(gpu) | | Mixed-gas Selectivity |
|--|---------------------------------|-------------------------------|-----------------------|
| | C ₂ H ₄ | C ₂ H ₆ | |
| Co(BF ₄) ₂ | 1.4* | 1.0* | 1.4* |
| Cu(BF ₄) ₂ | 0.5 | 0.3 | 1.5 |
| CuBH ₄ ((C ₆ H ₅) ₃ P) ₂ | Not soluble in casting solution | | |
| AgC ₂ F ₃ O ₂ | 2.8 | 1.2 | 2.6 |
| AgCF ₃ SO ₃ | 0.6 | 0.2 | 3.0 |
| AgPF ₆ | 3.6 | 0.3 | 11 |
| AgSbF ₆ | 2.4 | 0.2 | 14 |
| AgBF ₄ (standard carrier) | 30 | 1.0 | 30 |

Test conditions: feed pressure = 50 psig, T = 23°C. Mixture composition: 65% C₂H₄, 35% C₂H₆.

*Measured with pure gases at 50 psig and 23°C.

Another important criterion for evaluating an olefin carrier is its stability. As discussed in Section 6, membranes formed from Pebax[®] 2533+AgBF₄ are deactivated by light and reducing gases such as hydrogen, sulfur species, and acetylenes. This deactivation occurs because Ag⁺ carrier ions are reduced to silver metal or other reaction products that are not able to complex olefins. Such exposure causes Pebax[®] 2533+AgBF₄ membranes to turn black (due to the in-situ creation of silver metal particles) and gradually lose their high olefin/paraffin selectivity. An ideal carrier would exhibit greater stability than AgBF₄ while yielding membranes with at least comparable transport properties.

To see whether another silver salt has better stability than AgBF₄, a test was conducted with Pebax[®] 2533 membranes, one containing 80 wt% of AgBF₄ and another containing 80 wt% AgPF₆ (silver hexafluorophosphate) carriers. Membranes prepared with the different carriers were exposed to light and tested over a five day period. Both membranes gradually turned brown, suggesting that Ag⁺ ions were being reduced. Consistent with this observation, the ethylene permeances and ethylene/ethane selectivities decreased over time for both carriers. At the end of the exposure period, AgBF₄ membranes maintained significantly better performance than those prepared with AgPF₆. For example, the mixed-gas ethylene permeances of the membranes after five days were 10 gpu and 1.3 gpu for AgBF₄ and AgPF₆, respectively. This light-exposure test suggests that the best performing alternative carriers examined to date are not substantially more stable than AgBF₄. This result is not unexpected as both of these salts utilize silver ions as the carrier.

7.2 Permeation Properties of Membranes Containing Mixed Carrier Salts

To date, carriers other than silver have shown little promise by themselves. Work with mixed carriers has shown more potential, however. Table 10 presents data for Pebax[®] 2533 membranes containing various mixtures of both copper and silver carriers. Cu(I) ions have been reported in the literature to reversibly complex olefins and to resist acetylene poisoning. Because we had difficulty dissolving a Cu(I) salt in our polymer/solvent system (Pebax[®] 2533/ethanol), Cu(BF₄)₂, a Cu(II) salt, was used. As shown in Table 3, Cu(BF₄)₂ by itself was not effective at facilitating olefin transport. However, when blended with AgBF₄, it yielded membranes with

better performance than those containing the silver salt alone. For example, although 40 wt% AgBF₄ membranes exhibited a mixed-gas C₂H₄/C₂H₆ selectivity of only 6, membranes containing 40 wt% AgBF₄ and 40 wt% Cu(BF₄)₂ showed a mixture selectivity of 15. This performance enhancement is not specific to copper salts (or even metal salts), as demonstrated by the results with NH₄BF₄, also shown in Table 3. Pebax[®] 2533 membranes containing 40 wt% AgBF₄ and 40 wt% NH₄BF₄ showed a mixed-gas C₂H₄/C₂H₆ selectivity of 20. These findings suggest that the BF₄⁻ anion may play a more significant role in transport than previously believed.

Table 10. Mixed-gas Transport Properties of Pebax 2533 Membranes Containing Mixed Carrier Salts.

| Carrier | Mixed-gas Permeance (gpu) | | Mixed-gas C ₂ H ₄ /C ₂ H ₆ selectivity |
|---|-------------------------------|-------------------------------|--|
| | C ₂ H ₄ | C ₂ H ₆ | |
| 40 wt% AgBF ₄ | 3.9 | 0.7 | 6.0 |
| 80 wt% Cu(BF ₄) ₂ | 0.5 | 0.3 | 1.5 |
| 20 wt% AgBF ₄ + 60 wt% Cu(BF ₄) ₂ | 1.4 | 0.2 | 6.0 |
| 40 wt% AgBF ₄ + 40 wt% Cu(BF ₄) ₂ | 4.4 | 0.3 | 15 |
| 60 wt% AgBF ₄ + 20 wt% Cu(BF ₄) ₂ | 6.0 | 0.2 | 29 |
| 40 wt% AgBF ₄ + 40 wt% NH ₄ BF ₄ | 10 | 0.5 | 20 |
| 60 wt% AgBF ₄ + 20 wt% NH ₄ BF ₄ | 20 | 0.6 | 32 |

Membrane configuration: 1 x 0.5% Teflon AF2400 / 2 x 2% Pebax[®] 2533 + salt / PVDF. Test conditions: feed pressure = 50 psig, T = 23°C. Mixture composition: 65% C₂H₄, 35% C₂H₆.

To further investigate this mixed carrier discovery, several additional salts were examined. The results of mixed-gas tests are shown in Table 11. Consistent with our earlier measurements, some of these non-silver salts also improve performance when added to Pebax[®] 2533 + AgBF₄ membranes. For example, the membrane containing 40 wt% Ca(BF₄)₂ exhibited a mixed-gas ethylene/ethane selectivity of 27, nearly equivalent to a standard 80 wt% AgBF₄ membrane. Another interesting finding is that it appears the non-silver salt does not have to contain a BF₄⁻ anion to enhance membrane performance. One of the membranes containing Mg(CF₃SO₃)₂ also shows enhanced performance compared to a membrane with AgBF₄ alone. Generally speaking, this mixed carrier discovery offers the possibility to obtain better membrane performance using significantly less of the expensive silver salt.

Table 11. Mixed-Gas Transport Properties of Additional Pebax[®] 2533 Membranes Containing Mixed Carrier Salts

| Carrier | Mixed-gas Permeance (gpu) | | Mixed-gas C ₂ H ₄ /C ₂ H ₆ Selectivity |
|--|---------------------------|--------|--|
| | Ethylene | Ethane | |
| 40 wt% AgBF ₄ | 3.9 | 0.7 | 6 |
| 40 wt% AgBF ₄ + 40 wt% NaBF ₄ | 9.1 | 1.0 | 9.1 |
| 40 wt% AgBF ₄ + 40 wt% NH ₄ BF ₄ | 7.0 | 0.6 | 12 |
| 40 wt% AgBF ₄ + 40 wt% Fe(BF ₄) ₂ | 2.6 | .073 | 3.5 |
| 40 wt% AgBF ₄ + 40 wt% Mg(CF ₃ SO ₃) ₂ | 5.1 | 4.7 | 1.1 |
| 60 wt% AgBF ₄ + 20 wt% Mg(CF ₃ SO ₃) ₂ | 14 | 0.68 | 21 |
| 40 wt% AgBF ₄ + 40 wt% Zn(BF ₄) ₂ | 7.4 | 0.4 | 19 |
| 40 wt% AgBF ₄ + 40 wt% Ca(BF ₄) ₂ | 23 | 0.80 | 27 |
| 60 wt% AgBF ₄ + 20 wt% Ca(BF ₄) ₂ | 26 | 0.87 | 30 |
| 40 wt% AgBF ₄ + 40 wt% Al(CF ₃ SO ₃) ₃ | 43 | 43 | 1.0 |

Feed gas = 65% ethylene, 35% ethane: feed pressure = 50 psig; permeate pressure = 0 psig at room temperature.

The reason for the improved performance of mixed carrier systems is not well understood. Previously, it has been noted that metal salts can increase olefin sorption in aqueous silver salt solutions. It was suggested that the metal cations attract BF₄⁻ and water molecules, leaving Ag⁺ ions more exposed, which allows olefin molecules to interact with silver more easily. Based on this hypothesis, the charge-to-size ratio of the non-silver metal ion should be as high as possible. Comparing the data for mixed carriers with 40 wt% AgBF₄+40 wt% non-silver salt, the smallest divalent borofluorate salt, Ca(BF₄)₂, gives the highest ethylene permeance and selectivity. This result suggests that smaller salts, such as Mg(BF₄)₂ or Be(BF₄)₂, might enhance silver salt membrane performance even further.

An additional benefit of the mixed carrier systems is that they appear to degrade at a slower rate when exposed to light than membranes containing only AgBF₄. Because such behavior suggests a possible increase in membrane stability, this phenomenon was further investigated. Various coating solutions and membrane samples were prepared and images recorded. Figure 43(a) shows the membranes on the day they were made, while Figure 43(b) shows the membranes six days later. Our standard 80 wt% AgBF₄ membrane (shown on the left) appears dark brown in color almost immediately after coating. The dark brown color signifies the presence of silver metal particles, indicating that active Ag⁺ ions have been reduced to inert Ag⁰. Based on Figure 43, membrane samples containing Ca(BF₄)₂ or Zn(BF₄)₂ do not exhibit immediate silver carrier reduction. This suggests these salts have some potential capacity to stabilize Pebax[®] 2533+AgBF₄ membranes. Although not shown, this was not the case for NH₄BF₄-containing membranes, which rapidly turned black, much like the standard AgBF₄ membrane. In contrast,

both $\text{Al}(\text{CF}_3\text{SO}_3)_3$ and $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ also showed some capacity to mitigate light-induced silver reduction.

As discussed in Section 5, we found that adding an $\text{H}_2\text{O}_2/\text{HBF}_4$ mixture to our standard Pebax[®] 2533 + AgBF_4 membrane retarded Ag^+ ion reduction in freshly coated membranes. However, because H_2O_2 and HBF_4 are volatile liquids that evaporate over time, their beneficial effect was short-lived unless the membranes were stored in a sealed environment. $\text{Ca}(\text{BF}_4)_2$ and $\text{Zn}(\text{BF}_4)_2$ are solids, and thus not subject to this evaporative limitation. Consequently, they have greater potential as long-term membrane stabilizers. Figure 43 demonstrates this point, as these mixed carrier membranes, especially the one containing $\text{Ca}(\text{BF}_4)_2$, appear white after six days of light exposure. Over this time, our $\text{H}_2\text{O}_2/\text{HBF}_4$ -containing membranes would begin to turn black, indicating the presence of reduced silver.

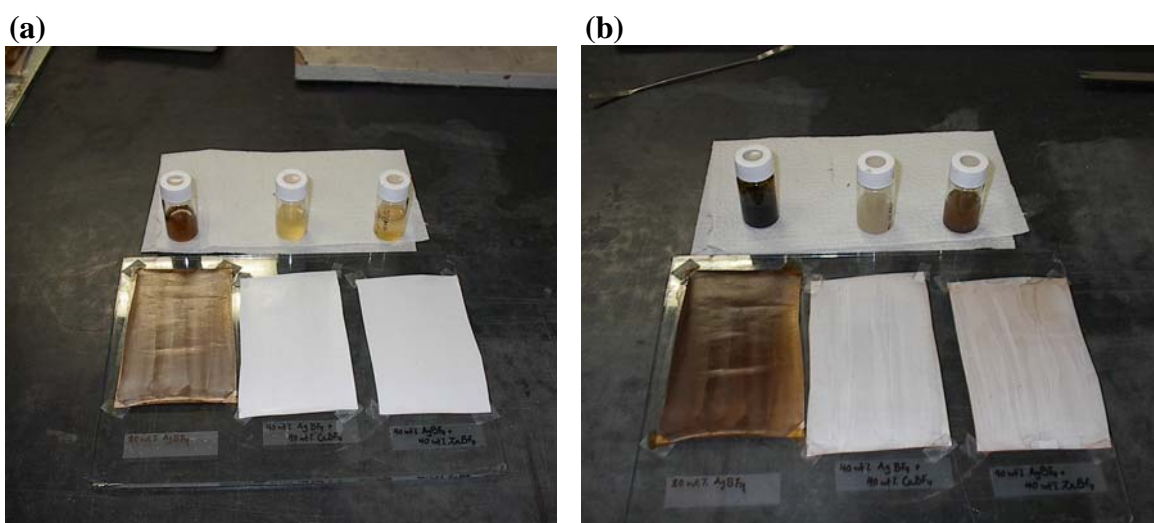


Figure 43. A comparison of membranes containing various mixed carrier salts on (a) the first day they were made and (b) six days after they were prepared. In both pictures, the composite Pebax[®] membrane on the left contains 80 wt% AgBF_4 , the one in the middle contains 40 wt% AgBF_4 +40 wt% $\text{Ca}(\text{BF}_4)_2$, and the membrane on the right contains 40 wt% AgBF_4 +40 wt% $\text{Zn}(\text{BF}_4)_2$. The corresponding solutions are shown above the membranes.

Although time did not permit a thorough aging study of the mixed carrier membranes, Figure 44 presents limited data for the most promising mixed carrier, $\text{Ca}(\text{BF}_4)_2$. Initially, the ethylene permeances of an 80 wt% AgBF_4 membrane (the control) and a 60 wt% AgBF_4 + 20 wt% $\text{Ca}(\text{BF}_4)_2$ are approximately equal, while that of a 40 wt% AgBF_4 +40 wt% $\text{Ca}(\text{BF}_4)_2$ membrane is about half as high. Over time, both of the higher permeance membranes show a decline in performance, while the ethylene permeance of the 40 wt% AgBF_4 +40 wt% $\text{Ca}(\text{BF}_4)_2$ membrane appears to be stable. However, the mixed-gas ethylene/ethane selectivities of all three membranes, which are initially between 25-30, decline over the course of the experiment. This decrease is most rapid for the 40 wt% AgBF_4 +40 wt% $\text{Ca}(\text{BF}_4)_2$ membrane. Interestingly, the reason selectivity decreases for this membrane is because ethane permeance increases, rather than that the permeance of the facilitated gas (ethylene) decreases. This would suggest that the

membrane ionic character is decreasing over time, which is somewhat different than the olefin-conditioning effect that impacts high silver salt content membranes. These mixed carrier membranes clearly warrant further investigation.

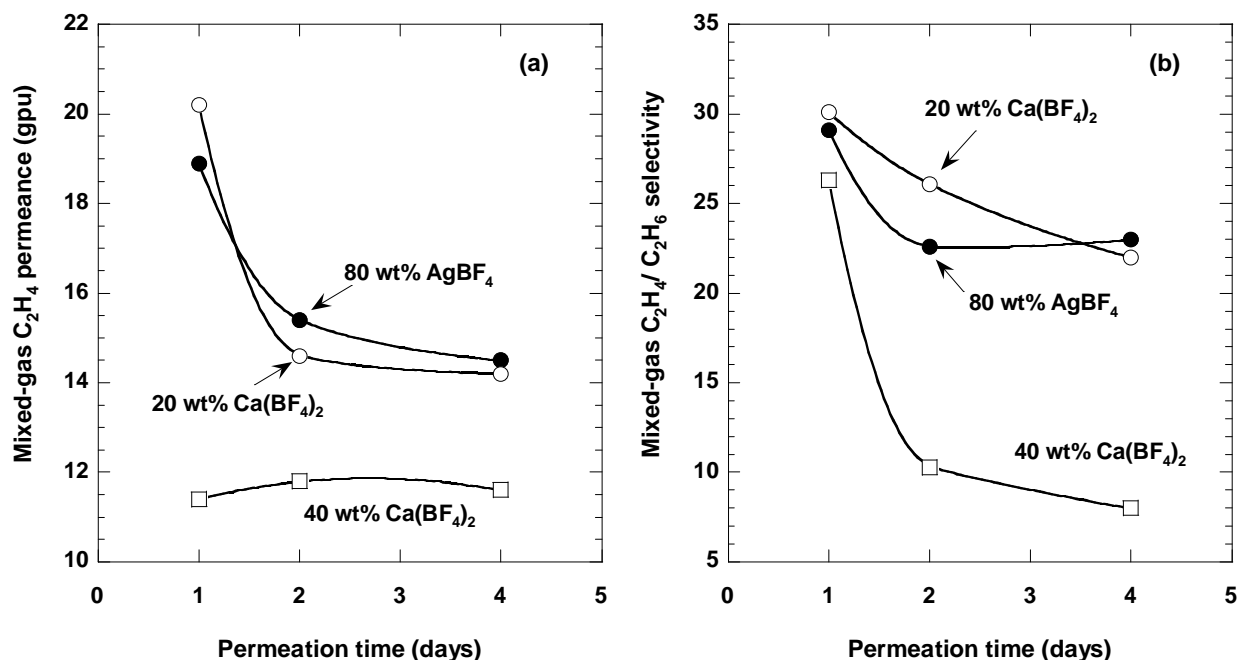


Figure 44. Mixed-gas (a) ethylene permeance and (b) ethylene/ethane selectivity as a function of permeation time for Pebax® 2533 composite membranes containing 80 wt% $AgBF_4$, 60 wt% $AgBF_4$ + 20 wt% $Ca(BF_4)_2$, and 40 wt% $AgBF_4$ + 40 wt% $Ca(BF_4)_2$.

7.3 Development of Non-Silver Salt Olefin Carriers

The industrial separation of olefins from paraffins using complexation agents has not yet come to fruition on an industrial scale. The perceived reasons for this are (1) a potential threat of explosion hazard with the current best-performing complexation agent - silver - or, less preferably, copper, and (2) deactivation of silver or copper complexing agents by potential impurities in the feed, particularly acetylene, hydrogen, and hydrogen sulfide (as described in Section 6). In this project, we began the work required to address these issues, using novel complexing agents with 100% selectivity for olefins over paraffins. Dr. Marianna Asaro of SRI International (SRI) led this research.

SRI performed the research in two tasks. The first task was to comprehensively review the literature on olefin complexation. Hundreds of olefin complexes exist, but almost none of them have been used to address this application. Hence most of the data of interest to make selections were unavailable. We therefore used what information was available to prioritize candidates and then undertook the second task, which was the synthesis of candidate complexes. The complexes were then introduced into MTR's membrane materials and the amount of ethylene uptake was compared to that obtained using only the membrane without any complexing agent

and to that obtained using the silver-loaded membrane system. The strategies employed in these Tasks are described below.

Task 1. Identification of Candidate Complexing Agents

Olefin complexes or olefin binding chemistries were identified through searching the literature and then reading the primary references. The complexation agents were evaluated according to the following criteria; the criteria are in approximate order of importance.

a. Reversibility of Olefin Binding

The potential efficacy of olefin uptake in a separation system depends fundamentally on the equilibrium constant of olefin binding, K_{BIND} , and the rate constants of olefin binding, k_{for} , and olefin dissociation, k_{rev} . The relationship between these parameters is shown in Equation (1):

$$K_{\text{BIND}} = \frac{k_{\text{for}}}{k_{\text{rev}}}$$

What the values of these parameters should be for a good olefin carrier in a solid polymer electrolyte membrane is not clearly established. The optimal equilibrium binding constant, K_{BIND} , for a liquid phase separation system has been estimated by Kemena et al as ~ 10 . The optimal complexation agent for a solid phase system, as in the present work, may be somewhat different than that for a solution phase system; however, the solution phase precedent was taken as a starting approximation for the solid phase work.

In principle, a complex having K_{BIND} of 10 would release 90% of its bound olefin with a pressure differential across the membrane of about 10 and 99% of its bound olefin with a pressure differential of about 100. Larger pressure differentials than these become uneconomical. Lower binding constants than ~ 10 can be used, with the caveat that as K_{BIND} approaches 0, the selectivity for olefin over paraffin imparted by the complexation agent also approaches zero.

The equilibrium binding constant K_{BIND} is a ratio of rates of the forward reaction (olefin binding) and the reverse reaction (olefin dissociation). The values of these kinetic constants are as important as their ratio. Both k_{for} and k_{rev} need to be large, with the former being ~ 10 times larger than the latter. The required magnitudes of these rate constants are highly specific to the type of separation system. The observed rate constant, k_{obs} , for any reaction is particularly affected by the medium and may differ substantially with different separator configurations (for example, membrane, packed bed, aqueous solution, etc.) due to differences in mass transfer characteristics or limitations.

Those few non-silver based systems that have been characterized for equilibrium binding of olefins have been studied in solution phase; in fact, most literature describing olefin complexes or complexation does not provide any data on equilibrium constant or rate constants of olefin binding. Nonetheless, we were able to down-select and prioritize by careful reading and deductive reasoning. For example, an olefin complex that was synthesized and then dried under a typical vacuum of 1 torr or below without change in composition is likely a poor choice

because K_{BIND} is presumably $\gg 10$ or the olefin would have been released. It is also possible to glean qualitative or quantitative information on olefin binding from spectroscopic results, particularly from the observation of olefin exchange by NMR spectroscopy. Such solution phase data are useful as guidelines to down-selection.

Complexes that display reversible olefin binding must do so by the appropriate mechanism to be useful for gas separations. Many olefin complexes exchange olefin associatively, only losing olefin after taking up another molecule such as solvent. Those that exchange or lose olefin dissociatively are much more attractive for reversible gas uptake applications.

In summary, the potential of a candidate complexing agent to display reversible olefin uptake was assessed by consideration of its equilibrium binding constant, kinetic constants, and reaction mechanism where such data were available or could be qualitatively assessed. Those systems where no such data were found could still be good candidates but were given lower priority in favor of those for which positive information was available.

b. Stability

The thermal and chemical stability of the candidate complexing agents were also important selection criteria in this work. The thermodynamics of olefin binding were considered first, as described under ‘Reversibility of Olefin Binding’. The thermal stability of the complexes toward other decomposition routes was considered next in the Task 1 screening; for example, when an olefin complex decomposes through some route other than loss of olefin.

The stability of complexes toward acetylene, other olefins such as propylene, hydrogen sulfide, acetylene, hydrogen, and oxygen were also canvassed in the literature screening. Typically, little if any of this information was available. Instability in the presence of oxygen, if present, is often noted in the literature, and occasionally competitive uptake experiments with ethylene and an acetylenic compound are provided. Stability toward hydrogen sulfide is almost never reported; however, some sense of this may be obtained by noting the stability toward water. Hence, down-selection based on stability toward potential contaminants was made primarily based on SRI’s two decades of previous experience with these types of complexing agents. In general, chemical stability is most likely to exist where chemical characteristics are relatively neutral. Thus the candidate complexes will likely be neither highly basic nor highly acidic and neither highly oxidizing nor highly reducing in character.

c. Polarity and Solubility

The next screening consideration was the polarity and solubility of the complexing agent, as it would affect compatibility with the MTR membrane systems. The ideal complexing agents would be soluble in water, alcohols or other polar solvents in which MTR’s preferred membrane materials could be dissolved. PEO-based membranes rather than Pebax[®]-based membranes were used for testing new olefin carriers because of their water solubility and easier analytical testing properties. The selection was not entirely limited to the more polar species, however, because MTR has a repertoire of other membrane polymers. An additional advantage of using polar solvents is that ethane has low solubility in polar environments.

Qualitative solubility information is often available in the literature. The preferred candidates based on solubility tended to be relatively polar, neutral species or cationic species with solubilizing counterions. Anionic candidates were few in number and were generally considered too chemically or thermally unstable for use in this application.

d. Ease and Cost of Synthesis

Ease of chemical synthesis was the final consideration in the screening process, albeit with less weight than the other criteria at this stage of development. The few commercially available complexes that bind olefins were considered and tested as appropriate. Most candidates would need to be synthesized, however, and only those that were deemed definitely unscalable (for plant use at industrial production levels) were rejected based on synthesis method. Likewise, the projected cost of the complexing agent was given low screening weight, because in our experience an expensive, but effective and long-lived complexing agent or catalyst is well-tolerated in the process economics. For example, the catalyst used for commercial preparation of the commodity chemical ethylene oxide can be as much as 35% silver by weight, but the material is sufficiently robust to provide favorable process economics.

Task 2. Synthesis of Candidate Complexing Agents

The candidate complexes were synthesized according to literature methods. The identity and purity of complexes were confirmed by

- NMR spectroscopy of organic segments of the complexing agents, including bound and free ethylene;
- IR spectroscopic analysis of various groups, particularly the $\nu_{C=C}$ stretch of the bound ethylene;
- UV/visible spectroscopy;
- observation of changes in absorption position depending on whether the ethylene was bound or unbound; and
- comparison to literature data for proof of identity.

Discussion of Screening and Synthesis Results

Approximately 250 olefin complexes or olefin binding chemistries were identified through literature search, reading the primary references in the initial literature search and perusing other references. These were grouped according to the categories shown in Table 12; the categories are numbered in order of Task 1 screening priority. Approximately 40 complexing agents were deemed of high interest, either based on data found in the literature or based on our experience.

Table 12. Categories of Olefin Complexes Considered for Olefin/Paraffin Separation. Categories are numbered in order of Task 1 screening priority.

| Priority | Category Description |
|----------|---|
| 1 | Cationic Olefin Complexes of Ru |
| 1a | Cationic Olefin Aqua Complexes of Ru |
| 1b | $[\text{Ru}(\text{amine})_n(\text{olefin})]_2$ |
| 2 | Neutral Olefin Complexes of Ru |
| 3 | Cationic Complexes of Rh/Ir/Co with Olefins |
| 3a | Cationic Olefin Aqua Complexes of Rh |
| 3b | Cationic Bis(olefin) Complexes of Rh |
| 4 | Neutral Olefin Complexes of Rh/Ir |
| 4a | Neutral Bis(Olefin) Complexes of Rh/Ir |
| 5 | Olefin Complexes of Fe |
| 6 | In-Situ Formation of Cationic CO Olefin Complexes of Groups 6 and 7 |
| 7 | Neutral Carbonyl Olefin Complexes of Groups 6 and 7 |
| 7a | In-Situ Formation of Neutral CO Olefin Complexes of Groups 6 and 7 |
| 8 | Group 6 Olefin Complexes with Oxy Ligands |
| 9 | Metallocenes with Olefin Ligands |
| 10 | Olefin Complexes of Co |
| 11 | Olefin Complexes of Ni |
| 12 | Olefin Complexes of Pt and Pd |
| 13 | Reversible Metal-Hydrogen (M-H) Insertion |
| 14 | Dithiolate Complexes |
| 15 | Metallocubanes |
| 16 | Complexes of Olefins & Lewis Acids |
| 17 | Special Reagents |
| 18 | Complexes of Olefins with Alkali Metals and Transition Metals |
| 19 | Complexation of Olefins with Main Group Elements |
| 20 | Olefin Complexes of Ag, Cu, Au, and Hg |
| 21 | Patents |

Project time and budget constraints considerably limited our experimental synthesis and testing efforts beyond the initial screening exercise. Consequently, priority was given to complexes for which some data were available. A total of eight complexes were synthesized and two additional complexing agents were purchased. Of these, four were selected for testing in MTR's membrane system. Some of the complexes that showed promise based on the membrane tests are the subject of an SRI patent application that is still in preparation, so the complexes are referred to below by their identification numbers. The discussion of each complex provides an example of the variation in information, synthesis, and results that were obtained in this section of our project.

a. Complex 14646-16 was selected for evaluation because it has good stability and was anticipated to have good compatibility with polyether membranes of interest for olefin/paraffin gas separations. Because this olefin complex is cationic, most of its salts will tend to have solubility in the polar solvents needed to dissolve the polymer and to cast the membrane. The ethylene complex of 14646-16 has been reported in the literature without equilibrium or rate constant data. The identity of the recrystallized ethylene complex was established by IR

spectroscopy ($\nu_{C=C}$ at 1537 cm^{-1} , weak, Nujol mull) and by NMR spectroscopy ($\delta = 3.18\text{ ppm}$ in D_2O , singlet, bound ethylene), and no side products were observed.

Complex 14646-16 is known to bind acetylene, forming a 1:1 adduct without formation of any acetylides or acetylene polymers. Based on a comprehensive investigation of the literature, we find that it is not feasible to predict, a priori, whether acetylene or ethylene binds more strongly (if at all) to a metal complex in a given environment. For candidates such as complex 14646-16, if ethylene binding experiments showed promise, we would then perform the ethylene/acetylene competition experiments within the membrane.

The BF_4 salt of complex 14646-16 was selected for synthesis because it had good solubility and by analogy to the preferred use of BF_4 in the silver system, where we believe that BF_4 exerts a synergistic effect with the complexation agent in olefin/paraffin separations.

The ethylene-bound form of complex 14646-16- BF_4 was co-dissolved in 24 ml of water at 2 wt% each of the complex and the PEO polymer. The membrane was cast and the solvent was evaporated at ambient temperature over several days. The initially light yellow, compound-loaded membrane slowly changed color to purple over this time period and the dried membrane did not show desorption of ethylene. We then prepared the PF_6 salt, 14646-16- PF_6 , and performed the casting in acetonitrile, with solvent removal over a few hours under reduced pressure. The resulting light yellow, loaded membrane was stable but did not show ethylene desorption. The fact that neither complex 14646-16 salt showed ethylene desorption suggests that K_{BIND} for this complex is too high for reversibility of complexation.

b. Complex 14646-37 was selected because it has good stability and is also commercially available. It is a neutral species that is not soluble in the polar solvents needed for PEO membranes, so we dissolved the ethylene-bound form of 14646-37 at 2 wt% contained metal in acetone and used ethylcellulose at 2 wt% to cast the membrane. The dried membrane formed a powder instead of a film, which suggests that the complex may have interacted with the polymer. The commercial ethylcellulose was 47% ethoxy-substituted, the rest being hydroxy-substituted. We suspect that these hydroxyls on the polymer bonded to the carrier complex and destroyed the film-forming ability of the system. We were unable to obtain sorption data on the powder.

c. Complex 14646-42 was selected because it has good stability and its direct precursor is commercially available. It is a neutral species that is not soluble in the polar solvents needed for PEO membranes, so we co-dissolved the unbound complex and polystyrene at 2 wt% each in a solution of 25 mL acetone and 5 mL toluene. The membrane was dried but failed to show ethylene uptake. This was surprising; however, prior work in our labs with the ethylene complex of 14646-42 was performed in ethanol/water solution phase and apparently that work does not transfer to the polystyrene membrane system.

d. Complex 14646-48 was selected because it has good stability and has an estimated solution phase equilibrium dissociation constant of about 0.04 M^{-1} . This corresponds to a K_{BIND} of about 25 M^{-1} , which is a bit larger than our target range of about $10 \pm 5\text{ M}^{-1}$ but might be sufficient for proof-of-principle. Complex 14646-48 was prepared in four steps from commercially available starting materials. The product was recrystallized and characterized for identity and purity by

proton NMR spectroscopy. Stability tests were not performed but we did note that the yellow solid was stable to air during handling.

A quantity of the ethylene-bound form of 14646-48 corresponding to 1.4 mmol of ethylene-binding capacity was co-dissolved with PEO polymer at 1.2% : 1.2% w/w concentration of contained complexation metal : PEO polymer. Acetonitrile was used as solvent. The dissolution was completed by allowing the mixture to agitate on a roller mill overnight. The compound dispersed well and formed a good film after casting and evaporation of the solvent. Initial studies showed no ethylene desorption. The sample was kept under reduced pressure for some days, whereupon loss of ethylene had occurred. The sample was cycled with ethylene atmosphere and showed re-uptake of ethylene (see Figure 41). These results suggest that the complex is able to reversibly uptake olefin and that a modified version of this complex having a somewhat lower value of K_{BIND} should be designed, prepared and tested. That work is fairly straightforward to do; however, the project ended before it could be performed.

Figure 45 shows an ethylene sorption isotherm for the PEO/complex 14646-48 blend. For comparison, ethylene sorption isotherms for pure PEO, PEO containing two compounds previously examined in this program, and PEO containing AgBF_4 are also shown. In contrast to previous complexes examined, 14646-48 appears to increase ethylene sorption when dispersed in PEO. This is an encouraging finding, although the amount of ethylene uptake is still more than an order of magnitude lower than that associated with PEO/ AgBF_4 blends.

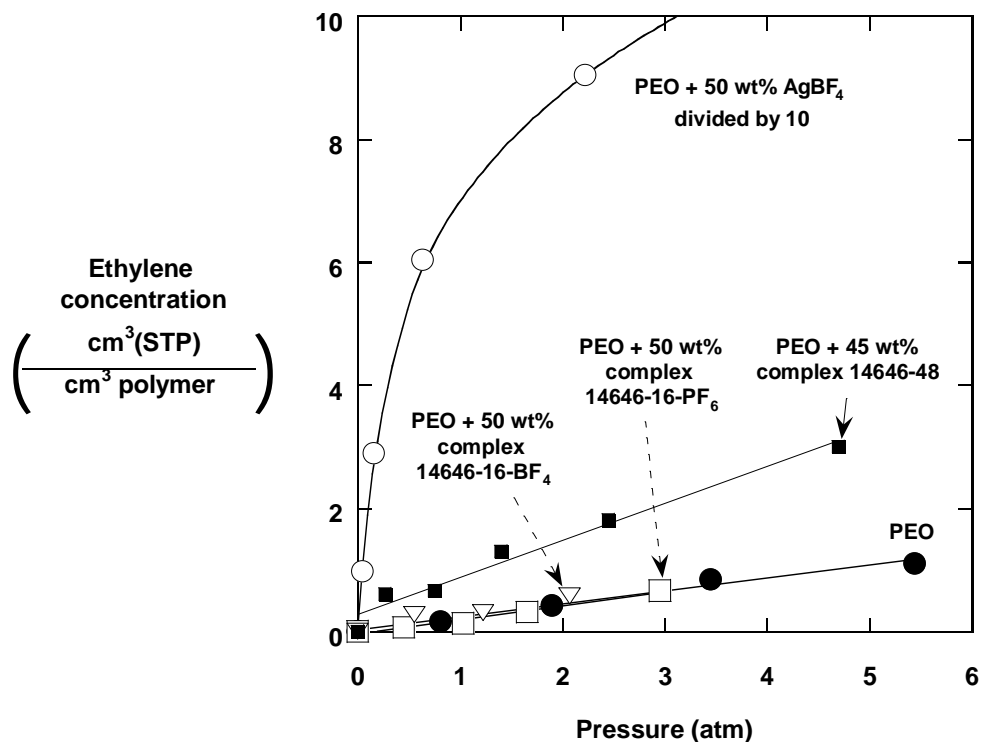


Figure 45. Ethylene sorption isotherms for PEO and PEO containing various olefin complexing agents. The ethylene uptake data for PEO + 50 wt% AgBF_4 have been divided by 10 for presentation purposes.

To test the feasibility of using complex 14646-48 as an olefin carrier in a facilitated transport membrane, we prepared PEO composite membranes containing 80 wt% of 14646-48. These membranes showed no selectivity for ethylene over ethane in pure-gas tests. It appears that the ethylene capacity of 14646-48 is not high enough or the binding constant is too great for effective use in a solid polymer electrolyte membrane.

e. Complex 14646-91 was selected because it has good stability and is of a similar structural type to 14646-48; however, we determined that it has a value of K_{BIND} of about 800 M^{-1} and so its ethylene complex is too strongly bound and is not a good candidate for this application.

Based on the number of issues identified in this project that would need resolving in order to use silver salts for olefin/paraffin membrane separations, the discovery of a new, stable olefin carrier could be the key breakthrough to allow commercialization of carrier-facilitated membranes. Certain of the complexes tested show good potential for successful development, and deserve further study. This would allow strengthening of the proof-of-principle determined during this project.

8. OLEFIN/PARAFFIN SEPARATION APPLICATIONS

8.1 Introduction

At the start of this program three target applications were identified as potential areas where facilitated transport membranes could be used for olefin/paraffin separations. The three initial target applications are briefly described below.

Steam Cracker Cold Trains. Steam crackers produce a mixture of hydrogen, carbon dioxide, light olefins, and paraffins. After treatment to remove carbon dioxide and other impurities, the gas is compressed to 500-600 psi and cooled, liquefied and separated in a series of large towers. This cold train represents the bulk of the capital and operating costs of the plant. We initially proposed using a membrane separation step to treat the gas produced by the steam cracker. The membrane unit was expected to cost approximately \$30-40 million. However, the associated cracker cold train would be significantly smaller, producing capital cost savings and very large energy savings.

Reactor Vent Streams. Technology for the recovery of propylene and ethylene from the paraffin vent streams of petrochemical reactors has the potential for widespread use. We estimate that as many as 200 U.S. petrochemical plants could adopt this technology. An additional 300-400 potential users are located outside the United States. Individually, these applications are small; taken together, they represent a significant opportunity for resource recovery. This gas is usually from a noble metal catalytic reactor; sulfur and acetylene levels are low. This application would also provide the opportunity to introduce and commercialize olefin/paraffin membrane separation technology on a small scale with favorable economics before trying to overcome the barriers involved in building the first membrane-based world-scale steam cracker gas separation plant.

FCC Off-gas. Most U.S. and European refineries use fluid catalytic cracker (FCC) units to convert heavy oil fractions to lower-molecular-weight hydrocarbons for the gasoline pool. In this process, a fraction of the feed is converted to hydrogen, methane, ethylene, propylene and paraffins. The hydrogen and olefins in this gas have considerably greater value when separated than when used as refinery fuel. A few refineries have installed turbo expander-distillation units to treat this gas, but most U.S. refineries continue to use this gas as fuel due to the high cost of liquefaction and distillation. Olefin/paraffin membrane separation technology could potentially expand the number of refineries capable of economically separating FCC off-gases.

8.2 Olefin Metathesis

During this project, a promising application requiring an olefin/paraffin separation technology was identified by our ABB Lummus partners. In this process, the streams of interest are *n*-butene/*n*-butane mixtures. Developing an economical method of separating these mixtures is important in olefin metathesis, used to produce polymer-grade propylene by combining the *n*-butene with ethylene. This separation is not commercially attractive using distillation. If successful, calculations show that a membrane process would increase reactant utilization of metathesis plants by 6%. The energy savings achieved by producing 6% more propylene from the same volume of feedstock are very large.

While butene/butane separations are required in metathesis operations, this separation is also important in the production of 1-butene for use as a polyethylene comonomer and polybutene-1 monomer; and 2-butene for use as a methyl ethyl ketone feedstock.

A process flow diagram of an olefin conversion metathesis plant is shown in Figure 46.^[40] Some plants are built as stand-alone units, but many are integrated with an existing steam cracker that produces the ethylene and butene feedstocks. In a metathesis unit, 0.74 tons of butenes, worth approximately \$200/ton are reacted with 0.31 tons of ethylene worth approximately \$500/ton to produce one ton of propylene valued at \$550/ton (2005 prices). As a result, a feed upgrade of \$247/ton is achieved. Propylene demand is growing at 6%/year in the U.S., and even more rapidly in other regions of the world. As a consequence of this growth, many metathesis plants are being installed. Total worldwide production of propylene by metathesis is 4.5 million tons per year — approximately 6% of total propylene production.

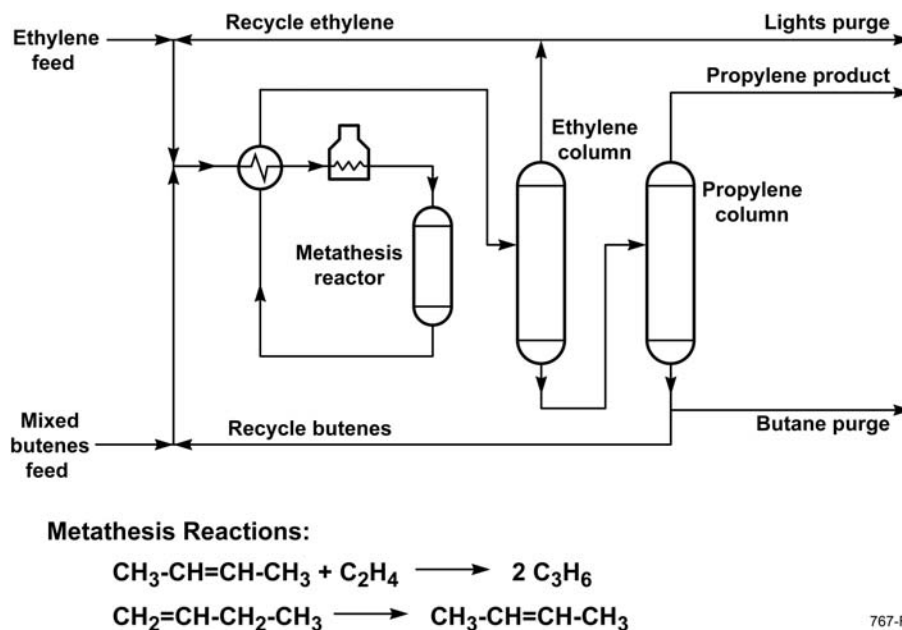


Figure 46. Process flow diagram of a metathesis olefin conversion process. Approximately 10% of the *n*-butene feedstock is lost with the *n*-butane purge.

In the process shown in Figure 46, ethylene and mixed butenes are heated and sent to a catalytic metathesis reactor. The catalyst promotes the reaction of ethylene and 2-butenes to produce propylene, and simultaneously isomerizes 1-butene to 2-butenes. Typical per-pass conversions of almost 60 to 70% are achieved with about 95% selectivity to propylene. The reactor product gas is cooled and fractionated to remove ethylene, which is recycled to the reactor feed. A small portion of the recycled ethylene is purged to remove methane, ethane and other light gas impurities. The ethylene column bottoms are then fed to the propylene column. There is no propane present, so it is not necessary to have a super-fractionator column to produce polymer-grade propylene. The bottoms from the propylene column contain all the unreacted butanes and are recycled to the front of the metathesis reactor. The *n*-butene feed to the process contains approximately 10% *n*-butane and small amounts of isobutane. This *n*-butane rapidly builds up in the recycle loop until the butene mixture entering the reactor contains as much as 25% butane. This high level of butane requires energy to heat the gas and lowers the production rate of the reactor. *n*-Butane levels are controlled by purging a portion of the butene recycle stream. This is a large purge stream and approximately 0.7 mols of *n*-butene are lost with every mole of *n*-butane purged (~ 2,000 kg/h of *n*-butene in a world-scale metathesis plant). The objective of our membrane process is to reduce the *n*-butene loss to 0.1 mol of *n*-butene/mol of *n*-butane purged (~ 300 kg/h).

Figure 47 shows the performance of Pebax[®] 2533+AgBF₄ membranes with a 50/50 *n*-butene/isobutane gas mixture as a function of temperature. The feed in these experiments was a 50/50 vol% C₄ mixture near saturation pressure (activity >0.95). The permeances for the olefin, 1-butene, are very high (>400 gpu) and decrease with increasing temperature. This temperature effect is typical for membranes where permeation is solubility controlled (rather than diffusion controlled as in size-sieving membranes). The extremely high permeance for 1-butene is likely

related to extensive membrane swelling caused by high sorption of this large penetrant. Even in this swollen condition the membrane still exhibits good selectivity for 1-butene over isobutane (about 8).

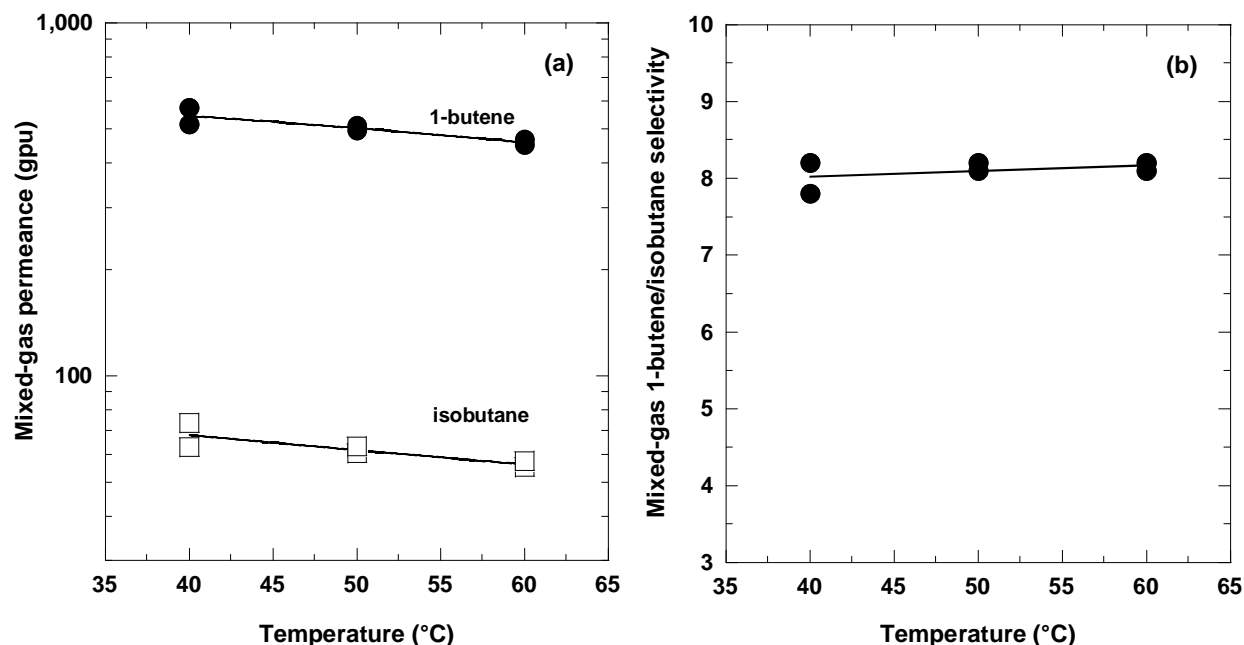


Figure 47. Mixed-gas 1-butene/isobutane (a) permeance and (b) selectivity as a function of temperature.

If stable facilitated membranes with the properties shown in Figure 47 were realized, the required membrane area would drop by nearly an order of magnitude, making the *n*-butene/*n*-butane membrane separation process that much more attractive. ABB Lummus estimates membrane recovery systems for olefin metathesis at approximately a \$150 million opportunity. If the membrane technology could be successfully developed for this first particularly attractive application, other related applications could be developed for upgrading butenes in refinery and other petrochemical operations.

In light of the facilitated membrane stability issue described throughout this report, it seems unlikely that this technology will be ready in the near future. Consequently, we are working on developing passive membranes that could be used for the metathesis olefin/paraffin application.

9. CONCLUSIONS

In this project, we continued the development of a new class of facilitated olefin transport membranes identified in a previous NSF project at MTR. These solid polymer electrolyte membranes initially showed promisingly high permeances and olefin/paraffin selectivities even in the absence of water. The focus of the research in this project was a detailed analysis of membrane time-dependent performance, including performance after exposure to carrier poisoning species.

We discovered that silver salt-based facilitated transport membranes are not stable even in the presence of ideal olefin/paraffin mixtures. For example, over a five-day period of continuous operation, the mixed-gas ethylene permeance of Pebax[®] 2533+80 wt% AgBF₄ membranes decreases from 50 to less than 1 gpu. Over the same time frame, the ethylene/ethane selectivity decreases from 40 to less than 2. This membrane performance decline appears to be caused by a previously unrecognized phenomenon that we have named olefin conditioning. As the name implies, this mechanism of performance degradation becomes operative once a membrane starts permeating olefins. Prior to olefin exposure, silver-salt membranes exhibit completely stable performance when exposed to inert (non-facilitated or non-poisoning) gases. Olefin conditioning is distinct from carrier poisoning in that it does not result in reduction of the silver carrier ion. In fact, visual inspection and FTIR analysis confirm that active silver ions are still present in olefin-conditioned membranes. Also, in contrast to carrier poisoning, olefin conditioning causes a decrease in the permeance of inert gases co-permeating with olefins.

Experiments conducted during this project have shown that olefin conditioning is accelerated by:

- Higher membrane silver salt content – for dry Pebax[®] 2533 membranes with less than 40 wt% AgBF₄, performance is stable over a one-week period. However, olefin/paraffin selectivities are not useful at these low silver loadings.
- Higher olefin feed pressure – at a fixed feed pressure, the rate of membrane performance decline increases with increasing olefin feed concentration.
- Higher temperature – at 5°C, membrane olefin permeance and olefin/paraffin selectivity appear to be relatively stable. The rate of performance degradation increases monotonically with increasing temperature.
- The presence of organic plasticizers or water – low-molecular-weight polyethylene oxide and water are plasticizers that swell the membrane and increase matrix mobility. Both of these additives enhance the rate of performance decline.

These results suggest that the structure of facilitated transport membranes changes over time due to olefin conditioning. When the membrane is exposed to an olefin, the polymer matrix becomes highly swollen as olefin sorbs into the membrane to react with silver ions. In this mobile environment, structural rearrangement that lowers gas permeance appears to occur within the membrane – perhaps by clustering of silver ions. This effect is independent of the matrix polymer (rubbery or glassy) or silver salt (AgBF₄, AgPF₆, or mixed carriers).

This project is the first study to identify olefin conditioning as a significant factor impacting the performance of facilitated olefin transport membranes. To date, we have not identified an effective strategy to mitigate the impact of olefin conditioning, other than running at low temperatures or with low olefin feed pressures. In our opinion, this issue must be addressed before further development of facilitated olefin transport membranes can proceed.

In addition to olefin conditioning, traditional carrier poisoning challenges must also be overcome. Light, hydrogen, hydrogen sulfide, and acetylene exposure adversely affect membrane performance through unwanted reaction with silver ions. For example, exposure to pure hydrogen at 35 psia caused reduction of silver ions to silver metal, resulting in an order-of-magnitude decrease in mixed-gas ethylene/ethane selectivity over a one-week period. Similar

results are obtained for exposure to 10 ppm hydrogen sulfide or acetylene. These harsh poisoning tests represent a worst-case exposure scenario but nonetheless demonstrate a need to improve the stability of the olefin complexing agent to develop membranes with lifetimes satisfactory for commercial application.

A successful effort to improve membrane coating solution stability resulted in the finding that membrane performance loss could be reversed for all poisoning cases except hydrogen sulfide exposure. A novel in-situ regeneration treatment with a peroxide/acid mixture in liquid or vapor form restored aged and poisoned membranes to nearly their initial performance values. This discovery offers the potential to extend membrane lifetime through cyclic regeneration. We also found that certain mixed carriers exhibited greater stability in reducing environments than exhibited by AgBF_4 alone. These results offer promise that solutions to deal with carrier poisoning are possible.

Efforts to identify a novel, non-silver olefin carrier met with some limited success. The best new carrier tested in this project reversibly sorbed ethylene, but at an insufficient level to enhance membrane olefin/paraffin selectivity. It is a significant challenge to find complexing agents that reversibly bind olefins while dispersed in a polymer matrix. However, the payoff for doing so would be large. As discussed above, carrier stability is still the primary technical hurdle blocking further development of silver salt-based facilitated transport membranes. If the stability problems could be largely circumvented by development of a new carrier, it would provide a clear breakthrough toward finally recognizing the potential of facilitated olefin transport.

During this project a promising application requiring an olefin/paraffin separation technology was identified by our ABB Lummus partners. In olefin metathesis, a process used to produce polymer-grade propylene by combining *n*-butene with ethylene, it is desirable to separate mixtures of *n*-butene/*n*-butane. This separation is not commercially attractive using distillation. Calculations show that a successful membrane process would increase reactant utilization of metathesis plants by 6%. The energy savings achieved by producing 6% more propylene from the same volume of feedstock would be very large. Our facilitated transport membranes show excellent separation properties for C_4 olefin/paraffin mixtures. However, in light of the stability problems of facilitated membranes, we are also examining high-performance passive membranes for this application.

The main achievement of this program was the progress made in gaining a more complete understanding of the membrane stability challenges faced in the use of facilitated olefin transport membranes. Our systematic study of facilitated olefin transport uncovered the full extent of the stability challenge, including the first known identification of olefin conditioning and its impact on membrane development. We believe that significant additional fundamental research is required before facilitated olefin transport membranes are ready for industrial implementation. The best-case scenario would be identification of a novel carrier that is intrinsically more stable than silver ions. Even if such a carrier is identified, development will be required to insure that the membrane matrix is a benign host for the olefin-carrier complexation reaction and shows good long-term stability.

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