Gas Sorption in Polymers, Molecular Sieves, and Mixed Matrix Membranes

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ABSTRACT: Gas sorption has been an underutilized technique for characterizing organic–inorganic hybrid (mixed matrix) membranes. Sorption in these membranes, which are composed of rigid inorganic domains, such as zeolites, dispersed in a polymer matrix, should be approximately additive. Sorption in the neat polymers and zeolites were first measured to demonstrate that sorption in mixed matrix membranes is approximately additive in the absence of other effects. Sorption in mixed matrix membranes was demonstrated to be additive. This extends to cases where sorption in one or both phases of the mixed matrix membrane is affected by an outside contaminant. For example, zeolite 4A is extremely hydrophilic and easily affected by contaminants from processing or from the test gases. Zeolite 4A encapsulated within a polymer matrix can still be affected by these same components, and this causes sorption lower than predicted based on that in unaffected polymers and sieves. This sorption analysis has proven to be very important in understanding the permeabilities and selectivities of mixed matrix membranes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 4053–4059, 2007

Key words: organic–inorganic hybrid; membranes; zeolites; gas permeation; gas sorption

GAS AND VAPOR SORPTION BACKGROUND

Although sorption in polymers and zeolites occur via different detailed mechanisms, both can be described with similar expressions, as demonstrated below. The sorption coefficient is defined as:

$$S = \frac{C}{p} \qquad (1)$$

The following discussion is for pure component sorption. Multicomponent sorption has also been addressed, but it is beyond the scope of this article.

According to the dual-mode model, for sorption in polymers, molecules may sorb into one of two "modes"[1] comprising "dissolved," or Henry's Law regions, and "hole," or Langmuir regions. The dual-mode model for penetrant "A" is expressed in terms of Henry's law coefficient, k_D, and Langmuir sorption parameters: the affinity, b, and hole saturation, C_H', constants:

$$C_A = k_{D,A} p_A + \frac{C_{H,A}' b_A p_A}{1 + b_A p_A} \qquad (2)$$

Sorption roughly correlates with the fractional free volume of a polymer.[2,3] The Langmuir mode occurs only in polymers below their glass transition temperatures, which have entrapped nonequilibrium "excess" free volume. The magnitude of the Langmuir saturation constant depends on the distance below the glass transition, as shown in Figure 1. The Henry's law coefficient and Langmuir affinity constants both increase with penetrant condensability.

Sorption in molecular sieves occurs at specific sites. Although Langmuir sorption in glassy polymers occurs at more-or-less fixed sites, these sites are randomly distributed throughout the polymer and their locations may slowly vary with time. Sorption in molecular sieves can be modeled using the same equation [eq. (2)] as for polymers with k_D set equal to zero, since there is no "dissolved" mode in zeolites. Nonetheless, it may be necessary to account for energetic heterogeneity of the sorption sites (i.e., different sites can have different energies of adsorption). Each type of site will then have its own affinity and saturation constants. It has proven sufficient to model sieve sorption with a single site for the zeolites under the conditions used in this work.

Gas sorption can be measured in several ways. Perhaps the two most common are gravimetric sorption and pressure decay sorption. Gravimetric sorption is typically used for highly sorbing gases and vapors (i.e., at low pressure). Pressure decay sorption is used for the remaining applications. The
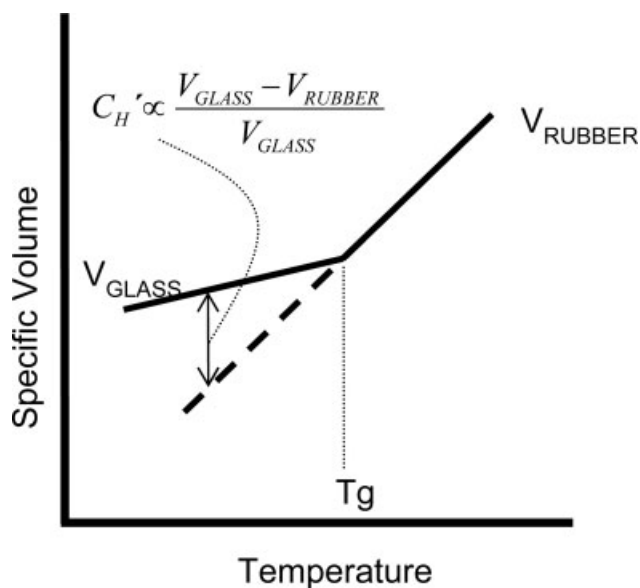
**Figure 1** Sketch demonstrating the nature of the Langmuir mode in polymers.

principle data obtained using sorption measurements is the sorption coefficient in the material. Provided sorption is not too fast and the sample is of uniform thickness, it is also possible to obtain the diffusion coefficient. This is done by fitting the experimental kinetic sorption curve with an appropriate theoretical expression that is a function of the diffusion coefficient.

Pressure decay sorption is useful for measuring the sorption of gases at pressures greater than 1 atm in polymers, sieves, and mixed matrix membranes. Equipment and operating techniques are well-documented in the literature.[4,5] Gas is introduced into a feed reservoir of known volume after complete evacuation of both reservoirs. After allowing the pressure in the feed reservoir to equilibrate for a few minutes, the valve between the sample and feed reservoirs is opened for 3 s to allow gas into the sample reservoir. Then, the valve is closed and the pressure in both reservoirs is monitored. The feed reservoir pressure should stabilize immediately, while the sample reservoir pressure will decrease a small amount due to sorption into the sample. Once the sample reaches equilibrium with the gas in the sample reservoir, a mole balance before and after the expansion gives the amount sorbed into the sample. Compressibility factors, given in the appendix, must be used to account for the nonideality of the gas phase. Finally, the pressure in the feed reservoir is changed and the whole cycle is repeated to derive the whole sorption curve. Kinetic sorption data were recorded using a PC running Labview® data acquisition software interfaced with a Keithley Instruments 2700 Multimeter.

To our knowledge, sorption in zeolites has not previously been measured with the pressure decay technique in this equipment. Zeolite powder is enclosed in a 0.5-μm sintered metal filter element (Swagelok® part number SS-2FK4-05), which is cylindrically shaped with one open end. After putting the sample into the filter element, the open end is covered with a piece of aluminum foil. Finally, a wire is wrapped around the filter element to hold the aluminum foil in place. The volume of each filter element, aluminum cover, and wire wrap was carefully calibrated since the unoccupied volume in the sample reservoir is an important parameter in the mole balance.

SORPTION OF GASES IN NEAT POLYMERS AND SIEVES

It was necessary to measure sorption of the neat polymer and pure sieve for later comparison with mixed matrix membranes. Equilibrium sorption of O_2, N_2, CO_2, and CH_4 in Ultem® (Fig. 2) and Matrimid® (Fig. 3) were measured. Oxygen sorption was not measured above 10 atm for safety reasons. Experimental equilibrium sorption curves are similar to those reported in the literature (see references in Table I). The experimental and literature regressed dual-mode parameters in Table I do not match well in some cases, because small curvatures or few data make an accurate fit difficult. The regressed parameters are quite dependent on the initial guesses used
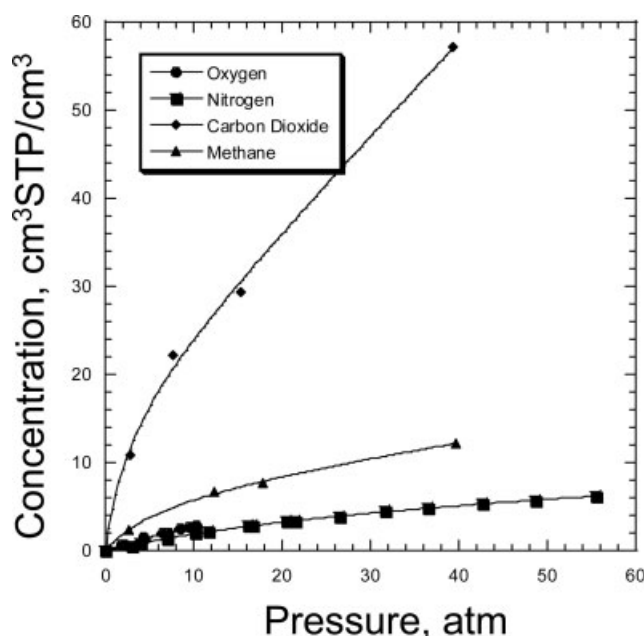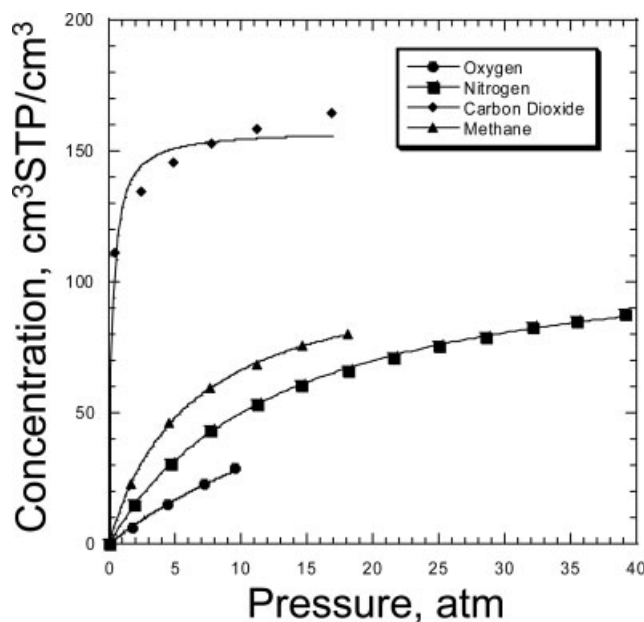

Figure 2 Sorption of O_2, N_2, CO_2, and CH_4 in Ultem at 35°C. Lines are fitted to the dual-mode equation [eq. (2)] with parameters given in Table I.
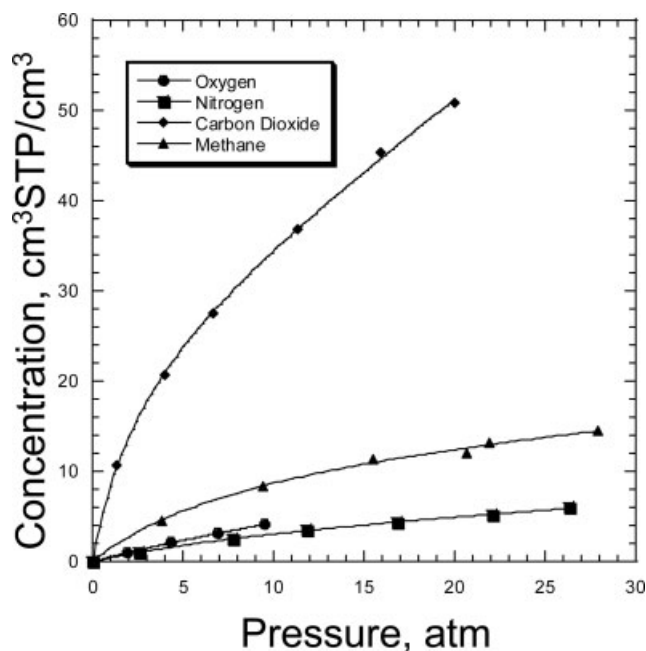
Figure 3 Sorption of O_2, N_2, CO_2, and CH_4 in Matrimid at 35°C. Lines are fitted to the dual-mode equation [eq. (2)] with parameters given in Table I.

Figure 4 Sorption of O_2, N_2, CO_2, and CH_4 in zeolite 4A at 35°C. Lines are fitted to the Langmuir equation [eq. (2)] with $k_D = 0$) with parameters given in Table II.

for the curve fit, but the resulting sets of parameters fit the data well and this is sufficient for this work.

Measuring ''normal'' sorption in the zeolites was not as straightforward. First, a method to contain the zeolites in the sorption cell had to be devised, as discussed earlier. Second, samples from the same batch of zeolite 4A initially appeared to give different sorption characteristics, even after the same activation treatment. Eventually, this was attributed to the contamination in the zeolite-processing equipment. This insight explains why poorer transport properties than expected were observed for some mixed matrix membranes. Equilibrium sorption in zeolite 4A and HSSZ-13 for selected gases is shown in Figures 4 and 5, respectively. The parameters for fitting these curves are given in Table II. Highly polar sorbates such as carbon dioxide (as in Fig. 4) and water typically display energetically heterogeneous surface

sites with respect to sorption, so the single-site Langmuir fits of their sorption are not as good as for the nonpolar molecules. Nonetheless, the quantity and quality of the data did not justify fitting a multiple site Langmuir equation with four parameters to be fit, and the single site model was sufficient for this work.

Equilibrium sorption for water and n-butane were measured as ''model'' contaminants likely to be present in air or natural gas separations. These data are shown in Figure 6. A log scale is used on the pressure axis so that the low pressure data can be distinguished. When plotted in this manner, a sigmoidal shape is typically observed instead of the classical Langmuir shape. Water sorption at 25°C was measured by Breck.[8] Water sorption in HSSZ-13 was measured using the gravimetric sorption technique.[9,10] Data from two samples are shown to

TABLE I
Selected Data for Gas Sorption in Selected Polymers at 35°C

Polymer	Gas	k_D (cm³ STP/cm³/atm)	b (1/atm)	C'_H (cm³ STP/cm³)	Reference
Ultem®	O_2	0.185	0.082	2.04	
	N_2	0.050 (0.063)	0.034 (0.045)	5.20 (4.15)	6,7
	CO_2	1.04 (0.758)	0.355 (0.366)	17.3 (25.02)	6,7
	CH_4	0.17 (0.207)	0.21 (0.136)	5.83 (7.31)	6,7
Matrimid®	O_2	0.245	0.054	5.31	
	N_2	0.120	0.087	3.94	
	CO_2	1.44	0.367	25.5	
	CH_4	0.136	0.105	14.3	

Literature values (where available) are given in parentheses.
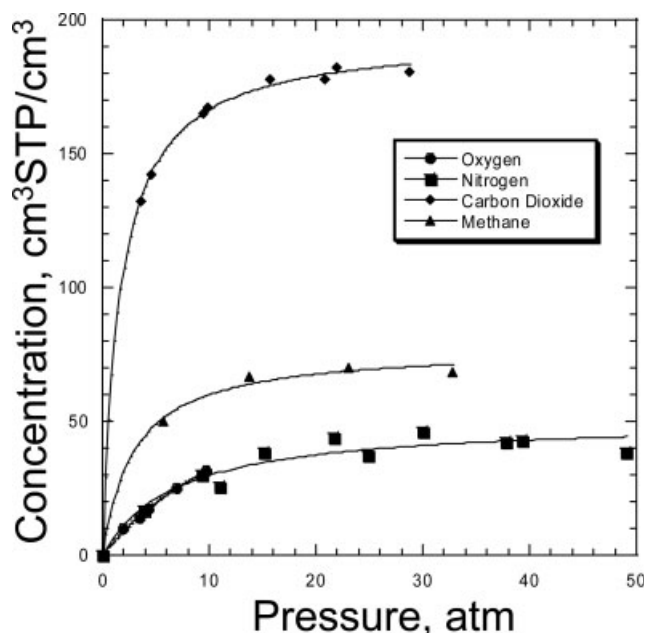
Figure 5 Sorption of O_2, N_2, CO_2, and CH_4 in HSSZ-13 at 35°C. Lines are fitted to the Langmuir equation [eq. (2)] with $k_D = 0$) with parameters given in Table II.

indicate the reproducibility of these measurements. Finally, *n*-butane sorption data in HSSZ-13 were provided by ChevronTexaco ETC. Increasing the temperature by 15°C causes an order of magnitude increase in the saturation pressure of *n*-butane. This illustrates the significant effect of temperature and the importance of characterizing membranes under realistic operating conditions. There is a dramatic difference between gas sorption (O_2, N_2, CO_2, and CH_4) and sorption of the condensable components (i.e., water and *n*-butane). Sorption is governed by the condensability of the penetrant and the affinity of the penetrant for the sieve. This explains why the

TABLE II
Langmuir Coefficients for Regressions of Penetrant Sorption in Zeolite 4A and HSSZ-13

| Sieve	Penetrant	b (1/atm)	C'_H (cm³ STP/cm³)	Reference
Zeolite 4A	Water, 25°C	(2510)	(537)	8
	Oxygen	0.041	98.8	
	Nitrogen	0.076	116	
	Carbon dioxide	4.27	158	
	Methane	0.164	107	
HSSZ-13	Water	47.0	432	
	n-Butane	615	66.7	
	Oxygen	0.056	89.4	
	Nitrogen	0.144	50.5	
	Carbon dioxide	0.607	194	
	Methane	0.340	77.6	

Literature values (where available) are given in parentheses.
Temperature is 35°C except where noted.

order of Langmuir *affinity* constants (*b* in Table II) in both zeolites is $H_2O > CO_2 > CH_4 > N_2 > O_2$, with the more hydrophobic HSSZ-13, having a higher affinity for *n*-butane than water. Zeolite 4A has silicon to aluminum ratio of one to one, whereas the HSSZ-13 used in this work typically has a ratio of around 25 to 1. The order of affinity constants in zeolites for nitrogen and oxygen is *opposite* to that of the polymers. Although nitrogen is less condensable, it has a higher affinity for the sieve than oxygen because its higher quadrupole moment allows for increased intermolecular interactions with the zeolite.

It is more difficult to determine the diffusion coefficient for gases in zeolites for two reasons: (i) in some cases, sorption occurs so quickly that it is impossible to accurately fit the data as a function of the diffusion coefficient and (ii) all the zeolite samples are polydisperse making it difficult to determine the characteristic length scale. Nonetheless, for slower gases in zeolite 4A, such as oxygen, it is possible to determine *relative* diffusion coefficients in the same large (~ 5 μm) sample activated or processed under different conditions. This has provided important insights into the nature of zeolites and the effects of various solvents and processing conditions, but these effects are discussed elsewhere.[11,12]
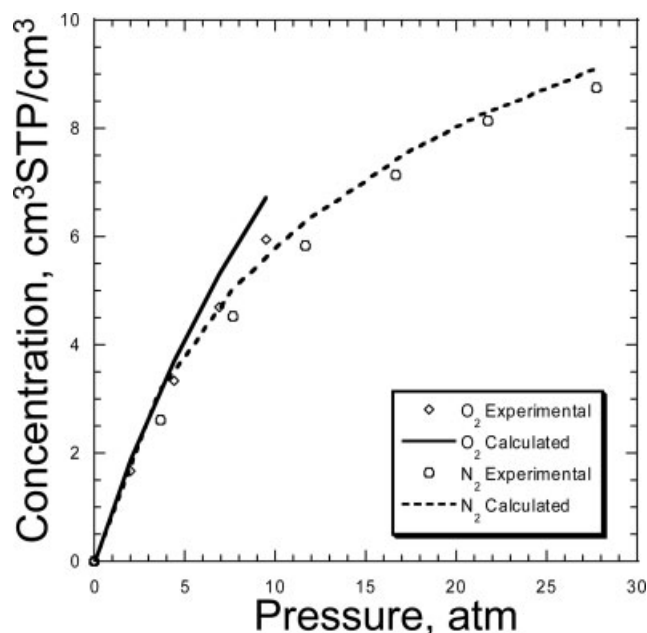
SORPTION OF GASES IN MIXED MATRIX MEMBRANES

Sorption of gases in mixed matrix membranes was studied to give additional information about their
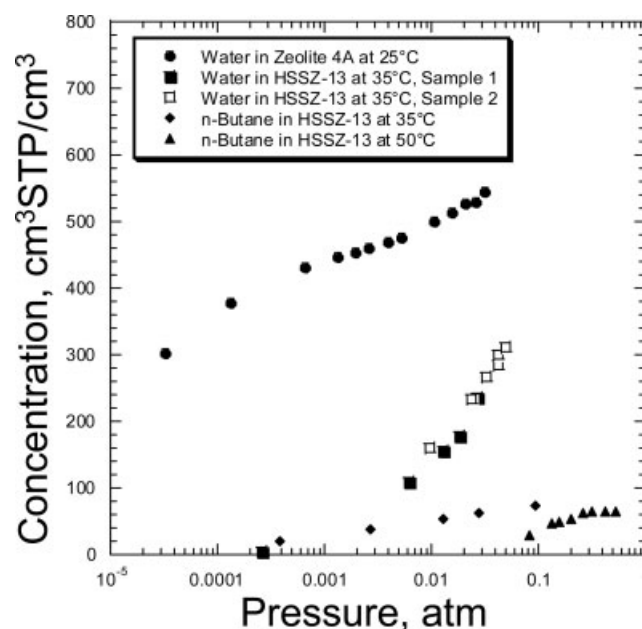
Figure 6 Sorption of water and *n*-butane in zeolite 4A and HSSZ-13 at selected temperatures. Note that the pressure is given in a log scale.

Figure 7 Demonstration of additivity of sorption in mixed matrix membranes. O_2 and N_2 sorption in 14.6 vol % HSSZ-13 dispersed in Ultem.

transport properties. It was expected that sorption in mixed matrix membranes, S_{MM}, should be additive, within acceptable error limits in the absence of unusual interfacial effects between the sieve and matrix or contamination of the sieve:

$$S_{MM} = \phi_{POLY}S_{POLY} + \phi_{SIEVE}S_{SIEVE} \qquad (3)$$

where ϕ is the appropriate volume fraction. This was previously demonstrated by Paul and Kemp for zeolite 5A dispersed in PDMS.[13] This was valid for some mixed matrix membranes. Figure 7 compares oxygen and nitrogen sorption for 14.6 vol % HSSZ-13 in Ultem with sorption calculated using eq. (3) and the Langmuir coefficients given in Tables I and II. Sorption is additive within the error of the measurements. A SEM of HSSZ-13 dispersed in Ultem is shown in Figure 8.

In contrast to HSSZ-13, some zeolites are easily "polluted" by contaminants present during processing or in the feed gases. Exposure of zeolite 4A-based mixed matrix membranes to a small amount of water in the feed gas makes them essentially impermeable.[14] During this work, we also discovered that a number of solvents used to process mixed matrix membranes based on zeolite 4A could also dramatically affect the sorption. Frequently, the result was reduced equilibrium sorption, but in some cases, the result was a reduction in sorption kinetics.[12] Because the sieves sorb much more gas than the same weight of polymer, approximately half of the total sorption in a $\sim$ 15 vol % sieve mem-

brane can be attributed to the zeolite. This makes it easy to diagnose inactive zeolites even after they are incorporated into mixed matrix membranes. The polymer matrix may afford some protection from contaminants, since it is expected to slow their diffusion into the membrane, but if given enough time, contaminants will still enter the zeolites. Of course, for the solvents used to process the dopes, the polymer matrix can afford no protection to the zeolites.

Figure 9 for 13.7 vol % zeolite 4A dispersed in Ultem cast from dichloromethane is an example of a membrane that sorbs significantly less gas than the additive assumption, indicating a problem with sorption in the zeolite. Figure 10 shows an example of zeolite 4A dispersed in Ultem. This sample exhibits a "sieve in a cage" morphology, which more clearly shows the zeolite structure. Oxygen sorption in this membrane is lower than the additive assumption, even after drying at 250°C for 12 h. If the zeolite phase of the membrane does not sorb enough gas, the membrane will be expected to exhibit lower permeability, and in fact, it did have a lower permeability than predicted.[11] Moreover, the reduced diffusion coefficients observed in pure zeolites may cause an even more adverse effect on mixed matrix membrane permeability. This membrane appeared to suffer from impermeable zeolites. The zeolites may not be completely impermeable, but even a 50% reduction in the permeability of the zeolite can have a dramatic effect on the transport properties of the resulting mixed matrix membranes as discussed later. The sorption rate of oxygen into the membrane
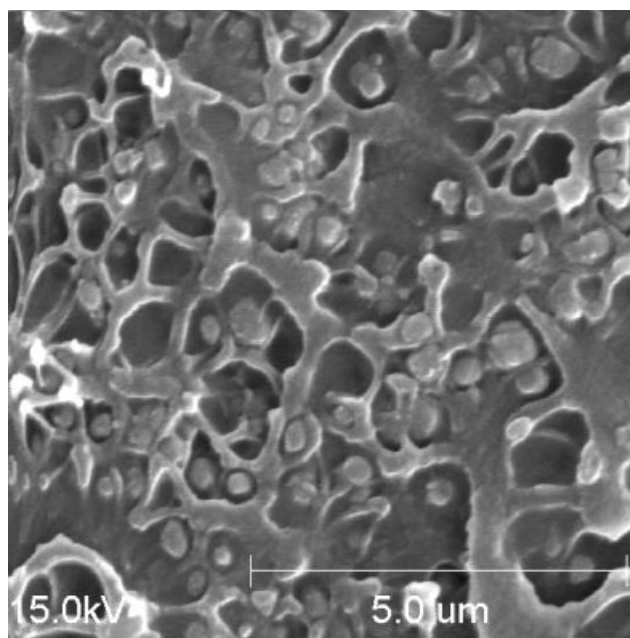
Figure 8 Mixed matrix membrane comprised submicron HSSZ-13 dispersed in Ultem.
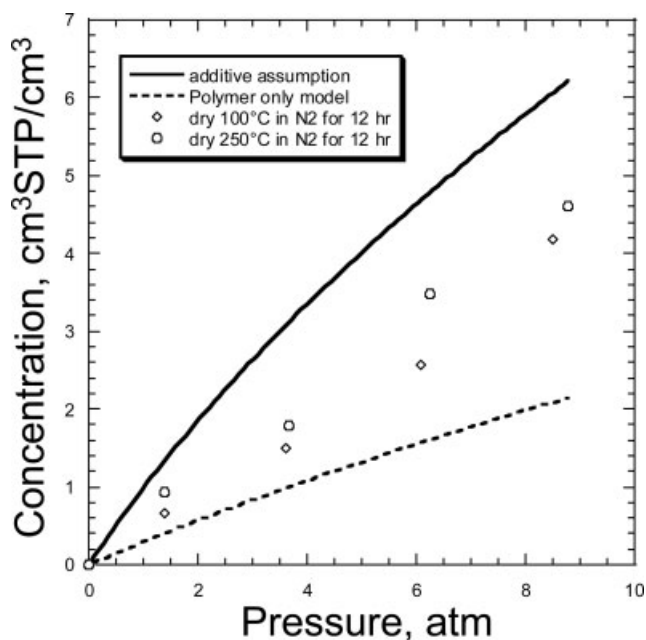
Figure 9 Oxygen sorption in 13.7 vol % zeolite 4A dispersed in Ultem cast from dichloromethane dried under different conditions.

is also significantly slower than expected, especially at higher equilibration pressures. This membrane was prepared without a silane coupling agent, eliminating the complications associated with silanation. However, it was also cast from dichloromethane, which could slow sorption into the zeolites enough to cause reduced transport properties.[12]

CONCLUSIONS

Examples of sorption in two polymers (Ultem and Matrimid), two molecular sieves (HSSZ-13 and zeolite 4A), and two mixed matrix membranes are presented. Matrimid and HSSZ-13 have not previously been characterized, nor has any data on mixed matrix membranes been presented.

This paper demonstrates that sorption in mixed matrix membranes is additive. Sorption in the Ultem-HSSZ-13 mixed matrix membrane was well predicted by a simple additive assumption of the sorption in the two neat phases. On the other hand, we demonstrated that mixed matrix membranes can suffer from the issues that affect their various constituent phases. The sorption in the zeolite 4A in the Ultem-zeolite 4A membrane was affected by some of the solvents used during processing of the membrane, and this caused the sorption of the mixed matrix membrane to *appear* lower than the additive assumption, which assumes that both phases of the membrane are pristine. Such effects have been shown to reduce the permeability and selectivity of mixed matrix membranes.[11] This again

demonstrates the importance of choosing the sieving phase wisely.

Even pristine mixed matrix membranes are known to exhibit permeabilities lower than that predicted by appropriate models.[15–17] These have been attributed to a rigidification of the polymer matrix near the sieve. This rigidification was not accompanied by a measurable change in the polymer sorption. The HSSZ-13 used in this work was submicron; so, much of the polymer was affected by the presence of the zeolite phase. Nevertheless, it is possible that a true nanosieve may affect the packing of the polymer and therefore the sorption of mixed matrix membranes.

APPENDIX

The compressibility factors are needed for the mole balance to determine the sorbed concentration using pressure decay sorption. The equations for compressibility factors at 35°C for the gases used in this work are given below. They were taken from Zimmerman,[18] who used a least squares routine to fit compressibility factors calculated using the DDMIX program available from the National Institute of Standards and Technology.

$$O_2: \quad z = 1 - \frac{3.635 \times 10^{-5}}{psia}P + \frac{4.757 \times 10^{-9}}{psia^2}P^2$$
$$+ \frac{1.132 \times 10^{-12}}{psia^3}P^3 \quad (A1)$$
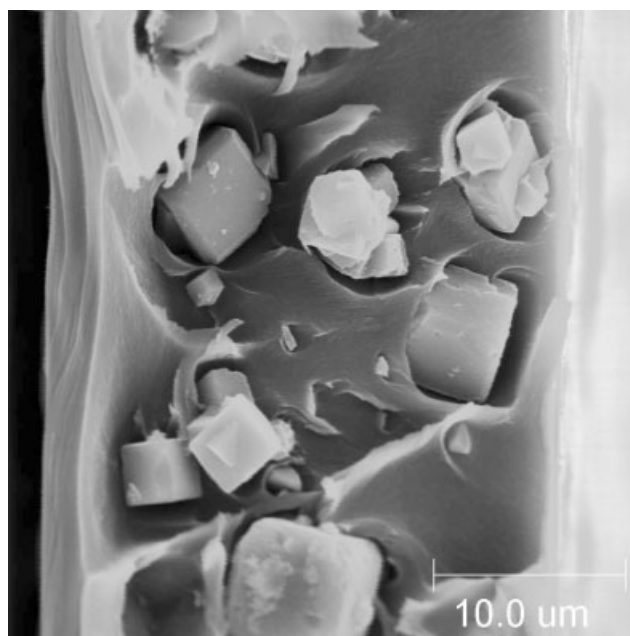
Figure 10 Mixed matrix membrane comprised of zeolite 4A dispersed in Ultem.

$$N_2: \quad z = 1 - \frac{8.589 \times 10^{-6}}{\text{psia}}P + \frac{1.078 \times 10^{-8}}{\text{psia}^2}P^2$$
$$- \frac{1.066 \times 10^{-13}}{\text{psia}^3}P^3 \quad (A2)$$

$$CO_2: \quad z = 1 - \frac{2.846 \times 10^{-4}}{\text{psia}}P - \frac{2.006 \times 10^{-7}}{\text{psia}^2}P^2$$
$$+ \frac{2.60 \times 10^{-10}}{\text{psia}^3}P^3 - \frac{2.154 \times 10^{-13}}{\text{psia}^4}P^4 \quad (A3)$$

$$CH_4: \quad z = 1 - \frac{1.049 \times 10^{-4}}{\text{psia}}P + \frac{3.818 \times 10^{-9}}{\text{psia}^2}P^2$$
$$+ \frac{5.202 \times 10^{-12}}{\text{psia}^3}P^3 \quad (A4)$$

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