# The Gluing of a Langmuir−Blodgett Bilayer

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In this paper, we introduce the concept of glued Langmuir−Blodgett (LB) bilayers, that is, LB bilayers that are composed of two monolayer leaflets, each of which is ionically cross-linked. We also report the first representative example, which uses calix[6]-arene **1** as the bilayer-forming amphiphile and poly(4-styrene-sulfonate) (PSS) as the glue. The fact that a single glued bilayer of **1**/PSS shows very high gas permeation selectivity and robustness should stimulate some rethinking of LB films for the creation of practical nanoscale devices.
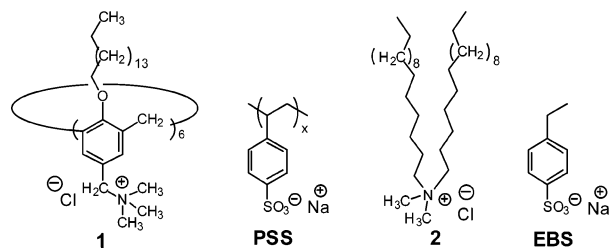
Langmuir−Blodgett films have been the subject of considerable interest for almost 70 years.[1−3] Despite this interest, problems with film quality and stability have hampered efforts that have been aimed at developing them from a practical standpoint.[3] A classic example can be traced to early pioneering studies by Katherine Blodgett, where it was suggested that LB films might find use as filters for molecular separations.[2] Since that time, many attempts have been made to reduce this concept to practice in the area of gas separations. To date, nearly all LB films that have been tested have shown gas permeation selectivities that approach values predicted by Graham's law. Such a finding indicates that diffusion takes place through defects in the film.[4]

Our own efforts in this area have led us to unique combinations of calix[6]arene-based amphiphiles and poly[1-(trimethylsilyl)-1-propyne] (PTMSP) supports.[5] Recently, we reasoned that a significant improvement should be possible using cationic calix-[6]arenes together with water-soluble polyanions. Specifically, we hypothesized that a polyanion should "glue together" such LB bilayers via ionic cross-linking, and help to fill void space within the assembly, the net result being enhanced stability, reduced defect formation, and increased permeation selectivity. In a broader context, we were intrigued with the concept of glued LB bilayers as a new strategy for stabilizing LB films. Although there have been several reports of the use of polyions to stabilize monolayers made from singly charged surfactants, to our knowledge, the combined use of a polyion and multiply charged surfactants (required for gluing) is without precedent.[6] Here, we show that such a strategy can result in LB films having attractive permeability and stability properties.

Calix[6]arene (**1**) was chosen for feasibility studies because of its ready availability from 5,11,17,23,29,35-hexa(chloromethyl)-
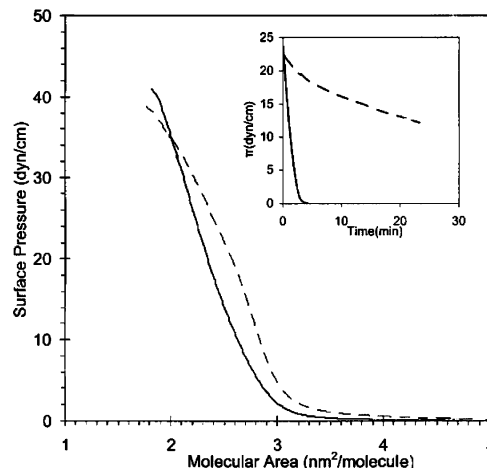
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**Figure 1.** Surface pressure−area isotherms for **1** over water (solid line) and 5.0 mM PSS (dashed line) at 25 °C; inset shows surface viscosity after monolayers were equilibrated at 22 dyn/cm for 60 min.

37,38,39,40,41,42-hexakis-*n*-hexadecyloxy-calix[6]arene by direct quaternization with trimethylamine.[7] A simple polyanion, PSS, was chosen as a glue on the basis of its commercial availability.

Compression of **1** on the surface of pure water produced stable monolayers having a limiting area of ca. $2.71 \pm 0.07$ nm$^2$/molecule (Figure 1). Subsequent expansion and recompression cycles yielded the same surface pressure−area curve. Compression of **1** over an aqueous subphase containing 5.0 mM of repeat units of PSS (average $M_W$ ca. 70 000, Polysciences) generated a similar surface pressure−area curve. In this case, compression beyond ca. 10 dyn/cm led to significant hysteresis such that subsequent expansion resulted in a sharp decrease in surface pressure (not shown).[8] This hysteresis implies that the polyanion enhances the cohesiveness within the monolayer by increasing the associative interactions between neighboring amphiphiles. Surface viscosity measurements, made in the absence and in the presence of PSS, also revealed enhanced cohesiveness. Thus, when a monolayer of **1** was compressed over pure water and exposed to a 6.0 mm slit opening of a canal viscometer, a precipitous decrease in surface pressure was observed. When PSS was present in the subphase, however, only a modest decrease in surface pressure with time was observed, reflecting a relatively high viscosity of the monolayer.

That PSS can be incorporated into a LB bilayer of **1** was established via ellipsometry and X-ray photoelectron spectroscopy (XPS) measurements. A LB bilayer of **1** was deposited onto a silylated silicon wafer using a 5 mM aqueous PSS solution (30 dyn/cm). Subsequent analysis by ellipsometry revealed a film thickness of $5.64 \pm 0.04$ nm.[9,10] A similar bilayer that was prepared in the absence of PSS showed a thickness of $4.80 \pm 0.16$ nm.[10] Thus, the polyanion contributes ca. 0.84 nm to the thickness of the bilayer. Further analysis of the glued bilayer by XPS yielded insight into the location of the polyanion, its relative quantity, and the extent

***Table 1.*** Fluxes across LB Bilayer/PTMSP Composite Membranes[a]

| LB bilayer | $10^6$ $P/l$ (cm$^3$/cm$^2$ s cm Hg) composite (PTMSP)[b] | | $\alpha_{He/N_2}$ $(P/l)_{He}/(P/l)_{N2}$ |
|---|---|---|---|
| | He | N$_2$ | |
| **1** | 513 (602) | 504 (643) | 1.02 |
| | 712 (871) | 706 (938) | 1.02 |
| **1**/PSS | 132 (602) | 0.56 (643) | 235 |
| | 154 (602) | 0.67 (643) | 231 |
| | 118 (602) | 0.48 (643) | 245 |
| **1**/EBS | 376 (521) | 67 (556) | 5.6 |
| | 295 (521) | 69 (556) | 4.3 |
| **2**/PSS | 566 (602) | 590 (643) | 0.96 |
| | 780 (871) | 820 (938) | 0.95 |

[a] Normalized fluxes were calculated by dividing the observed flux by the area of the membrane and the pressure gradient used (10 psig). Transfers were made using a surface pressure of 30 dyn/cm (25 °C). [b] Numbers in parentheses refer to the bare PTMSP; slight variations are due to variations in the thickness of the support.

of ion exchange between PSS and **1**. By using various "take-off" angles, one can assess atomic compositions at different depths.[11] On the basis of a plot of nitrogen (N) and sulfur (S) content versus takeoff angle, it is clear that both of these elements are buried within the LB film. The fact that the N/S atomic ratio ($0.38 \pm 0.09$) shows little dependency over the entire range of takeoff angles further indicates that both of these atoms lie at similar depths. Because no chlorine could be detected by XPS, and because the atomic percentage for Na (1.23%) plus N (1.58%) is very close to the atomic percentage of S (3.16%, 90° takeoff angle), we conclude that ion exchange is essentially complete and that the glued film contains ca. a 2-fold excess of sodium 4-styrenesulfonate groups. Finally, whereas an unglued bilayer of **1** can be readily removed from the surface of a silicon wafer by rinsing with chloroform, a PSS-glued analogue remains intact. These results demonstrate that gluing significantly enhances film stability.

The quality of these glued and unglued LB films was then assessed by measuring their permeation selectivity with respect to He and N$_2$. For this purpose, cast films of PTMSP were used as support material. Specific experimental procedures that were used were similar to those previously described.[5] Deposition of a bilayer of **1** on PTMSP resulted in reduced normalized fluxes for both He and N$_2$, and a He/N$_2$ selectivity of 1.02 (Table 1). When PSS was included in the bilayer, a significant decrease in the normalized flux for He was observed, as well as a very dramatic decrease in the normalized flux for N$_2$, the net result being a permeation selectivity of ca. 240. If one assumes that the resistance of this composite is equal to the resistance of the support plus the resistance of the glued bilayer, then the averaged normalized flux values for He and N$_2$ across this bilayer are 174 and 0.57 cm$^3$/cm$^2$ s cm Hg, respectively. These values translate into an intrinsic He/N$_2$ selectivity for the bilayer of ca. 305, which clearly reflects a very high quality film.

To put this permeation selectivity into perspective, a defect-free LB film made from more than 20 bilayers (60 nm in thickness) of a polymeric surfactant has shown a He/N$_2$ selectivity of 24 on the basis of a solution-diffusion mechanism of permeation.[12] The high selectivity of our single glued bilayer of **1** is a likely consequence of its permanent nanoporous structure, and its stability due to ionic cross-linking (gluing), which result in a more effective discrimination between He and N$_2$ on the basis of their size (i.e., the kinetic diameters for He and N$_2$ are 0.260 and 0.364 nm, respectively).[5a]

Finally, to confirm the gluing effect, we examined a related bilayer in which PSS was replaced by the sodium salt of 4-ethyl-benzene sulfonate (EBS), that is, a monomer analogue that is incapable of cross-linking the calix[6]arene assembly. Permeation measurements made for **1**/EBS revealed a moderate reduction in the normalized flux for He and N$_2$, and a He/N$_2$ selectivity of ca. 5. From these results, we conclude that ionic cross-linking is, indeed, a major contributor to the extraordinary selectivity found with **1**/PSS. The modest increase in selectivity of bilayers of **1**/EBS relative to bilayers of **1** is presumed to reflect the additional mass that EBS contributes to the assembly. As a further control, we examined a related membrane using *N*,*N*-dimethyl-*N*,*N*-dihexa-decylammonium chloride (**2**) in place of **1**. Similar to **1**/EBS, this combination of singly and multiply charged counter*ions* (**2**/PSS) precludes the possibility of ionic cross-linking. The poor selectivity that we have observed with this membrane is a likely consequence of film defects that are formed within a less cohesive assembly. As expected, monolayers of **1**/EBS and **2**/PSS showed negligible surface viscosities. The fact that PSS does not significantly increase the viscosity of monolayers of **2**, but does significantly increase the viscosity in monolayers of **1**, clearly reveals the "gluing" effect.

The He/N$_2$ selectivity of 305 that we have measured for a single glued bilayer of **1**, which is less than 6 nm in thickness, is extraordinary. These findings should encourage the exploration of ionic cross-linking as a new strategy for improving the quality and stability of LB films.

**Supporting Information Available:** Synthesis of **1**, XPS and stability data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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