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Selective Dampening of the Gas Permeability of a Langmuir−Blodgett Film Using Moist Permeants

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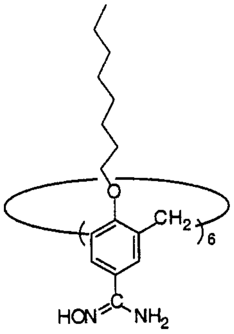
Abstract: The permeability of helium across a composite membrane derived from six monolayers of 5,11,17,23,29,35-hexaamidoxime-37,38,39,40,41,42-hexakis(1-octyloxy)calix[6]arene (**1**) and poly[1-(trimethylsilyl)-1-propyne] cast film has been found to be significantly reduced when the film is exposed to moisture. In sharp contrast, the permeability of nitrogen across this same composite was unaffected by moisture. These results, by themselves, provide compelling evidence for the existence of t*wo distinct pathways for diffusion*: one that strongly favors the transport of He over N_2, and a second that is much less selective. Unusual pressure effects that have been observed for the normalized flux of He support a model in which this smaller permeant can diffuse through individual calix[6]arenes.

Introduction

For the past 12 years, we have been exploring Langmuir−Blodgett (LB) films derived from amphiphilic calix[*n*]arenes as ultrathin membranes for gas separations.[1,2] In particular, using surfactants such as 5,11,17,23,29,35-hexaamidoxime-37,38,39,40,41,42-hexakis(1-octyloxy)calix[6]arene (**1**), and cast films of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) as support material, we have succeeded in creating membrane separators having thicknesses that are without precedent.[1g] Our presumption has been that diffusion *through* the surfactants makes an important contribution to the overall permeability of these assemblies.



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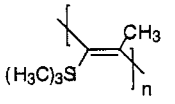
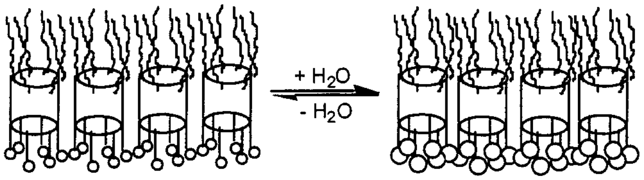


PTMSP

Scheme 1



Recently, it occurred to us that exposure of such film to humidity could improve their selectivity features. Specifically, we hypothesized that by using water as a co-permeant, a steady-state buildup of hydration would reduce the effective diameter of the molecular pores (Scheme 1). We further reasoned that this reduction in size would have a greater influence on the permeability of larger gases than on smaller ones, the net result being improved selectivity.[3] To our chagrin, *we have observed exactly the opposite behavior*. These findings, together with unusual pressure effects that have been observed for the permeation of helium, suggest the existence of a unique pore structure within these films. A model for this pore structure is briefly described.

Experimental Section

Silylated ATR Crystal. A trapezoidal silicon ATR crystal (Harrick Scientific Corp; single pass; 50 mm × 20 mm × 1 mm; $\theta = 45\%$; native oxide thickness of ~1.7 nm) was cleaned by immersing in a piranha solution [a 4/1 (v/v) solution of concentrated H_2SO_4 and 50% H_2O_2: *Caution: this solution reacts violently with organic materials*] for 24 h, followed by rinsing with purified water (Millipore, Milli Q). Both sides of the crystal were then silylated by dipping it into a heptane/octadecyltrichlorosilane (OTS) solution (made from 15 mL of heptane and 2 drops of OTS) for 10 min. After silylation, the thickness of the hydrocarbon layer, as determined by ellipsometry, was 43 Å.

Fabrication of Langmuir−Blodgett Films. Using standard Langmuir−Blodgett methods, the silylated ATR crystal was dipped, verti-

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(1) (a) Markowitz, M. A.; Bielski, R.; Regen, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 7545. (b) Lee, W.; Hendel, R. A.; Dedek, P.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc*. **1995**, *117*, 10599. (c) Conner, M.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 1178. (d) Markowitz, M. A.; Janout, V.; Castner, D. G.; Regen, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8192. (e) Hendel, R. A.; Nomura, E.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc*. **1997**, *119*, 6909. (f) Hendel, R. A.; Zhang, L.-H.; Conner, M. D.; Hsu, J. T.; Regen, S. L. *Langmuir* **1998**, *14*, 6545. (g) Zhang, L.-H.; Hendel, R. A.; Cozzi, P. G.; Regen, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 1621.

(2) For a review of organic membranes for gas separations, see: (a) Stern, S. A. *J. Membr. Sci*. **1994**, *94*, 1. (b) Koros, W. J.; Fleming, G. K. *J. Membr. Sci*. **1993**, *83*, 1. (c) Koros, W. J. *Chem. Eng. Prog*. **1995**, *91*, 68. (d) Robeson, L. M.; Burgoyne, W. F.; Langsam, M.; Savoca, A. C.; Tien, C. F. *Polymer* **1994**, *35*, 4970. (e) *Polymers For Gas Separations*; Toshima, N., Ed.; VCH Publishers: New York, 1992. (f) Robeson, L. M. *J. Membr. Sci*. **1991**, *62*, 165.

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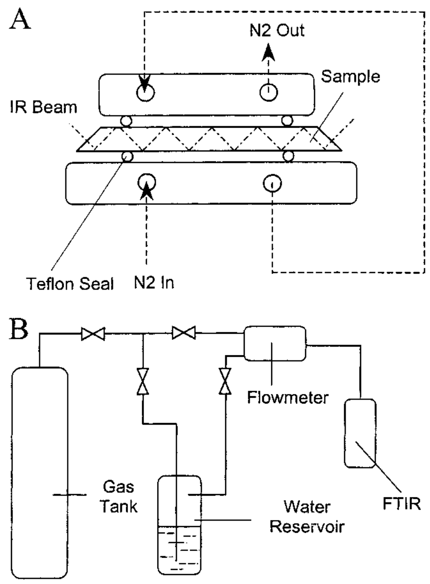

Figure 1. Schematic diagrams of (A) the vapor exposure cell used to control the relative humidity of the sample surface and (B) the experimental arrangement used in these studies.

cally, down and up through a monolayer of **1** that was maintained at 40 dyn/cm at the air−water interface.[1e] After deposition of an individual bilayer, the film was allowed to dry in air for 3 h prior to the next dipping. A total of nine bilayers were transferred; the transfer ratio in all cases was 1.0 ± 0.1. The thickness of the deposited film, as judged by ellipsometry, was 303 Å, which corresponds to 33.7 Å/bilayer. Examination of CPK molecular models indicate a bilayer thickness of **1** equaling 38 Å, when arranged in a fully extended conformation.

FTIR Measurements. ATR IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer that was equipped with a DTGS detector. In each case, 1024 scans were taken at 4.0-cm^{-1} resolution. Specific humidities were produced by mixing a stream of dry N_2 with a stream of water-saturated N_2. This mixed gas then flowed over the sample in a specially designed cell. The humidity was measured by an electronic hygrometer. Samples were allowed to equilibrate for 30 min before recording a spectrum.

Gas Permeation Measurements. Gas permeation measurements were carried out using procedures similar to those previously described.[1e]

Results and Discussion

Reversible Hydration of LB Films of 1. To establish that LB films of **1** can readily undergo reversible hydration, we examined their ability to take up water, as judged by their attenuated total reflectance (ATR) spectra, using carefully controlled relative humidities.[4] For this purpose, 18 monolayers of **1** were transferred to an ATR crystal, which had been made hydrophobic via silylation with octadecyltrichlorosilane. Relative changes in water content were then measured by ATR IR using a specially designed apparatus that is illustrated in Figure 1.[4]

Initially, we recorded a background spectrum for the silylated ATR crystal (without the LB film) at relative humidities of 2, 50, and 96%. This crystal was then removed from the cell and an LB film deposited onto its surface by standard Langmuir−Blodgett procedures. After the sample was allowed to dry for 12 h in a clean desiccator, a spectrum was recorded under a stream of dry N_2. The relative humidity (RH) was then increased to 50%. In Figure 2 is shown the resulting O−H stretching region of the LB film at 50% RH. It should be noted that this spectrum includes a background subtraction for the silylated ATR crystal at 50% RH and the dry LB film, which was recorded immediately after removal from the desiccator. When the relative humidity was changed to 96%, and then to 2%, the resulting spectra showed increased and decreased absorbances, respectively (Figure 2). These results clearly show that the LB film can readily undergo reversible hydration when it is exposed to moisture.

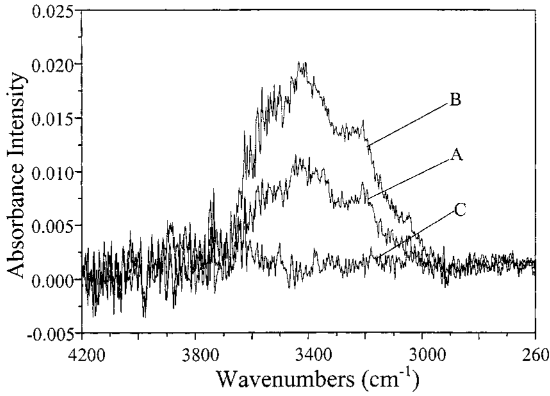

Figure 2. Infrared spectra of 18 monolayers of **1** on a silylated, silicon ATR crystal, which was exposed to relative humidities of (A) 50, (B) 96, and (C) 2%. For each spectrum, a background spectrum for the silylated ATR crystal at the given relative humidity, and also the spectrum of the LB film that was recorded after removal from a desiccator, have been subtracted.

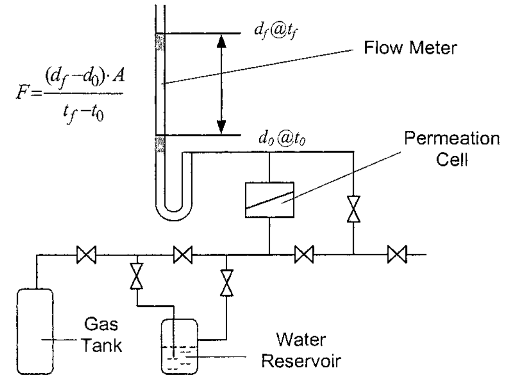

Figure 3. Schematic representation of the home-built apparatus that was used to measure permeation rates of gases under moist conditions.

Moisture Effects on Gas Permeability. To explore the effects of water on membrane permeability, six monolayers of **1** were deposited onto cast films of PTMSP using procedures similar to those previously described.[1e,5−7] Helium and nitrogen were chosen as permeants since it is known that solubility contributions to their permeability are minimal.[2f] In all cases, normalized fluxes (P/l) were determined by measuring the volumetric flow rate (F) of the permeant gas through the membrane and dividing this quantity by the membrane's cross-sectional area (A) and by the pressure gradient (Δp) employed (eq 1); P represents an intrinsic permeability coefficient that

$$(P/l) = F/(A\Delta p) \qquad (1)$$

characterizes the specific membrane−permeant combination, and l corresponds to the membrane thickness; permeation selectivities were calculated from the ratio of $(P/l)_{He}/(P/l)_{N_2}$.

Gas permeation measurements were carried out in one of two ways: (i) a pressure gradient of the permeant gas (10 psig) was applied directly across the composite membrane or (ii) the permeant gas (10 psig) was first passed through a reservoir containing water (Figure 3). In the latter case, the relative humidity in the He or N_2 stream was ∼75%, which corresponds

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[4] MacNeill, B. A.; Simmons, G. W.; Ferguson, G. S. *Mater. Res. Bull.* **1999**, *34*, 455.

Table 1. Hydration Effects on the Permeability of LB Films of 1[a]

monolayers (no.)	permeant	1/*F* (s/mL)	$P/l \times 10^6$ [cm^3/(cm^2·s·cmHg)]	$(P/l)_{He}/(P/l)_{N_2}$
Initial Exposure to Dry Permeant				
0	He	2.8	738	0.90
	N_2	2.55	810	
6	He	24	86	73.6
	N_2	1766	1.17	
6 (dupl)[b]	He	20	103	70
	N_2	1400	1.47	
Subsequent Exposure to Moist Permeant				
0	He	2.8	737	0.90
	N_2	2.51	823	
6	He	83.3	24.8	20.8
	N_2	1733	1.19	
6 (dupl)[b]	He	77	26.8	18.2
	N_2	1403	1.47	
Return to Dry Permeant				
0	He	2.83	730	0.90
	N_2	2.45	807	
6	He	24	84.9	72.6
	N_2	1766	1.17	
6 (dupl)[b]	He	19.2	108	71.7
	N_2	1377	1.5	

[a] All gas permeation measurements were made at 22 °C using a membrane area of 9.36 cm^2 and a pressure gradient of 10 psig. Values were obtained from 5 to 10 measurements; the error in each case was <5%. All LB transfers were made using a subphase temperature of 25 °C, a constant surface pressure of 40 dyn/cm, and a dipping speed of 4 mm/min; the spreading solution was $CHCl_3$/ CH_3OH (5/1, v/v), which contained 1 mg of surfactant/mL. Cast films of PTMSP were 15 μm in thickness. [b] Duplicate experiments were made using a second LB/PTMPS composite, which was fabricated under identical conditions.

to a water content in the vapor phase of 1.4 mol %. Control experiments were also carried out in which the effect of water on the permeability of He and N_2 across bare PTMSP was determined.

Our principal results are summarized in Table 1. In brief, composites made from six monolayers of **1** on PTMSP resulted in a significant reduction in the permeability of He and N_2, relative to bare PTMSP, and a He/N_2 selectivity of ~70. Subsequent exposure of this composite to these same two gases, after they were first passed through an aqueous reservoir, resulted in a 70% *reduction in He permeability but no alteration in the permeability of* N_2. Returning the permeant streams to the dry state brought the helium-normalized flux and the He/N_2 selectivity back to their original values; i.e., this effect by water was completely reversible.

Pore Structure Within LB Films of 1. The fact that exposure of the LB film toward water "dampens" its permeability with respect to He is fully consistent with our hydration hypothesis (Scheme 1). The fact that the membrane's permeability toward N_2 is unaffected by the presence of water, which leads to an overall decrease in selectivity, further indicates the existence of at least *two distinct permeation pathways*, i.e., one that is selective for He and is being dampened by water and another that is less selective and less capable of being dampened. Given the fact that the kinetic diameter of He (2.60 Å) is smaller in size than that of N_2 (3.64 Å), these results imply that the selective permeation pathway has a smaller pore diameter. In addition, since the kinetic diameter of H_2O (2.65 Å) is almost identical to that of He, and since the water content in the vapor phase is only 1.4 mol %, a blocking action by individual water molecules, which are not part the hydration shell of the calix[6]arene, is highly improbable.

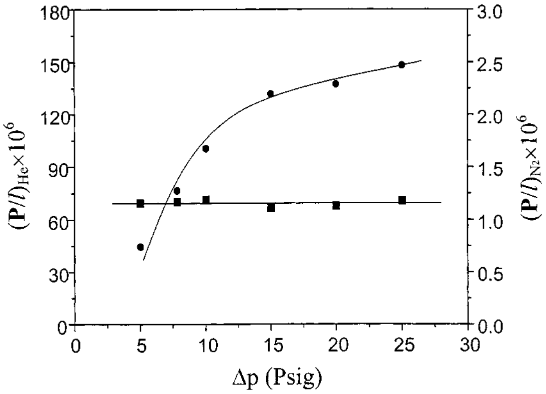
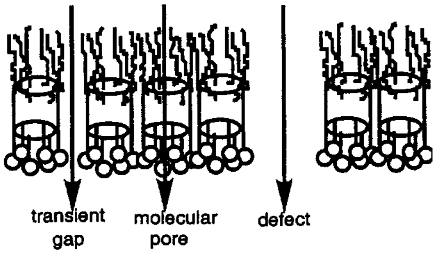


Figure 4. Plot of normalized flux (*P*/l) for He (●) and N_2 (■) through a composite membrane, formed from six monolayers of **1** and 15-μm-thick PTMSP, as a function of Δ*p*. The units of normalized flux (*P*/*l*) are cm^3/(cm^2 × s × cm Hg).

Scheme 2



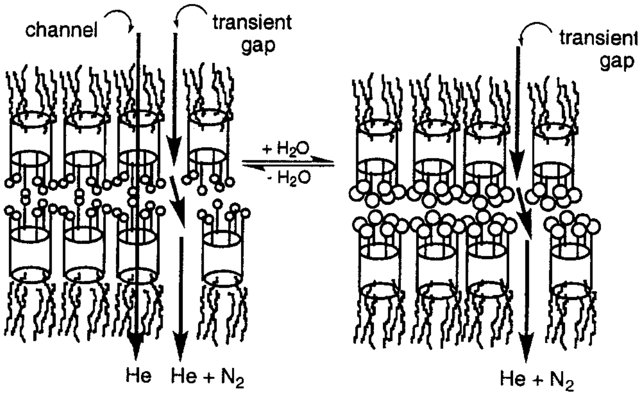
What are the different permeation pathways that exist? Three possibilities include the following: (i) molecular pores, (ii) transient gaps that develop between neighboring calix[6]arenes as a result of thermal motion, and (iii) defects within the film. In Scheme 2 we show a stylized illustration that depicts each type of pore.

Which of these openings is being dampened by water? Film defects can be ruled out as a possibility because their diameters, by definition, are much greater than the diameter of the permeants and because they are expected to exhibit a maximum permeation selectivity that is governed by Graham's law. This translates into a He/N_2 selectivity of 2.6, which is much less than what we have observed. Distinguishing between transient gaps and molecular pores, however, is considerably more difficult. Examination of CPK molecular models of the calix[6]arene framework indicates a *maximum* molecular pore diameter of ~4.8 Å. Depending upon the average conformation of the calix[6]arene in the assembled state, the internal diameter of these molecular pores could be less than this value. It is conceivable, in fact, that this pore diameter could approach the kinetic diameter of N_2 (3.64 Å). Because of their dynamic nature, the average pore diameters of transient gaps are even more difficult to judge.

Despite these difficulties, an unusual pressure effect on the normalized flux of helium points toward molecular pores as being the likely pathway that is dampened by water. In previous studies, we have found that composites made from LB films of **1** and PTMSP show unusual pressure effects.[1b] Specifically, we found that the normalized flux for He increases, significantly, with increasing pressures but that the influence of pressure on the normalized flux of N_2 was only modest.[1b] A more detailed investigation of these pressure effects has revealed that the changes in the normalized flux for nitrogen are, in fact, negligible (Figure 4). Very similar results have been obtained for LB films made from an analogous calix[6]arene bearing *n*-dodecyl chains.[8] In theory, an increase in a pressure gradient that is applied across a membrane should produce a proportional increase in the volumetric flow rate, *F*, and leave the normalized flux, P/l, unaltered (eq 1). Thus, the normalized flux of gas across a given membrane is a characteristic of that particular membrane. Any change in the normalized flux is a likely reflection of a change in membrane structure.

A simple model that can account for this sharp difference between He and N_2 is one that assumes that (i) He is capable of diffusing through the calix[6]arenes but N_2 diffuses through it very slowly if at all (i.e., the internal diameter of the hydrated calix[6]arene is greater than the kinetic diameter of He, but equal to or less than that of N_2) and (ii) the degree of alignment of the calix[6]arenes between the monolayers increases with an increasing helium pressures.[9] Thus, as the extent of calix[6]arene alignment increases, the resistance toward helium flow decreases, leading to an increase in the normalized flux for helium. Since the N_2 molecule is unable to diffuse through the calix[6]arene, a similar increase in the N_2 pressure would not be expected to change its normalized flux. In the case of N_2, the only permeation pathway that would be available to it would be through transient gaps that are short-lived compared with the permanent pore of the calix[6]arene. A stylized illustration of this model, which includes the formation of channels, transient gaps, and hydrated molecular pores is shown in Scheme 3.

Scheme 3. Hypothetical Diffusion through and between Porous Surfactants



Conclusions

Gas permeation measurements have been carried out for He and N_2 across Langmuir−Blodgett films of **1** in the presence and in the absence of moisture. Whereas the permeability of N_2 was unaffected by moisture, the permeability of He was significantly reduced. This sharp difference provides compelling evidence for the existence of t*wo distinct pathways for diffusion*: one that strongly favors the transport of He over N_2, and a second one that is much less selective. The normalized fluxes of He and N_2 across these LB films, as a function of the pressure gradient that is used, support a model in which He (but not N_2) can diffuse through the calix[6]arenes. Diffusion of N_2 across the film is likely to pass through transient gaps that develop between neighboring calix[6]arenes.

If our model for gas transport through composites of **1**/PTMSP is correct, then one would expect that the elimination of transient gaps by covalent cross-linking should produce a membrane that is impermeable toward nitrogen, but permeable toward He. Such a membrane would also be expected to have potential for separating H_2 and N_2, a gas pair that has considerable commercial importance.[10] Efforts aimed at exploring such a possibility are currently in progress.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) How an increase in the pressure gradient might increase the extent of calix[6]arene alignment is not presently clear. Two scenarios that seem possible are as follows: (i) a transport-induced mechanism, in which the flow of helium through the calix[6]arenes exerts an "atomic-like shear force", that tends to produce a minimum energy state of the assembly by minimizing its barrier toward helium and (ii) a more general, pressure-induced mechansim in which the LB film is compressed, leading to increased hydrophobic interactions between calilx[6]arenes in adjacent monolayers that are maximized through alignment

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