

Effect of Humidified Feeds on Oxygen Permeability of Mixed Matrix Membranes

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Abstract: Hybrid inorganic/organic membranes, often called mixed matrix membranes, are composed of (inorganic) molecular sieves dispersed in a continuous (organic) polymer matrix. Recent studies have demonstrated that mixed matrix membranes have the potential to exceed the performance of conventional polymer membranes while maintaining their processability. Because water vapor can be present in air and in natural gas feeds, it is an ideal candidate for studying the effects of strongly sorbing minor components on mixed matrix membranes. Water vapor has been shown to cause complex but predictable effects on mixed matrix materials. In this article simple models are proposed to describe the behavior of mixed matrix membranes with

humidified feeds to assist in interpreting observed performance. This research has shown that mixed matrix membranes composed of zeolite 4A dispersed in poly(vinyl acetate) are adversely affected by water adsorbed in the pores of zeolite 4A. On the other hand, a novel, more hydrophobic molecular sieve, SSZ-13, appears to be an ideal candidate for mixed matrix membranes because it has improved transport properties over zeolite 4A and is less affected by sorbed water. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1574–1580, 2003

Key words: gas permeation; membranes; zeolites; composites; humidity

INTRODUCTION

The trade-off between permeability and selectivity of polymeric membranes is a well-known phenomenon. Since Robeson developed his most recent “upper-bound” curves for polymeric membranes, in 1991, to illustrate this trade-off,¹ there has been relatively little progress toward creating polymers with properties beyond this boundary. On the other hand, membranes composed of zeolites or carbon molecular sieves (CMS) have excellent theoretical properties; however, these properties have been difficult to attain for zeolite membranes. The defect pathways created along crystal growth boundaries dramatically reduce the observed performance of zeolite membranes.^{2,3} These problems, coupled with processing requirements, make zeolite membranes unlikely candidates for industrial-scale gas separation, although they may be useful as specialized sensors. Similarly, although car-

bon molecular sieves are amorphous, they are extremely brittle, so processing requirements also make CMS membranes unlikely candidates for industrial scale gas separations, although research in this area continues.⁴ Mixed matrix membranes, composed of molecular sieves dispersed in a continuous polymeric phase, combine the favorable attributes of both phases, organic and inorganic.^{5,6} Including the molecular sieving phase in the membrane imparts excellent selectivity, while the continuous polymeric phase allows mixed matrix membranes to be fabricated with conventional polymer processing techniques. The present study concentrated on mixed matrix membranes in which crystalline zeolites are the dispersed phase, although mixed matrix membranes with carbon molecular sieves have also been prepared.⁷

Many factors contribute to overall membrane performance. The permeability and selectivity can change dramatically with operating conditions, which has major implications for membrane performance. For example, the operating temperature can have a large effect on the permeability of membranes because permeation is an activated process. The operating pressures, both upstream and downstream, are also important considerations. One important factor that is sometimes overlooked is the effect of minor compo-

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TABLE I
Selected Properties of Polymers and Molecular Sieves Used in This Work

Temperature	Material	Oxygen permeability (Barrers)	Selectivity, (O ₂ /N ₂)	Density, dry (g/cm ³)	Pore size (Å)
25°C	Zeolite 4A	0.72	38	1.52	3.8
35°C	Poly(vinyl acetate)	0.5	5.9	1.19	
	Zeolite 4A	0.77	37	1.52	3.8
35°C	SSZ-13	10	40	1.51	3.8†
	15% SSZ-13 in poly(vinyl acetate)	0.61	6.4	—	—

† The pore size of SSZ-13 was assumed to be the same as that of a chabazite structure (3.8 Å).

nents in the feed gas. Condensable linear and aromatic hydrocarbons present in trace amounts in natural gas streams can have detrimental effects on many gas separation membrane materials.⁸ Similarly, water can dramatically affect the permeability and selectivity of many gas separation polymers.⁹ Water will be present in both air and natural gas feeds, which are among the applications to which mixed matrix membranes are particularly well suited. Gas sorption in zeolite 4A was reduced by preadsorption of water, a more strongly adsorbed molecule, at 1%–2% relative humidity,¹⁰ so it is reasonable to hypothesize that water would dramatically affect the transport properties of mixed matrix materials containing zeolite 4A. Funke et al. reported a 60% decrease in the nitrogen permeance of α -alumina-supported silicalite membranes for humidified nitrogen feeds.¹¹ Unfortunately, they did not report the humidity of the feed, and they stated that their silicalite may have been contaminated by aluminum from the α -alumina support, making it more hydrophilic. The current study determined the effect of a model penetrant, water, present in both air and natural gas, on mixed matrix membranes composed of hydrophilic (zeolite 4A) and hydrophobic (SSZ-13) zeolite molecular sieves dispersed in poly(vinyl acetate).

EXPERIMENTAL

Materials were dried in a vacuum oven overnight prior to the formulation of the casting solutions. Poly(vinyl acetate) (PVAc), $M_w \approx 500,000$, was obtained from Aldrich (Milwaukee, WI) and dried at 100°C prior to use. Zeolite 4A was obtained from Advanced Specialty Gas Equipment (South Plainfield, NJ) and dried at 250°C prior to use. The hydrogen counterion form of SSZ-13 was provided by the Chevron Texaco Energy Research and Technology Company (Richmond, CA) and used without additional drying when formulating the membranes or was dried at 200°C prior to measuring the water vapor sorption. Zeolite 4A has a Linde Type A (LTA) structure, whereas SSZ-13 has a CHAbazite (CHA)-type structure. SSZ-13 has a high silicon:aluminum ratio (16:1),¹² and

this is probably the source of its hydrophobicity, as water sorption in zeolites increases with increasing aluminum content.¹¹ Zeolite 4A has a silicon:aluminum ratio of 1:1.¹³

Table I gives selected properties of the molecular sieves and poly(vinyl acetate). PVAc has a glass-transition temperature (T_g) between 28°C and 31°C.¹⁴ The combination of a low T_g polymer and processing conditions, discussed later, was developed to allow the PVAc to conform to the sieve surface before the PVAc vitrified, resulting in well-adhered polymer-sieve interfaces. Mahajan measured the permeability and selectivity of PVAc.¹⁵ The permeability and selectivity of zeolite 4A were determined by calculating diffusion and sorption coefficients from zeolite diffusion data and then multiplying them to get the permeability.⁶ As detailed oxygen permeation data or combined sorption and diffusion data are unavailable for SSZ-13, the oxygen permeability was determined indirectly by measuring the permeability of the mixed matrix membranes, which have known polymer phase permeabilities, and then using an appropriate model to calculate the SSZ-13 permeability. This procedure is subject to some uncertainty; however, the model and experimental results have been shown to fit relatively well for mixed matrix membranes prepared with zeolite 4A dispersed in PVAc.¹⁵ The transport properties for SSZ-13 reported in Table I represent the average of several films. The polymer density was taken from the literature,¹⁴ and sieve density can be calculated from diffraction data available in the literature. X-ray diffraction data from the International Zeolite Association were used for zeolite 4A,¹⁶ and neutron diffraction data for SSZ-13 are available from Smith et al.¹² The pore sizes shown in Table I for zeolite 4A¹⁷ and chabazite¹⁶ are reported in the literature.

Measurement of water vapor sorption

The water adsorption curve for zeolite 4A was taken from Breck¹³; however, data for adsorption by SSZ-13 were unavailable. Therefore, the amount of sorbed water in SSZ-13 as a function of the water vapor

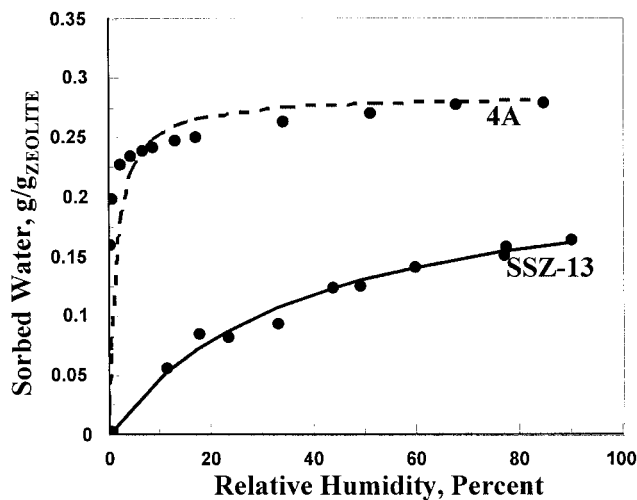


Figure 1 Adsorption curves for water in zeolite 4A (25°C) and SSZ-13 (35°C). The data for zeolite 4A was taken from Breck, while the data for SSZ-13 represents experimental data. Continuous line, Langmuir regression of SSZ-13 sorption; dashed line, Langmuir regression of 4A sorption.

pressure was measured with a McBain balance, described elsewhere.^{18,19} This is a gravimetric technique, in which the weight of a sample in a constant volume chamber is recorded as a function of the water vapor pressure in the chamber. In this apparatus materials typically are suspended from a quartz spring. The deflection of the spring is carefully calibrated so that the change in length of the spring can be correlated with the weight change from the gases sorbed by the material. A known amount of water vapor pressure was introduced into the chamber, and after equilibrium, the pressure and deflection of the spring were recorded.

Figure 1 contrasts the sorption curves for water vapor in zeolite 4A and SSZ-13. Note that the temperatures for the two cases are slightly different, for reasons discussed later. The data taken from Breck for zeolite 4A and the experimental data for SSZ-13 were fitted with the Langmuir equation to determine the affinity constant, b , and the maximum weight of water adsorbed per gram of zeolite, x_M . The constants from these least-squares regressions are shown in Table II. There is some error involved in fitting the points read from the figure in Breck for zeolite 4A, but this should lead to only a minor overestimation of the permeability of zeolite 4A at low relative humidity (and a slight underestimation above about 7% relative humidity) in the equilibrium adsorption model discussed below. When using the fitted Langmuir sorption curve, this error is proportional to the difference between the measured and fitted sorption curves. However, in applying the equilibrium adsorption model to zeolite 4A, this has been circumvented by interpolating the experimental data rather than using the Langmuir fit. The

higher affinity constant of water for zeolite 4A arises from its more hydrophilic character. The CHA and LTA structures have similar volumes of pores accessible to water (0.45 cc/g),¹³ so it is interesting to note that SSZ-13 and zeolite 4A did not have similar water sorption capacities, as indicated in Table II. Sorption is expected to be lower at higher temperatures, but this was also an indication of the decreased hydrophilicity in SSZ-13.

Film formulation and preparation

The casting suspension was prepared in two parts. The solvents were first filtered through 0.2- μ m PTFE (Cole-Parmer, Vernon Hills, IL) filters to remove any dust or particulates. Dried molecular sieves were then dispersed in dichloromethane (4A; EM Sciences, Gibbstown, NJ) or isopropanol (SSZ-13; Fisher Chemicals, Fairlawn, NJ) using a sonicator (Sonics & Materials, Inc., Danbury, CT) with a 6-mm microtip. This difference in sieve solvent should not inhibit comparison of membranes prepared with these two sieves as both solvents were chosen because they are too large to enter the sieve pores and any trace solvent should be removed from the matrix phase when the membranes are dried. The sieve suspensions were sonicated at 20 kHz for 1–2 min. Concurrently, a solution of dried PVAc in dichloromethane was prepared. The ratio of sieve to polymer was set by the desired loading in the membrane, whereas the preferred ratio (by weight) of total solids to solvent was about 1:4. This ratio was found to yield good films when cast; lower ratios produced extremely viscous suspensions, and higher ratios produced dilute suspensions, which allowed the sieves to settle to the bottom of the membrane. The exact solvent-to-solids ratio in the casting suspension was difficult to control as some of the solvent evaporated during sonication because of its high volatility. After the sieve suspension was sonicated, the PVAc dissolved in dichloromethane was added to the sieve suspension. The resulting polymer-sieve-solvent mixture was then placed on a mechanical roller to gently mix the suspension until it was homogeneous.

Once the suspension was homogeneous, it was removed from the mechanical roller and set on the bench to degas for at least 10 min to allow any entrapped air bubbles to escape. PVAc membranes cast

TABLE II
Langmuir Coefficients for Water Sorption in Zeolites

	Affinity Constant, b ($\%^{-1}$)	Capacity, X_M ($\text{g}_{\text{WATER}}/\text{g}_{\text{ZEOLITE}}$)
Zeolite 4A, 25°C	0.778	0.286
SSZ-13, 35°C	0.026	0.230

Estimates are based on regressions of the data in Figure 1.

on glass are difficult to remove, so membranes containing PVAc were prepared on Teflon[®]-coated glass plates. Casting was completed in a glove bag presaturated with dichloromethane in order to control the solvent evaporation rate from the nascent film. Films were cast with a 10- or 12-mil (1 mil = 0.001 in) doctor's knife and then covered with an inverted funnel while still within the glove bag. The spout of the funnel was covered with aluminum foil. These additional measures were taken to more carefully control the solvent evaporation rate and to prevent any dust from settling on the surface of the nascent film.

After the film was cast, it was allowed to dry overnight in the glove bag. The Teflon[®]-coated glass plate, with the film still attached, was then placed in a vacuum oven and dried overnight at 50°C, above the T_g of PVAc. To prevent unnecessary stresses at the interface because of rapid cooling, the oven was allowed to cool to at least 30°C before the glass plate was removed. The film could be easily removed from the Teflon[®]-coated glass plate by using a razor to carefully delaminate the film at one end and then gently lifting the film off the surface.

Measurement of permeability and selectivity with pure gases

Because mixed matrix membranes prepared with SSZ-13 have never been characterized, oxygen and nitrogen permeabilities of these materials were first obtained with pure gases in the standard constant-volume, variable-pressure testing apparatus (described by others).²⁰ The SSZ-13-containing membranes were tested at 35°C with ~65 psia feed gas. The permeability and selectivity reported in Table I represent average values from several films. Although higher zeolite loadings likely could have been achieved using the methods of Mahajan,¹⁵ 15 vol % loading samples were prepared because they are simpler to formulate and provide sufficient information from which to draw conclusions regarding the utility of SSZ-13 in mixed matrix membranes. Scanning electron microscopy showed that all these membranes had good adhesion between the polymer and the sieve, with no voids between the phases, which would lead to artificially high permeability.

Measurement of oxygen permeability with humidified feeds

The measurement of oxygen permeability using humidified oxygen was performed with an Oxtran 100A permeation device (Mocon, Minneapolis, MN). In this device a sweep stream of 2% hydrogen in nitrogen carries the oxygen permeate to a nickel-cadmium fuel cell, which accurately determines the oxygen content in the sweep stream. The output voltage from the fuel

cell can be converted into an oxygen permeability value. Both the oxygen and nitrogen/hydrogen sweep streams are humidified in separate bubblers filled with DI water before contacting the membrane. For experiments with 4A-filled PVAc membranes, salt solutions were used to regulate the relative humidity in the feeds; however, this corroded the oxygen detector. After obtaining a new sensor for experiments with SSZ-13-filled PVAc membranes, the relative humidity was regulated by controlling the temperature of the bubblers with constant-temperature water baths surrounding the outer surface of each bubbler. The relative humidity was also monitored using a RH-30-2 humidity sensor from Omega (Stamford, CT). The sensor tip was enclosed in a plastic fitting with a small holdup volume attached with a short tube to the outlet of the Oxtran. The humidity measurements from the sensor were in good agreement with those expected based on the bubbler temperatures. The zeolite 4A-filled membranes were tested at 25°C so the sorption data from Breck could be used, whereas the SSZ-13-filled membranes were tested at 35°C, which is a standard testing temperature for gas separation membranes. This difference in temperature had no bearing on the conclusions regarding the utility of the molecular sieves as mixed matrix inserts.

MODELS

Several models were considered to assist in the interpretation of the humidified oxygen permeation data. The so-called Maxwell model can be used to predict the properties of a heterogeneous, or mixed matrix, membrane if the permeabilities and selectivities of the polymer and the sieve are known.²¹ The model is given below:

$$P_M = P_P \left(\frac{P_S + 2P_P - 2\phi_S(P_P - P_S)}{P_S + 2P_P + \phi_S(P_P - P_S)} \right) \quad (1)$$

where P is the permeability, ϕ_S is the sieve volume fraction, the subscript M is the mixed matrix membrane, the subscript P is the polymer, and the subscript S is the sieve. This model was originally developed by Maxwell to predict the conductivity of a material composed of conducting spheres dispersed in a matrix with a different conductivity,²² but it has also been shown to work reasonably well for predicting the permeability of two-phase membranes.^{21,23} Other models, such as the effective medium field theory²⁴ and a model by Bruggemann²⁵ can be used, but at best, they provide only a marginally better practical description of the results than does Maxwell's model.^{21,23} Therefore, Maxwell's model was used because of its simplicity relative to the other models and its ease of modification.

The oxygen permeability of pure poly(vinyl acetate) was measured as a function of humidity at both temperatures, so the polymer permeability, P_p , was known. As discussed earlier, it is not possible to prepare a defect-free membrane of pure zeolite 4A or SSZ-13 to directly characterize permeability as a function of humidity. Therefore, three models were considered for describing the performance of the sieves with humidified feeds. The first model assumed that humidified feeds had no effect on the permeability of the sieves, so sieve permeability was constant at the unhumidified value shown in Table I. This is the open model. The closed model assumed that the sieves had a very strong affinity for water, such that their pores filled with water, so that oxygen permeability through the sieves was zero.

Equilibrium adsorption model

Because the open and closed models represent the extremes in potential sieve behavior, a third model was developed for an intermediate case, one in which permeability in the sieve was assumed proportional to the fraction of the pore structure not occupied with water. This latter case is called the equilibrium adsorption model and is shown in eq. (2). In each case the appropriate model for sieve permeability is used in the Maxwell model to calculate the overall permeability for the membrane.

$$P_s(\%rh) = P_s(0\%) \times \left(1 - \frac{x}{x_M}\right) \quad (2)$$

where x is the amount of water sorbed as a function of pressure and x_M is the saturation capacity, which can be found in Table II. More complex models might be envisioned, but these simple descriptions serve to bound the expected behavior that might be observed.

RESULTS AND DISCUSSION

Permeation through pure poly(vinyl acetate) with humidified oxygen

Knowledge of the permeability of pure poly(vinyl acetate) with humidified oxygen was required to interpret mixed matrix performance. It was necessary to obtain these data at both temperatures to "subtract out" the behavior of the polymer phase in mixed matrix membranes in order to ascertain the behavior of the sieves. As noted earlier, performing the measurements at two temperatures did not affect the conclusions regarding the utility of the two sieves as sieving phases in mixed matrix membranes. Figure 2 shows the oxygen permeability of PVAc as a function of relative humidity at both 25°C and 35°C. Data for relative humidities greater than about 65% were not

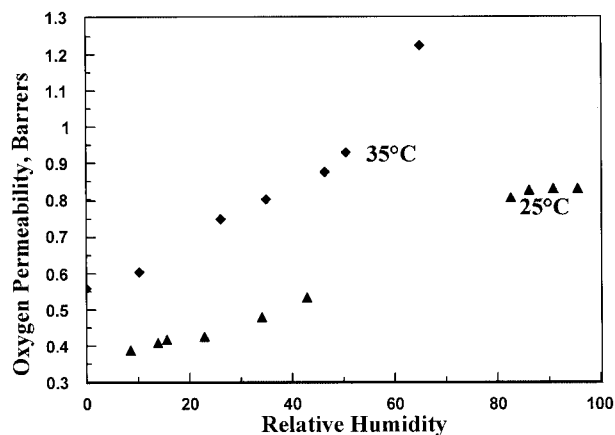


Figure 2 Oxygen permeability of pure PVAc at 25°C and 35°C as a function of relative humidity.

obtained at 35°C because water vapor partial pressures at these relative humidities exceed saturation at room temperature, so it was difficult to prevent condensation in the system. The upswing in oxygen permeability measured at 35°C between 50% and 65% relative humidity can potentially be explained by swelling of the matrix by sorbed water,²⁶ with a concomitant increase in oxygen permeability.

Although the two experimental temperatures straddled the T_g , swelling by water led to a lower T_g in PVAc,²⁷ so it is likely that the polymer phase was rubbery under most of the experimental conditions studied. Increased chain mobility caused by swelling allows for an increase in the diffusion coefficients of many penetrants in many polymers, and the same was probably true of PVAc. Permeability is the product of the diffusion coefficient and the sorption coefficient, so an increase in the diffusion coefficient should lead to increased permeability. Nevertheless, the important effect investigated here is that of water on the molecular sieving phase, the subject of the next section.

Permeation through mixed matrix membranes with humidified oxygen

Table III shows oxygen permeability as a function of relative humidity in the oxygen feed for zeolite 4A-filled PVAc, including model predictions for each of the cases discussed above. Note that the experimental data and modeling predictions for 1.5% relative humidity are for a PVAc film with 40 vol % 4A, whereas the data at 10% relative humidity correspond to 25 vol % 4A film. A higher zeolite loading was used at the lower humidity to increase the sensitivity of the zeolite to the measurement, and the different loadings are reflected in the model predictions shown in Table III. The results clearly show that the equilibrium adsorption model most closely paralleled the experimental observations for zeolite 4A. From these observations it

TABLE III
Summary of Experimental Data and Model Predictions for Zeolite
4A-Filled PVAc Membranes Tested at 25°C

Relative humidity	Zeolite fraction	Permeability (barrer)			
		Open model	Equilibrium adsorption model	Closed model	Experimental data
1.5%	40%	0.50	0.30	0.20	0.33
10%	25%	0.51	0.30	0.27	0.28

Note the similarity between the experimental data and the oxygen permeabilities calculated using the equilibrium adsorption model.

can be inferred that oxygen permeation in zeolite 4A was reduced by water adsorbed on the pore walls of the zeolite, even at very low relative humidities. This is consistent with what is shown in Figure 1, that zeolite 4A is about 85% saturated with water even at 10% relative humidity.

Although not studied here because of limitations of the Oxtran apparatus, pore blockage should affect the faster gas (oxygen) more than the slower gas (nitrogen) because a higher portion of the faster gas permeates through the sieves. This would likely lower the observed selectivity for mixed matrix membranes containing hydrophilic sieves such as zeolite 4A. This effect makes the use of zeolite 4A as a molecular sieving phase in mixed matrix membranes less attractive in practical applications. Water has been shown to be excluded from membranes by coating with a very hydrophobic layer such as Teflon[®] AF²⁸, but this adds complexity. Alternatively, a pretreatment stage can be added to remove the water from the feed stream before it contacts the zeolite 4A-containing membrane. Water removal from the feed could potentially be accomplished with another membrane module. However, both alternatives would increase the cost of a

membrane separation system if the mixed matrix membrane contains zeolite 4A.

A more desirable alternative is to utilize a molecular sieve that is not so adversely affected by water, such as SSZ-13. It can be seen in Figure 3 that the experimental results for a 15 vol % SSZ-13 in PVAc film were most closely approximated by the open or equilibrium adsorption models. This indicates that the sieves were unaffected or relatively unaffected by the presence of water impurities in the feed gas. In this case, it was necessary to perform experiments well above the range tested for zeolite 4A because of the lower affinity of water for SSZ-13. Humidity greater than about 65% could not be accurately maintained in the Oxtran. Two separately prepared films were tested in order to get an estimate of the errors involved in these measurements, and the error certainly did not affect the conclusion that SSZ is less severely affected by water sorption. The last data point was slightly higher than the prediction for completely open sieves. This could be because of experimental error or because of a change in the morphology of the membrane at high relative humidity, which is unaccounted for by any of our models. Nevertheless, it is clear that a complete "shutdown" of SSZ-13 by sorbed water did not occur, contrary to the results with zeolite 4A.

The oxygen permeability of mixed matrix membranes composed of PVAc at a constant sieve loading increased with increasing relative humidity, as shown in Figure 3. As water swelled PVAc, the diffusion coefficient of oxygen was increased, and hence so was the oxygen permeability, as shown in Figure 2. Typically, such swelling causes plasticization and disproportionate increases in the diffusivities of the slower penetrants, such as nitrogen, so that the overall effect is decreased selectivity.²⁹ In more rigid glassy polymers the major effect of water is the occupation of sorption sites usually available to other penetrants,^{9,30} so the decline in selectivity may be less severe. Pye et al. found only a small depression in H₂/CH₄ selectivity³¹ in several glassy polymers in the presence of ~50% relative humidity. A relatively unaffected sieve in a rigid matrix, therefore, may provide the very desirable combination of excellent theoretical transport

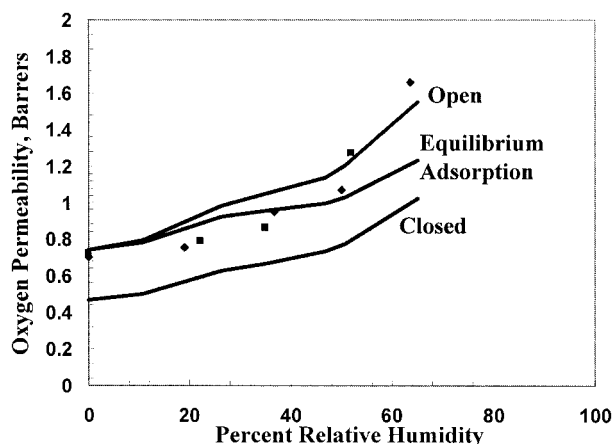


Figure 3 Effect of feed humidity on the oxygen permeability of a ~15 vol % SSZ-13 in PVAc membrane. Experiments were performed at 35°C (◆: Film 1 data; ■: Film 2 data).

properties *and* the ability to substantially maintain them in the presence of water. However, given the complex effects on both polymer and sieve permeabilities that arise with the introduction of water, this hypothesis requires additional study.

CONCLUSIONS

These results have illustrated the effects that impurities and/or minor components in a feed gas can have on organic/inorganic hybrid (mixed matrix) membranes. Specifically, they showed that water can affect both the polymer and sieve phases. Water clearly led to swelling and concomitant increased oxygen permeability in poly(vinyl acetate). Water adsorbed into the pores of hydrophilic molecular sieves can cause a decrease in the permeability of oxygen, and this will likely reduce the overall selectivity of a mixed matrix membrane prepared with such a sieve. As expected, the permeability reduction was much more pronounced in the more hydrophilic zeolite 4A than in the hydrophobic SSZ-13. Models were presented to separate the competing effects of increased permeability from swelling of the polymer matrix and decreased permeability caused by blockage of the sieve with adsorbed water. Both systems were best modeled by the equilibrium adsorption model, which assumes that oxygen permeability in the sieve is proportionately reduced by the amount of water sorbed. A more complicated model can be envisioned, perhaps incorporating competitive Langmuir sorption isotherms for water and oxygen, but the current data do not justify such a complex model, and the more simplistic model clearly shows that the permeability in the sieves was decreased by the presence of sorbed water within the pores. Using the equilibrium adsorption model for the sieve, the overall effect of water on the mixed matrix membranes could be elucidated. In mixed matrix membranes the SSZ-13 sieves appeared to be relatively unaffected by water, making SSZ-13 an ideal candidate for air separation with mixed matrix membranes. However, membranes containing zeolite 4A will suffer from pore blockage unless action is taken to exclude water from the membrane. It appears that sieve hydrophilicity must be added to the many considerations required to formulate a viable mixed matrix membrane.

This work also demonstrated the utility of SSZ-13 as the molecular sieving phase in mixed matrix membranes. This sieve also better maintains these properties with humidified feeds, so it looks quite promising as a potential molecular sieving phase. Continuing research seeks to formulate these sieves into glassy polymers, which provide better baseline transport properties, and to test these membranes in the presence of water. These membranes will also need to be tested for performance in the presence of condensable hydrocarbons if they are to be used for natural gas processing. It is envisioned

that the more hydrophobic interior of SSZ-13 will make it more susceptible to condensable hydrocarbons, which are typically found in natural gas streams. Sorbed condensable hydrocarbons in SSZ-13 would presumably have an effect similar to the sorbed water in 4A, so a more hydrophilic sieve may be required for natural gas separation. This hypothesis is the subject of continuing research.

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