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# Porous and Glued Langmuir-Blodgett Membranes

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## Objectives

The long-range goal of this program is to create porous and glued Langmuir-Blodgett (LB) films that can be used as ultrathin membranes for the separation of  $H_2$  from  $CO_2$ . The immediate objective of this research is to expand the scope of porous and glued Langmuir-Blodgett bilayers by synthesizing analogs that are based on (i) hydrogen bonding, (ii) covalent bond formation, and (iii) post-gluing protocols.

## Technical Barriers

The thickness of polymer-based membranes is a major factor that determines their utility for gas separations. Specifically, thin membranes are preferred because they allow for a high flux of gaseous permeants, and a high overall productivity. Based on current technologies, it has proven difficult to prepare defect-free membranes that are thinner than ca. 100 nm. This program is aimed at creating porous and glued Langmuir-Blodgett membranes that are less than ca. 6 nm in thickness, which are free of defects and exhibit  $H_2/CO_2$  permeation selectivities in excess of ca. 100.

## Abstract

Research that has been carried out over the past 18 months has demonstrated the feasibility of creating glued Langmuir-Blodgett bilayers based on hydrogen bonding, covalent bond formation and post-gluing protocols. Specifically, monolayer assemblies derived from calix[6]arene-based amidoximes have been stabilized by use of poly(acrylamide). In addition, poly(allylamine) has been used to stabilize monolayers of calix[6]arene-based aldehydes via Schiff base formation. A protocol has also been devised in which calix[6]arene-based surfactants are transferred from the air/water interface and “glued” in a gluing-chamber. Preliminary gas permeation measurements have established that these

hydrogen-bonded and covalently-bonded thin films are free of defects, but that  $He/CO_2$  selectivities are less than what has been obtained by ionic crosslinking.

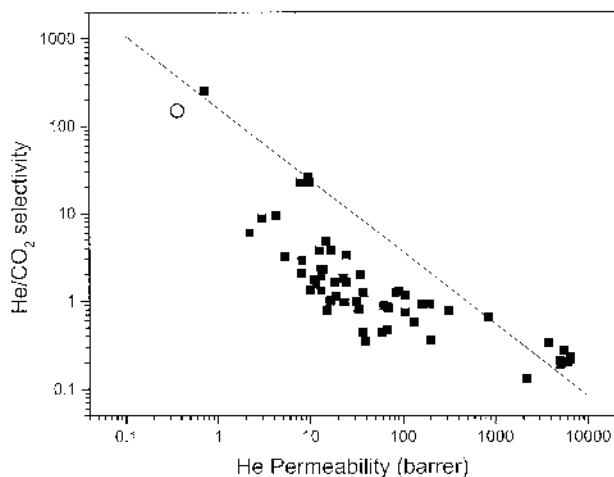
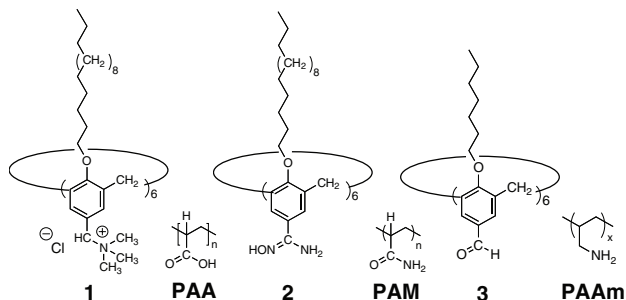
## Progress Report

**Glued Langmuir-Blodgett Monolayers.** We have recently introduced the concept of “glued” Langmuir-Blodgett (LB) monolayers, whereby water-soluble polyelectrolytes are used to ionically crosslink LB monolayers of surfactants bearing multiple counterions.<sup>1-3</sup> We have also shown that such gluing eliminates film defects, as evidenced by changes in their barrier properties. For example, single LB bilayers made from **1**, which have been ionically cross-linked with poly(acrylic acid) (PAA), exhibit  $He/CO_2$  permeation selectivities as high as 150 (Chart 1).<sup>4</sup> This degree of  $He/CO_2$  selectivity for a membrane that is less than 6 nm in thickness is without precedent. In these model studies, helium was used as a simulant for hydrogen because it is noncombustible and because He and  $H_2$  are of similar size and diffusivity.

To place the permeation properties of these glued LB bilayers into perspective, a “trade-off” plot for  $He/CO_2$  selectivity versus helium permeability is shown in Figure 1 for a series of representative polymers that have been reported in the literature. Also included is a solid line, which corresponds to a theoretical “upper bound”; that is, the maximum selectivity and permeability that is predicted from a solution-diffusion transport mechanism. To our knowledge, the only polymer that has a  $He/CO_2$  selectivity that is as high as our glued bilayer is poly(acrylonitrile); both lie close to the upper bound and both have a  $He/CO_2$  selectivity that is in excess of 100. A key difference between the two materials, however, is that only the glued bilayer can be fabricated as defect-free membranes with extreme thinness, down to 5.6 nm. In principle, materials of this type could lead the way to improved membranes for hydrogen purification.

**Glued Langmuir-Blodgett Monolayers Via Hydrogen Bonding.** During the current grant period, we have expanded the concept of glued LB bilayers beyond that of ionic crosslinking. Specifically, we have demonstrated the feasibility of using hydrogen bond interactions between a nonionic, water-soluble polymer [i.e., poly(acrylamide) (PAM)] and a surfactant monolayer made from calix[6]arene **2** to produce a glued LB thin film. Table 1 shows normalized fluxes that have been measured across single LB bilayers derived from calix[6]arene **2** in the absence and in the presence of PAM. As is evident from these data, the introduction of PAM substantially increases the permeation selectivity of

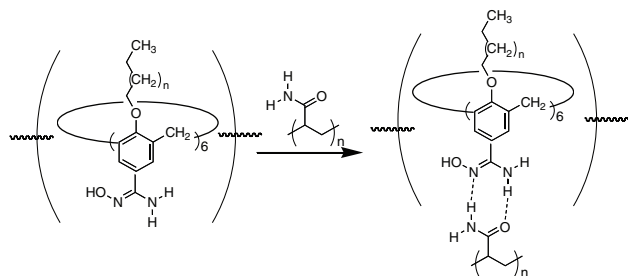
**CHART 1**



**FIGURE 1.** Comparison of He/CO<sub>2</sub> selectivities versus the permeability coefficient,  $P$ , for He for a broad range of organic polymers.<sup>4</sup> The open circle represents the permeability properties of a glued bilayer derived from **1** and PAA.

the film for He versus CO<sub>2</sub>, as well as for He versus N<sub>2</sub>. Although the He/CO<sub>2</sub> selectivity is not as high as that found with **1**/PAA, it is still in excess of that predicted for Knudsen diffusion based on Graham's law. This demonstrates that the film is free of defects. In principle, further improvements should be possible through a manipulation of the structure of the surfactant and/or polymer; e.g., by varying the size of the calix[ $n$ ]arene framework, modifying the hydrophobic/hydrophilic balance of the polymer, etc.

**SCHEME 1**



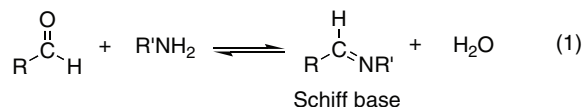
**TABLE 1.** Normalized Flux of He, N<sub>2</sub> and CO<sub>2</sub> Across Glued and Unglued LB Bilayers of **2**<sup>a</sup>

Calix[6]arene	PAM <sup>b</sup>	10 <sup>6</sup> P/l -----cm <sup>3</sup> /cm <sup>2</sup> -s-cmHg-----				
		He	N <sub>2</sub>	CO <sub>2</sub>	$\alpha_{\text{He/N}_2}$	$\alpha_{\text{He/CO}_2}$
2	---	162	12.9	214	13	0.76
2	1.0	90	0.44	15.4	205	5.8
2	5.0	88	0.43	6.30	205	14.0

<sup>a</sup> LB bilayers made using a surface pressure of 30 dyn/cm (25°C). Normalized flux values ( $P/l$ ) are the observed flux divided by the area of the membrane (9.36 cm<sup>2</sup>) and the pressure gradient (10 psi) employed;  $l$  is the thickness of the composite; the thickness of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) supports in all cases was ca. 30  $\mu$ m.

<sup>b</sup> Repeat unit concentration (mM) in the aqueous subphase.

**Glued Langmuir-Blodgett Monolayers Via Covalent Bond Formation.** The reaction of primary amines with aldehydes to form Schiff bases is well-established (eq. 1). Because of its simplicity, mildness and effectiveness, Schiff base formation has been widely used to immobilize proteins and a variety of other molecules onto organic and inorganic surfaces. For these same reasons, we chose Schiff base formation as a basis for gluing LB monolayers.



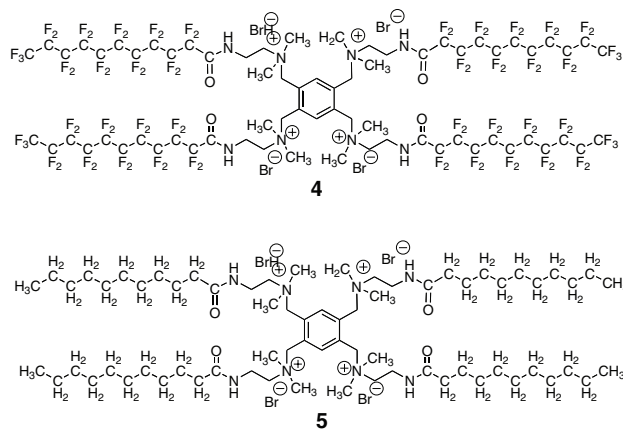
Examination of the monolayer properties of calix[6]arene **3** over an aqueous poly(allylamine) (PAAm) subphase has revealed effective crosslinking when the pH of the subphase was  $\geq 9.5$  (Chart 1). Detailed characterization of these glued assemblies has been carried out by a combination of atomic force microscopy (AFM), water contact angle measurements, ellipsometry, X-ray photoelectron spectroscopy (XPS), and attenuated total reflection IR (ATR-IR) spectroscopy, after being deposited onto a silicon wafer that had been silylated with *n*-octadecyltrichlorosilane (OTS). In preliminary studies, we have found that deposition of a glued LB bilayer made from **3** and PAAm onto poly[1-(trimethylsilyl)-1-propyne] (PTMSP) supports exhibit barrier properties that are similar to those of glued bilayers derived from **2** and PAM, with a He/CO<sub>2</sub> permeation selectivity of ca. 15.

**Post-Gluing.** In preliminary studies, we have developed a post-gluing procedure. Specifically, monolayers of **3** are first transferred to a hydrophobic substrate [e.g., a silicon wafer that had been silylated with *n*-octadecyltrichlorosilane (OTS)] via a single vertical LB down-trip, and then removed from the aqueous subphase (vertical up-trip) after the surface

pressure has been reduced to 0 dyn/cm. Rapid immersion into an aqueous solution containing poly(allylamine), followed by rinsing, has afforded surfaces that are similar in quality to those films that have been glued, directly, in the LB trough.

## Future Directions

**Glued Langmuir-Blodgett Bilayers From Fluorocarbon-based Surfactants.** In principle, a reduction in solubility contributions for CO<sub>2</sub> should lead to higher He/CO<sub>2</sub> permeation selectivities. To explore this possibility, we will first synthesize and compare glued bilayers derived from surfactants **4** and **5**. Although these are not porous surfactants, if we observe significantly higher He/CO<sub>2</sub> permeation selectivity with **4**, we will then synthesize analogous calix[6]arene-based surfactants, bearing fluorocarbon chains. Our main interest in **4** and **5** is that such compounds should be readily accessible in only a few synthetic steps; the synthesis of calix[6]arene analogs would, however, be significantly more involved.



**Hollow Fibers.** Ultimately, we propose to extend our glued and porous LB membrane chemistry to hollow fiber technology, where very high surface areas are possible.

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