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## THE FORMATION OF CHEMICALLY MODIFIED $\gamma$ -ALUMINA MICROPOROUS MEMBRANES

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### ABSTRACT

A technique for the chemical modification of 40 $\text{\AA}$   $\gamma$ -alumina membranes with Tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane is presented. The modification is carried out in order to reduce the membrane's pore size so that selective separation of low molecular weight liquid mixtures may be possible. Pure gas permeability measurements with He, H<sub>2</sub>, Ar, and SF<sub>6</sub> are reported for an unmodified and two modified membranes which varied in their reaction times from one day to two weeks. The permeability measurements indicate that the short-term modification produced a membrane that still had an appreciable amount of surface flow, while the membrane modified for two weeks had a hindered surface transport. Also reported are data on the separation of toluene from a high molecular weight (M~660) lube oil. The data indicate an increase in selectivity due to the short-term modification; however, after the two-week modification, the selectivity drops to near unity.

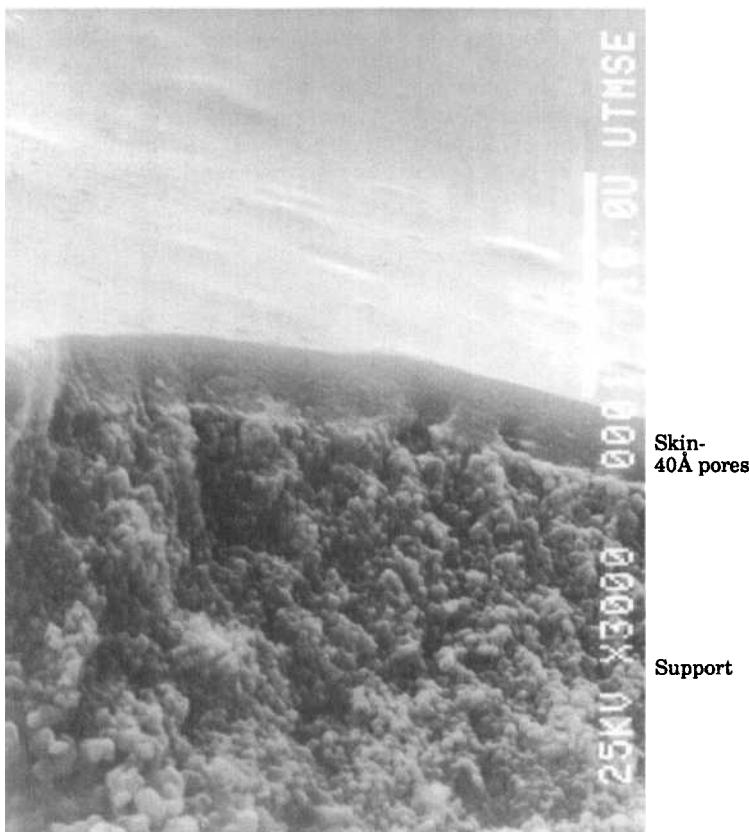
### INTRODUCTION

At present, commercially available alumina ultrafiltration (UF) membranes, known for their high-temperature stability and chemical inertness, have a minimum pore dimension of 40 $\text{\AA}$ , adequate for rejecting molecules having a molecular weight of about

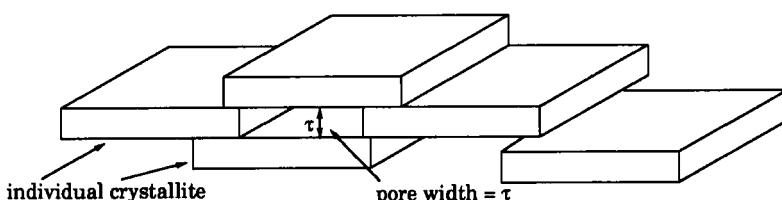
3,000 daltons or greater. The possibility of using alumina membranes for separation of lower molecular weight liquids will only exist if this lower limit of 40Å is further decreased. This can be accomplished in two ways: either by casting membranes that have inherently smaller pores or by chemically modifying the existing pore structure and reducing its size. Membranes with pores as small as 25Å have been cast under laboratory conditions (1); however, still much smaller dimensions are needed to affect most liquid-liquid separations. This paper focuses on the second option and presents a technique that utilizes silanes for the chemical modification of commercially available alumina membranes. The modified and unmodified membranes have been characterized with pure gas permeation measurements, along with scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS). In addition, preliminary permeability and selectivity data are presented concerning the separation of a solvent, toluene, from a lube oil. This mixture is frequently found in combination with methyl-ethyl ketone for use in the process of solvent dewaxing and has been the subject of research with polymeric materials (2,3).

The synthesis of supported alumina UF membranes has been extensively treated by Leenaars (4) and Anderson (5). The method employed for the synthesis is the sol-gel technique, resulting in an asymmetric membrane structure with the selective skin layer being composed of  $\gamma$ -alumina crystallites. Figure 1 is an SEM of this alumina membrane. The pores in the skin have been shown to be the result of the crystallites arranging as a "card-pack" type structure, leaving rectangular voids having a minimum dimension  $\tau$ , as shown in Figure 2.

Hydroxyl groups are present on the surface of these crystallites (and thus the pore wall) and can act as reactive sites for modification of the pore structure with chloro- or alkoxy silanes. This reaction leads to the formation of an Al-O-Si bond and the liberation of HCl or H-OR. Several researchers have focused on the derivitization of surface hydroxyl groups with silanes to produce chromatographic columns (6) or to modify the surface of electrodes (7,8). The substrates treated with silanes have been varied and include silica (6), tin oxide (8), ruthenium oxide (7), gold (9),  $\alpha$ -alumina (9) and others. Recently two groups have attempted this modification on alumina membranes. Shimizu et al. investigated the modification of  $\alpha$ -alumina microfiltration membranes with ethoxy and chlorosilanes for use as a membrane bioreactor (10). Sugawara et al. looked at formation of a composite membrane by interfacially polymerizing silanes on anodically formed alumina membranes (11).



**Figure 1.** SEM of 40Å alumina membrane. It is evident that the membrane is highly asymmetric.



**Figure 2.** The formation of slit shaped pores due the 'card-pack' arrangement of the individual crystallites. Taken from ref. (1).

While the work of Berendsen (6) cited above dealt mainly with changing the chemical nature of silica by silanation, he also reported data showing the effect of silane chain length on the resulting pore radius of derivitized silica. He concluded that the pore radius could be decreased as silanes are introduced into the pore. Whereas this study utilized silanes that had an aliphatic hydrocarbon tail, our research focuses on the control of the slit width by modification with *rigid* perfluorinated silanes.

## THEORY

### Gas Transport

The permeation of pure gases is useful for characterization of microporous membranes (12) and has been studied using both the unmodified and modified membranes considered in the present study. For membranes with pores of 40 Å or less with negligible support resistance, flow will be governed by Knudsen diffusion for non-condensable gases at low pressure since the mean free path is much greater than the pore size. The equation describing Knudsen permeability can be shown as:

$$P = \frac{4 \epsilon \bar{v} f(r)}{3 R T L K_g^2} \quad (1)$$

where  $\epsilon$  is the porosity,  $R$  is the gas constant,  $T$  is the absolute temperature,  $L$  is the thickness of the selective layer,  $K_g^2$  is the tortuosity of the medium, and  $f(r)$  is a function which describes the characteristic dimension of the pore for transport. In general, this is related to the frequency of collisions between the penetrant and the pore wall. For a cylindrical pore,  $f(r)$  is equal to  $r/2$ , where  $r$  is the radius. For a slit with an aspect ratio close to unity,  $f(r)$  is approximately equal to  $\tau/4$ . However, as the aspect ratio increases,  $f(r)$  tends to increase somewhat above  $\tau/4$  (13).

The quantity  $\bar{v}$  is the average molecular velocity and can be further defined as:

$$\bar{v} = \left( \frac{8 R T}{\pi M} \right)^{1/2} \quad (2)$$

where  $M$  is the molecular weight of the gas. It is therefore evident that the Knudsen selectivity for a given gas pair, temperature, and membrane is simply related to their respective molecular weights, assuming no dependence of the penetrant's size on transport.

Complications arise when using gases that tend to adsorb on the surface of the pore and undergo surface diffusion. Surface diffusion is an additional mechanism of gas transport and can greatly enhance gas permeability above the Knudsen prediction. It is a function of the amount of surface area of the medium, the condensibility of the gas, and interaction potential between the gas and solid. It can be expressed by Fick's law in two dimensions:

$$J = -\rho(1 - \epsilon) \frac{D_s}{K_s^2} \frac{dq}{dl} \quad (3)$$

where  $\rho$  is the density of the medium,  $D_s$  is the surface diffusivity,  $K_s^2$  is the surface tortuosity, and  $dq/dl$  is the surface concentration gradient. For a linear pressure gradient the surface permeability can be shown to be:

$$P = \rho(1 - \epsilon) \frac{D_s}{K_s^2} \frac{dq}{dp} \quad (4)$$

where the gradient  $dq/dp$  is found from the equilibrium adsorption isotherm.

In the absence of laminar flow, any deviations from Knudsen selectivity between two gases can be attributed to surface diffusion. Therefore, the total flow is a sum of Knudsen and surface components and a general expression for selectivity between gas "a" and "b" can be written as:

$$\frac{P_a}{P_b} = \frac{\beta M_a^{-0.5} + P_{a,SD}}{\beta M_b^{-0.5} + P_{b,SD}} \quad (5)$$

where  $\beta$  is a constant for a given membrane and temperature and  $P_{a,SD}$  and  $P_{b,SD}$  are the permeability components due to surface flow of gas "a" and "b", respectively. Therefore, if it can be assumed that one of the gases has no surface flow, such as is the case with helium,

then the amount of surface flow of the other gas can be easily determined.

### Liquid Transport

The Carman-Kozeny equation has been commonly used to described the flow of liquids in porous media (14). It is an extension of the Hagen-Poiseuille equation, defined on the basis of a hydraulic diameter. When combined with Darcy's law, the pressure normalized flux, permeability, is shown to be:

$$P_{CK} = \frac{\epsilon D_h^2}{16 K \mu L} \quad (6)$$

where  $K$  is the Kozeny constant, which takes into account the tortuosity and "shape factor" of the material,  $\mu$  is the liquid viscosity, and  $D_h$  is the hydraulic diameter of the medium. It is further defined as:

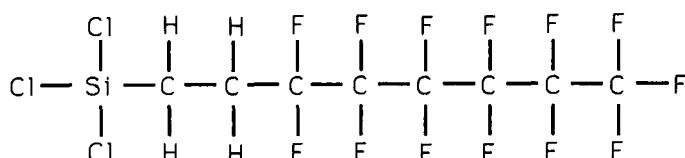
$$D_h = 4 \frac{\text{void volume}}{\text{surface area of channels}} \quad (7)$$

Although this equation is derived for creeping flow, it has been found that in pores of 40 Å or less the permeability is not proportional to the bulk viscosity (15,16). Debye and Cleland's investigation with hydrocarbons and "Vycor" glass concluded in the idea that this deviation is due to a slipping adsorbed layer of molecular thickness at the pore wall. Although this view was in agreement with their data, it is not known if it can generally be applied to situations such as the one discussed in this paper.

## EXPERIMENTAL

### Materials

The silane used in this study is Tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane (Petrarch, Inc.) and will be referred to as TDFS. The structure of TDFS is:



The alumina membranes (Alcoa) used in this work are composite cylindrical tubes with an inside diameter of 7 mm and an outside diameter of 10 mm. They are composed of a  $\gamma$  - alumina skin and an  $\alpha$  - alumina support. The skin is about 5  $\mu\text{m}$  thick with a rated pore (slit) size of 40 $\text{\AA}$ . The support was graded so that the pore size closest to the skin was 0.2  $\mu\text{m}$ , then 0.8  $\mu\text{m}$ , with the bulk of the support containing 10  $\mu\text{m}$  pores.

The gases used in this study are  $\text{H}_2$ , He, Ar, and  $\text{SF}_6$ . All are ultra high-purity grade (99.999%), except for  $\text{SF}_6$  (99.8%), and are sent through a molecular sieve drying column prior to any use. The liquids used are toluene and a deasphalted, dewaxed oil (M-660). The toluene was research grade and was used without further purification.

### Gas Permeation and Modification

Pure gas permeation measurements and the membrane modification were carried out in a apparatus shown in Figure 3. For permeation measurements, a connection is broken at point A and tubing is connected to a bubble flowmeter. An unmodified membrane is securely placed in the stainless-steel housing and valves 1 and 2 are closed. A pure, dry gas is introduced at 23 °C and a feed pressure of 5 psi is reached. Feed pressure is monitored with the indicated pressure transducer. The permeate flowrate is measured until steady state is reached, at which point the next gas is introduced.

After all gas permeabilities have been measured, the connection at point A is rejoined, and valve 1 is opened while valves 2 and 3 are closed. The three-way valve is directed toward the vacuum. The entire system is traced with heating tape and insulation and heated to 190-200 °C, as vacuum is pulled. This is done for about 24 hours to remove any adsorbed moisture from the system and membrane. After this period, the three-way valve is closed as valve 2 is opened, introducing dry argon into the system. After a positive pressure is registered on the feed pressure gauge, the three-way valve is opened to the cold trap, and the argon purge proceeds at about 225 cc/min. The purge proceeds for about 12 more hours, still at 190 - 200 °C, to insure the removal of the moisture.

After this period, the heating tape and insulation is removed from all components except the membrane housing, where the temperature is kept at 50 °C. The cold trap is submerged in a dewar flask containing a mixture of dry ice/isopropanol. The argon flowrate is reduced to about 35 cc/min and the effluent is bubbled into the water

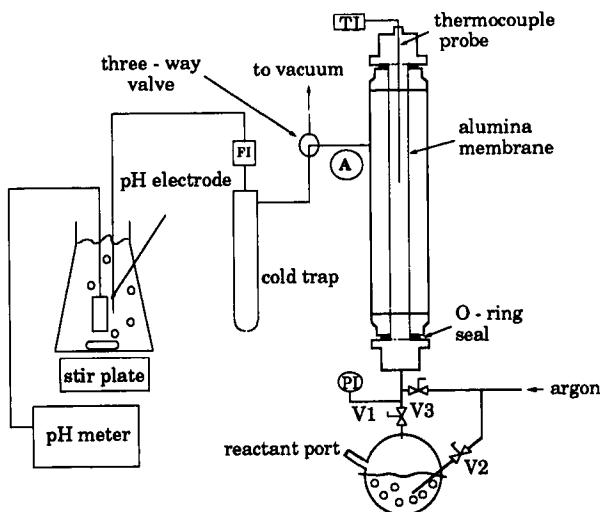


Figure 3. Equipment for the modification of alumina membranes. The reaction is monitored by observing the change in pH and feed side pressure.

bath. At this time, the initial pH and feed pressure are recorded. The reactant is then carefully introduced into the reactant flask using air-sensitive transfer techniques. About 5-10 cc are added so that the argon can bubble through the reactant, carrying its vapor into the bore of the membrane. The reactant, TDFS, and argon then permeate through the pores, where TDFS can react with the available hydroxyl groups, liberating HCl. The permeate, consisting of HCl, unreacted TDFS, and argon proceed to the cold trap where the unreacted silane is trapped out. The argon/HCl mixture is then bubbled into the water bath where HCl dissolves, registering a change in pH. As the reaction proceeds, this pH continues to decrease as the feed pressure increases, for a constant flow rate of argon.

It would be convenient if the evolved HCl data were able to be directly translated into the number of molecules that reacted in the membrane pores. Much work has been done on quantifying the number of OH groups on  $\gamma$ -alumina (17), and for our treatment conditions, this number is fairly well known. However, it is also known that  $\alpha$ -alumina contains OH groups on its surface as well (18,19). The literature reports these values as well; however, there is a substantial amount of scatter. Moreover, an accurate value of the surface area of our support material is not known, and since this makes up the majority of the membranes volume, any error in it will cause the total number of OH groups to be off. Therefore, the pH cannot be used to quantify the number of TDFS groups on the surface,

but it in combination with the pressure measurement can be an excellent qualitative measure of the extent of reaction.

The reaction can proceed to any desirable degree. As will be shown in the Results and Discussion section, the pH will eventually stop changing and the pressure will not continue to increase, signifying the reaction has gone to its fullest extent. When the reaction has proceeded to the desirable point, valves 1 and 2 are closed as valve 3 is opened. This allows clean argon to sweep away any unreacted TDFS vapor from the membrane. At this point, the connection at point A is broken again and a bubble flow meter is connected. The flowrate is measured until steady state is attained and then repeated with the remaining gases.

### Liquid Permeation

The system designed to evaluate liquid permeability is shown in Figure 4. It is most commonly operated at total recycle to keep a near constant feed composition. For normal operation, the membrane is installed and vacuum is pulled for 24 hours with valves 1, 2, and 3 closed. This is done to remove all the air from the pores. For the purpose of this paper, toluene is present in the feed tank and the lines are full up to valve 1. After evacuation for 24 hours, valve 1 is opened followed by valve 2, as the feed pump is turned on. This introduces toluene to the membrane, where it permeates into the vacuum line and is trapped out. After a few minutes, the vacuum line is closed.

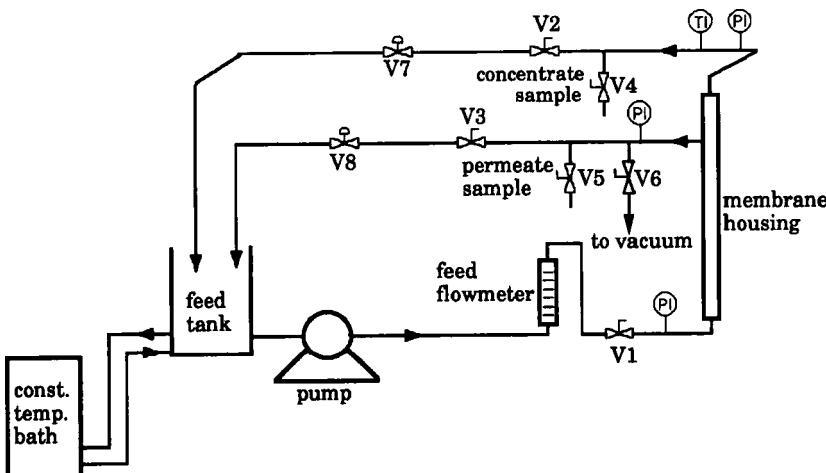


Figure 4. Equipment for toluene/oil permeation studies.

The permeate then fills up the permeate line until the permeate pressure reaches the feed pressure, the point at which the membrane is considered wet. Permeate flowrate is determined gravimetrically, and permeate and feed samples are collected and subjected to vacuum distillation for weight fraction analysis.

For all determinations, crossflow velocity is fixed at about 1.6 m/s, leading to a Reynolds number of about 18,000. Temperature is held at 23 °C. Forthcoming research will look at the dependence of crossflow velocity and temperature on permeability and selectivity.

## **RESULTS AND DISCUSSION**

The modification of the pore structure is expected to proceed by the mechanism shown in Figure 5a. TDFS reacts with the available hydroxyl groups and liberates HCl. It has been shown with the reaction of trifunctional silanes and silica that not all three reactive groups bind to the surface (6). Although the density of OH groups on alumina may be somewhat larger (6,17), it is assumed that there will be 1-2 unreacted chlorines per silane as well. When exposed to the atmosphere, these will likely hydrolyze.

Figure 5b shows how this reaction could affect the membrane's pores. Since it is thought that the pores have a relatively large aspect ratio, about 10 to 15 (1), the reaction of TDFS affects primarily the slit width,  $\tau$ , and not the breadth of the pore. Although from a distance, the modified pore may appear to be evenly coated with TDFS, the inset provided in Figure 5b shows that due to steric hindrance not all available OH sites are likely to be reacted. This leaves voids in between the TDFS groups, and the effect of these voids on permeability and selectivity is discussed below.

The bound TDFS groups are rigid since there is essentially no rotation of the C-F backbone due to hindering by the large fluorine atoms. The most flexible link is the Si-C bond, which can freely rotate. However, since the silane is highly fluorinated it has a low affinity for the native alumina. In addition, as the surface becomes more packed with silane groups, the rotation becomes hindered and thus it is believed that the silane resides in a near-vertical position, making full use of its length of 12 - 13 Å.

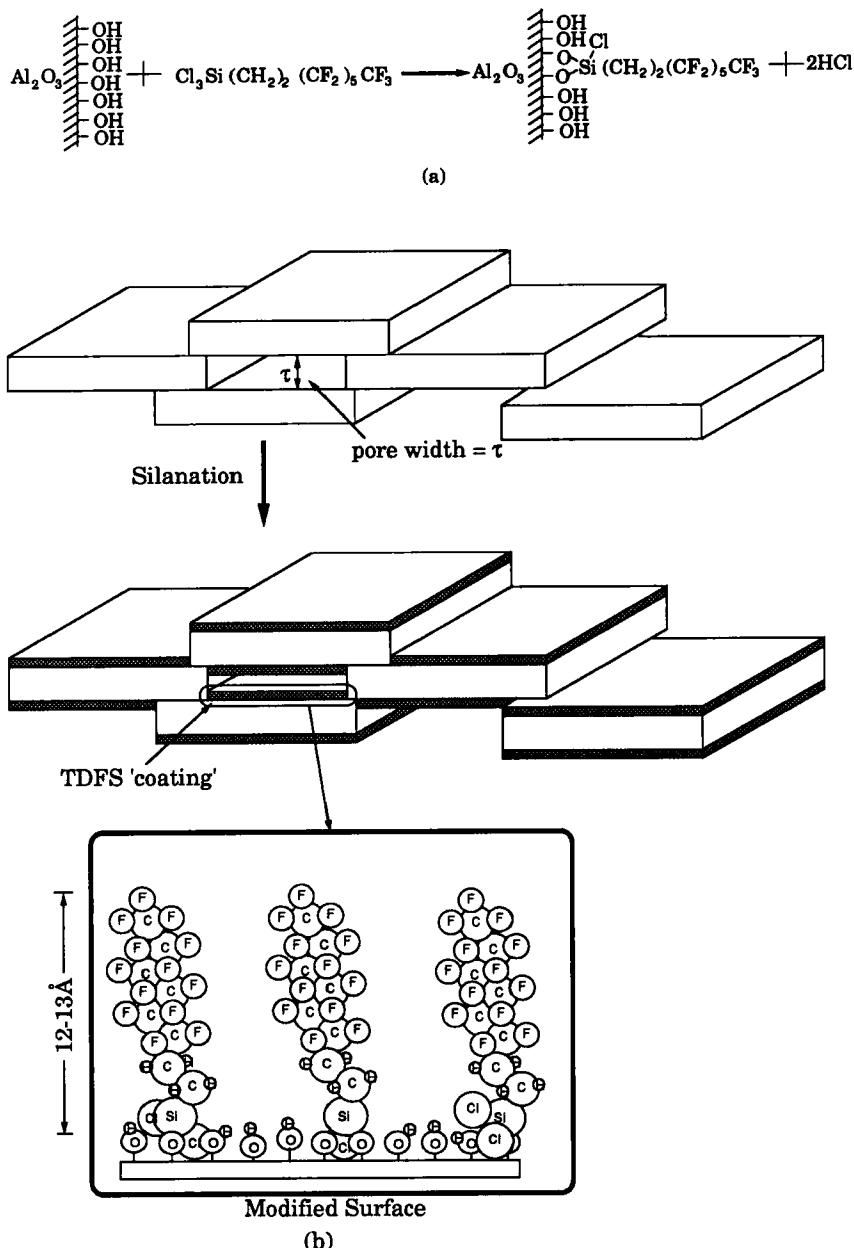


Figure 5. Reaction of TDFS with membrane: (a) microscopic representation depicting reaction with surface hydroxyl groups and formation of HCl; (b) representation of how this reaction can decrease the slit width of the pore. The exploded view of the pore surface shows how there may be gaps between the bonded TDFS groups, as opposed to a dense covering.

### **Modification**

The results of three types of membranes are presented in this paper. They include type A, an unmodified membrane; type B, a membrane modified for 24 hours; and type C, a membrane modified for 14 days. The time-dependent variables used to characterize the extent of modification for membranes B and C were evolved HCl and feed-side pressure. Figure 6 shows the relationship between these variables for these two membranes. As is clear from the graphs, both the pressure and the amount of HCl evolved increase with time, apparently reaching a limit near the 14-day period for the 50 °C reaction conditions used here. The pressure is seen to increase very rapidly at first due to the onset of the larger TDFS molecules invading the pores; however, the amount of evolved HCl does not increase substantially until about 12 hours have passed. The reason for this is unclear at this time. Overall, these data suggest that as the reaction is proceeding, the resistance of the membrane is increasing, presumably due to a decrease of the effective pore size. However, two other possibilities must be considered. If there was residual moisture on or in the membrane during the reaction, the trifunctional silane could have polymerized either on the surface with a film extending across the mouth of the pores, or polymerized in the pores themselves. The formation of a polymeric film was definitely ruled out after SEM and XPS were used to analyze the surface.

SEMs were taken of the membrane surface and cross section before and after modification. These are shown in Figure 7. It can be seen that the two materials are nearly identical and detection of a polymeric substance is not possible. Since a thin polymer skin may be beyond the detection levels of this microscope, XPS was employed to get a closer look.

XPS is a surface-sensitive technique, able to examine about the first 100-200 Å of substrate, and determine the material's surface composition. This technique has been used by Murray et al. (20) to determine if polymerization occurred during treatment of electrodes with silanes and can therefore be directly applied to the situation at hand.

Since XPS is able to determine the material's surface composition, the modified and unmodified membranes can be compared by selecting an element that is common to the surface of both materials. Aluminum is a fairly obvious choice since it is not added to the surface during the reaction, nor is it depleted. The appearance of a polymeric skin on the surface would greatly decrease the signal intensity of aluminum for membrane B as compared to

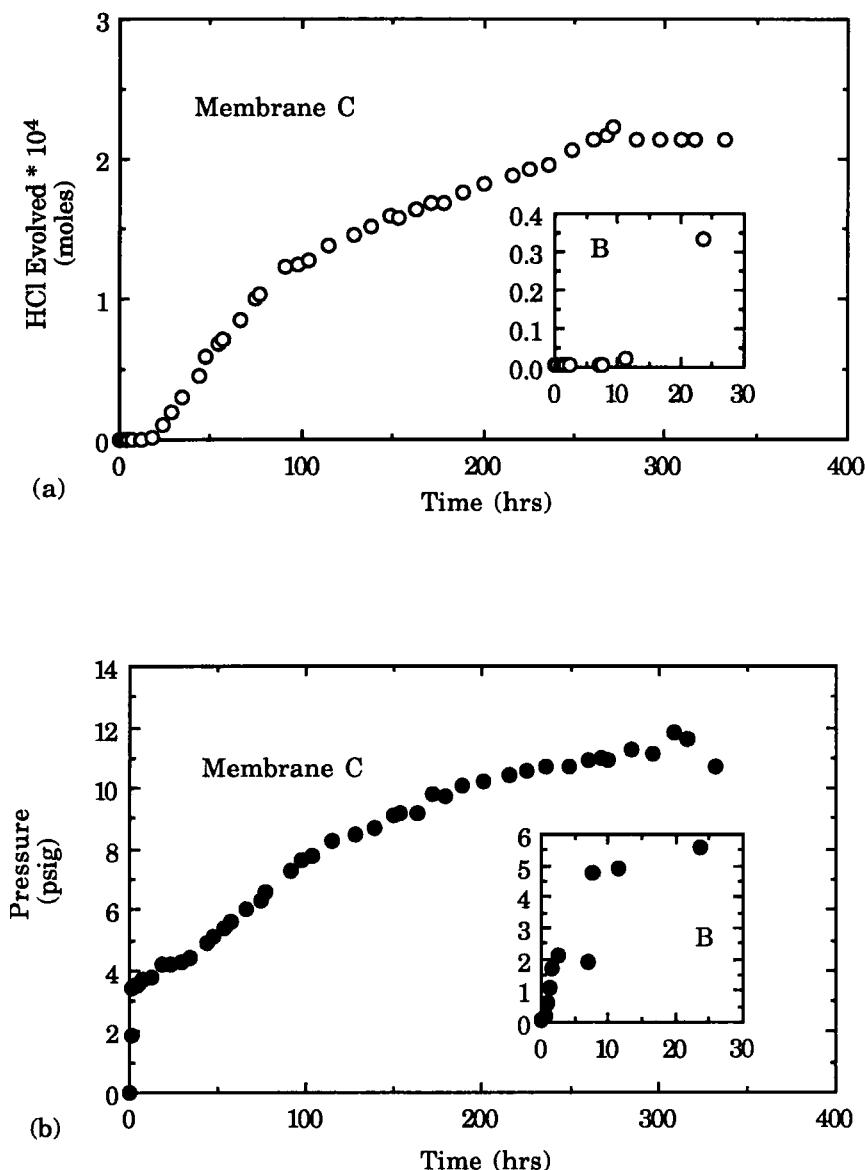
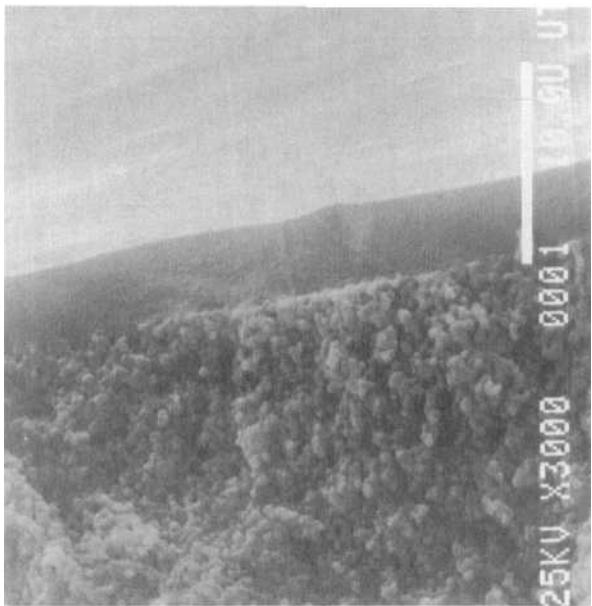


Figure 6. The effect of reaction time on (a) HCl production and (b) argon feed pressure. The insets are short reaction times, characteristic of membrane B.



(a)



(b)

Figure 7. SEMs taken (a) before modification and (b) after a 24 hour modification to check for polymerization. It is evident that no large-scale polymerization of the reactant took place.

membrane A. This can be shown by the following equation:

$$\frac{I_B}{I_A} = \exp(-d/\lambda) \quad (8)$$

where  $I_B$  and  $I_A$  are the Al 2p signal intensities (peak areas) of membrane B and A, respectively,  $d$  is the average silane layer thickness and  $\lambda$  is the escape depth of an emitted photoelectron through it. Experimentally, the value of  $I_B/I_A$  is determined to be 0.66, and using the method described by Penn (21), the value for  $\lambda$  is estimated to be about 24 Å. The value of  $d$  then comes to about 10 Å, and therefore silane monolayers or submonolayers are present on the membrane surface.

Although it can be concluded that there is no polymerization on the surface of the membrane, it cannot be assumed that the same holds true for the membrane pores on the basis of the XPS measurements alone. Since the membrane pores have a very complicated structure and path length, occlusions could occur at points in the pore that may not be "visible" to XPS. In order to investigate this possibility, future work is proceeding toward carrying out the modification with a monofunctional silane. This reactant is exactly the same as TDFS, except that two of the reactive chlorines are replaced by methyl groups. This structure guarantees that no polymerization will take place, and agreement between those reaction results and the present data will ensure that no polymerization is occurring with the present reactant.

### Pure Gas Permeability

Results are presented in Table 1 for the pure gas permeability and permeability ratio (selectivity) of H<sub>2</sub>, He, Ar, and SF<sub>6</sub>. The resistance of the support has been proven by experimentation to be negligible so that the majority of the pressure drop takes place across the selective skin (22), and due to the relatively large mean free path of all gases, laminar flow can be neglected. This is confirmed for H<sub>2</sub> and He since experimentally it is shown that the selectivity of H<sub>2</sub>/He is approximately equal to its ideal Knudsen value of 1.41. While transport of these non-condensable gases is based solely on Knudsen diffusion, the occurrence of surface flow greatly affects the membrane's permeability and selectivity to more condensable gases, as will be shown below.

TABLE 1

Permeability and Selectivity of various gases in  
Membranes A, B, and C

Membrane	Permeability * 10 <sup>8</sup> (mol/cm <sup>2</sup> sec cmHg)				Ideal Selectivity		
	H <sub>2</sub>	He	Ar	SF <sub>6</sub>	H <sub>2</sub> /He	He/Ar	He/SF <sub>6</sub>
A	380.0	268.0	95.6	73.3	1.4 (1.4)	2.8 (3.2)	3.7 (6.0)
B	11.3	7.8	6.8	5.9	1.4	1.1	1.3
C	3.3	2.0	0.9	0.7	1.7	2.1	2.9

Values in parentheses are the  
Knudsen values

For all gases the permeability decreases in going from membrane A to B to C. In the case of membrane A, He and H<sub>2</sub> behave according to Knudsen; however, Ar and SF<sub>6</sub> show a higher permeability than the Knudsen prediction as revealed by the permeability ratio of He to these two gases. In this case, the permeability of SF<sub>6</sub>, which is due to surface flow calculated by equation 5, amounts to 40% of its total flow, while Ar has 11.3% going to surface flow. This is consistent with the higher critical temperature of SF<sub>6</sub>, making it more condensable than Ar.

Upon modification, membrane B shows a He permeability which is 3% of membrane A, while membrane C is about 0.8% of A. These permeability decreases may be rationalized with the aid of Figures 8a and 8b. Figure 8a represents how a modified pore may look if its surfaces were completely coated with TDFS. As stated previously, this type of representation is highly unlikely due to steric hindrance by the bulky silane. A more realistic view is given by Figure 8b, where the groups are not tightly packed, but rather have some amount of space between them. It is thought that the spacing between groups is smaller in membrane C compared to B since the density of groups on C is greater.

Due to this arrangement, the penetrant would not only be undergoing collisions with the pore wall, but rather it can also penetrate into the TDFS occupied region where it can undergo several collisions between individual silanes. It is thought that the average distance between these groups is sufficiently small to cause the penetrant's collision frequency to greatly increase, resulting in the observed permeability decrease. This average distance is not only

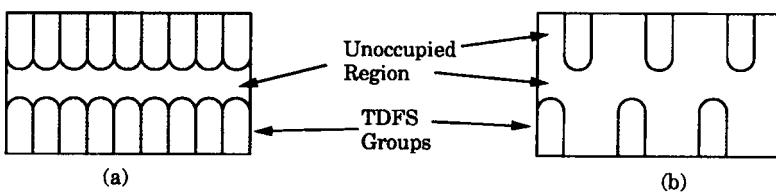


Figure 8. Representation of modified pore opening: (a) if TDFS groups were to form a new, impenetrable surface in the pore and (b) if reacted groups had a gap between them. This gap would allow transport of the penetrant in the region occupied by TDFS.

determined by the distance between silane groups on the same surface, but also between silanes that lie on the pore's top and bottom surface. This is very important to keep in mind since the membrane does not consist only of 40 Å pores, but rather a distribution. In fact, Leenaars (1) shows that a large fraction of the pores lies below the rated pore size, with only a few above. The distance between silanes that lie on the top and bottom pore surfaces is smaller in the smaller pores, and thus the penetrant's collision frequency is increased much more in these smaller pores. As a result, the permeability can be greatly decreased by modification, the effect being amplified for membrane C since the penetrant's collision frequency would be larger due to its higher density of TDFS as compared to membrane B.

The permeability due to surface diffusion can be affected by the presence of TDFS as well. It can be shown that as the surface area of the pores increase, the contribution of surface permeability can increase as well. As Figure 8b depicts, the inclusion of TDFS in the pore apparently increases the surface area. However, the inclusion of these groups would seemingly also increase the tortuosity that a surface-flowing molecule may see. Therefore, as discussed below, the amount of permeation due to surface flow may in fact decrease upon modification.

### **Selectivity**

The selectivity data can also be employed to get a better idea of how the modified pore may look. The selectivity to He/Ar and He/SF<sub>6</sub> seem to decrease from membrane A to membrane B, but then increase in the case of membrane C. If equation 5 is applied to these data, the basis for this behavior can be seen. For example, consider gas "a" to be He and "b" to be SF<sub>6</sub>. For a given membrane and temperature,  $\beta$  is a constant. If there was no surface flow of SF<sub>6</sub>, then it would be expected that the selectivity would be the Knudsen value.

This is obviously not the case, and can be accounted for by considering the added surface flow of SF<sub>6</sub>. This contribution of surface flow to the total flow in the case of membrane B is apparently larger than in A, assuming that the Knudsen permeability of both He and SF<sub>6</sub> decreased by the same amount. Therefore, as stated above, the addition of TDFS into the pore could cause an increase in the collision frequency of the gas phase molecules, while the TDFS groups may be spaced out far enough so as to not greatly affect the surface tortuosity of the pore.

For the case of membrane C, where it is believed that there is a higher density of TDFS on the pore's surface, the selectivity of all gas pairs increases. Again assuming that the Knudsen permeability decreases the same for He and SF<sub>6</sub>, then this increase in selectivity can arise due to a smaller contribution of surface flow of SF<sub>6</sub> to its overall permeability relative to its surface flow contribution in membrane B. It is thought that this decrease in surface permeability comes about due to an increase in surface tortuosity upon modification from B to C, caused by the greater density of TDFS. The same trend is found for Ar and can be explained in the same manner.

It is also observed that the H<sub>2</sub>/He selectivity increases above its Knudsen value for membrane C. A possible reason for this increase in selectivity is that the Knudsen permeability of H<sub>2</sub> in membrane C has been decreased so much that its surface flow is finally becoming a significant part of the total flow. This would result in a H<sub>2</sub> permeability which is higher than that Knudsen prediction, and thus an increased selectivity.

#### Separation of Oil/Toluene Mixture

In order to further evaluate our modified alumina membranes, preliminary work has begun in investigating the industrially important separation of a lube oil from toluene. Mixtures of lube oils and solvents represent fairly low molecular weight mixtures that are presently separated by flash distillation. However, work done by Bitter (2,3) has shown that the separation of Bright Stock oil from a 50/50 mixture of toluene and methyl ethyl ketone is possible with a silicone rubber-based membrane. He reports a permeability of 2 kg/m<sup>2</sup> hr bar at 40 bar, along with a separation factor of about 11 for a 10 wt% oil mixture (2), assuming a specific gravity of 0.86. Similarly, the data reported below are for a 10 wt% oil mixture, however, the solvent consists only of toluene. In addition, the lube oil used in our study is believed to be of about the same molecular weight and distribution as Bitter's; however, it was produced by a different company.

The resulting permeability and selectivity of membranes A, B, and C to this mixture, along with the pure toluene permeability, are reported in Table 2. Predictably, the pure toluene permeability decreases from membrane A to B to C. However, the results of the mixture are not as straight forward. The membrane's selectivity does increase due to the 24 hour modification, but upon further treatment, the selectivity is seen to diminish to unity. In parallel, the permeability of membrane B to the mixture is about 10% of A's, while membrane C is essentially equal to B. This equality is simply due to the fact that membrane C permeates a higher percentage of oil relative to B. While there is a large reduction (~75%) in toluene permeability between membranes B and C, it is not expected that the same reduction in toluene permeability would be seen with the mixture. If this was the case, then the selectivity would fall well below unity. Overall, it is obvious that these results cannot compete in terms of selectivity or permeability with Bitter's membrane; however, slight changes in our modification reaction may help boost the selectivity.

While these results are quite perplexing at first glance, the concepts developed with the gas permeability data can be employed in attempting to rationalize what may be occurring in the case of liquid permeation. The selectivity of membrane A is 1.4, which implies that the size of the oil molecule is large enough to be partitioned between the bulk feed and the pore. Upon modification for 24 hours, the

TABLE 2

Permeability and Selectivity of Toluene and Toluene/Oil Mixture with Membranes A, B, and C

Membrane	Permeability		Selectivity *
	(kg/m <sup>2</sup> hr bar)	( $\omega_{tol}/\omega_{oil}$ ) Permeate	
	Toluene	Toluene/Oil	( $\omega_{tol}/\omega_{oil}$ ) Feed
A	3.02	0.38	1.4
B	0.21	0.03	1.8
C	0.05	0.03	1.0

\* Selectivity is defined on a weight fraction basis

membrane's selectivity increases about 30% to 1.8, apparently due to the inclusion of TDFS into the pore. The picture developed from the gas data of this partially modified pore was one that had TDFS groups spaced out on the pore's surface so that the gas phase Knudsen transport was greatly reduced, but the surface flow of condensable gases, such as SF<sub>6</sub>, was not hindered to a great extent. In a similar manner, liquid toluene may be able to enter and flow through the TDFS occupied region, while the larger oil molecule is much more restricted. In essence, we have created a selective **region** in the pore. The center of the pore, which is thought to be unoccupied, should also be selective since it is now an open channel having a width much smaller than its initial width, depending on the pore size distribution.

From the gas data, membrane C was believed to have closely packed TDFS groups that greatly hindered the surface transport of SF<sub>6</sub>. Therefore, not only the large oil molecule but also toluene may experience highly hindered transport through the TDFS occupied region. We then speculate that the primary channel for transport through the pore is the unoccupied bore in the center of the pore. Again, since this region is much more narrow than it was when unmodified, it should be more selective.

However, as the data indicate, the membrane's selectivity is unity. At least two possibilities exist for this behavior which include (1) flow-induced deformation and (2) favorable adsorption of oil at the mouth of the pore and in the pore due to the presence of TDFS. Flow-induced deformation is caused by applying a strain to a flexible molecule, resulting in an elongated structure with a greatly reduced sieving dimension. This may tend to diminish the membrane's selectivity since this deformed molecule could now transport through the unoccupied region of the pore. The strain is induced by high solvent velocities. The effect of pore size and solvent flow rate on selectivity under conditions producing deformation has been studied by Long and Anderson (23) for relatively large pore sizes (400-1600 Å), with high molecular weight polystyrene ( $M \sim 1 \times 10^6$ ), and very dilute concentrations. Their data indicate that for a given flowrate and size of polymer the selectivity increases as the pore size decreases. Only for very high flowrates does the selectivity actually decrease, presumably due to deformation of the polymer. Utilizing their criteria for a high flowrate, our flow conditions are well below this, implying that flow-induced deformation should not occur in our case. However, to our knowledge, systems representing our conditions of high concentration and very small pores have not been studied. These conditions may lead to violating the assumption of continuum flow, and it is not certain what effect non-continuum flow would have on the structure of the larger oil molecule.

The second possibility for a diminished selectivity comes from the idea that the oil may have a tendency to adsorb favorably over toluene in the pore due to the presence of TDFS. This would result in a higher concentration of the oil in the membrane than in the bulk feed, causing the selectivity based on the feed concentration to decrease. This idea is based on solubility parameters. Highly fluorinated materials, such as teflon®, have a solubility parameter of about  $12.7 \text{ (J/cm}^3)^{0.5}$ , while toluene's is reported to be  $18.3 \text{ (J/cm}^3)^{0.5}$  (24). Based on simulated distillation data, we have estimated the oil's solubility parameter to be on the average about  $16 \text{ (J/cm}^3)^{0.5}$ . Since the parameter for the oil is closer to teflon® than toluene's, we may conclude that it may favorably adsorb into the pore.

For the above case of liquid transport, no mention has been made of the actual mechanism of transport. In the modified membranes, the mechanism may involve combinations of pressure-driven Poiseuille flow, hindered transport (molecular sieving), and concentration-driven diffusion, the degree of which varies from pore to pore. This variance comes about since there is an actual pore size distribution in the membrane, as previously stated. Therefore, the macroscopic theories such as the Carman-Kozeny theory, the theory of Debye and Cleland, and the theory of hindered transport, which make use of bulk-phase solvent viscosities and continuum flow, may not generally apply to the situation at hand.

However, what has been learned is that by partial modification the membrane's selectivity is effectively increased. By using this same type of modification procedure with longer silanes that extend across the width of the pore, this effect could possibly be greatly amplified. This would result in a fairly open, porous pore, as shown in Figure 9. However, transport of larger molecules, such as lube oil, would be hindered in their transport to a much greater degree than

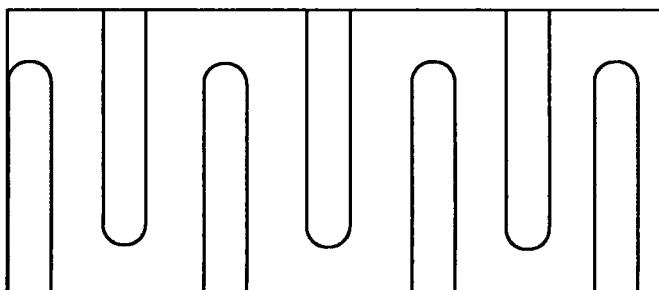


Figure 9. Representation of pore opening if longer chain silanes were utilized at short reaction times.

smaller molecules such as toluene. The arrangement of the silanes in such a pattern would also decrease the possibility of flow-induced deformation since there would not be a continuous, unoccupied region remaining in the pore.

Future work will focus on synthesis of this structure and deducing the transport mechanism of both the unmodified and modified membranes. Work done by Leenaars et al. (15) on unmodified alumina membranes shows a dependence of the permeability on the penetrant's size. We will extend this research to cover our modified membranes and explore the possibility of hindered solvent transport and diffusional flow. This work will utilize well defined polymers to better investigate the effects of permeate velocity and crossflow velocity on selectivity. In addition, since the primary advantage of the alumina membrane is its high-temperature stability relative to polymers, research will be carried out to investigate the thermal stability of the added silane groups.

### **CONCLUSIONS**

It is possible to chemically modify  $\gamma$  - alumina membranes with TDFS in a way that the process can be monitored. The short-term modification seems to produce a membrane with spaced TDFS groups on the surface, capable of affecting toluene/oil separation. Further modification seems to increase the likelihood of events such as shear deformation and oil adsorption.

Although the data presented above cannot compete in terms of selectivity with the polymeric materials currently available, it has provided us with an excellent framework with which a new class of membrane materials can be created. Using this framework, it seems possible that a good separation can be achieved by using our present modification procedure, but with longer silanes that extend across the width of the pore that are not tightly packed. In essence, a membrane could be produced that contained silanes spaced far enough apart to allow one component to pass through, while restricting another, on a molecular level.

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