FEATURE ARTICLE

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# Don't forget Langmuir–Blodgett films

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**Langmuir-Blodgett (LB) films have been investigated, extensively, over the past 70 years. Despite considerable efforts aimed at exploiting their nonlinear optical, piezoelectric, pyroelectric, semiconducting, sensing and barrier properties, problems associated with film quality and stability have hampered their practical development. This feature article highlights one recent advance in the LB area (*i.e.*, the ionic cross-linking of LB films or "gluing"), which has resulted in single bilayer membranes possessing extraordinary quality and stability. The gluing of LB films provides new opportunities for an old technology that has been waning in recent years.**

## Introduction

In the 1930s, Irving Langmuir and Katherine Blodgett introduced a method for fabricating monolayer and multilayer arrays of surfactants.[1–3] Since that time, this Langmuir–Blodgett (LB) technique has been used, extensively, to construct a wide variety of organized thin films.[4] Typically, LB films are fabricated by dipping a solid support, vertically, through a surfactant monolayer at an air–water interface. For example, a single "down-trip" of a hydrophobic support from air into water results in the monolayer being transferred, such that the hydrocarbon tails are in intimate contact with the support and the polar head groups extend outward towards the bulk aqueous phase (Fig. 1). A subsequent "up-trip" generally deposits a second monolayer with a head-to-head orientation with the first deposited monolayer. Further dipping can then lead to multilayers of the surfactant.[4]

In recent years, there has been a steady shift away from the LB technique towards self-assembly methods for the fabrication of monolayer and multilayer arrays (Fig. 2). Two reasons for this shift are a greater robustness of self-assembled materials relative to most LB films, and also their ease of preparation. In contrast to the LB method, which requires a film balance and careful control over surface pressures during dipping and transfer, self-assembly is carried out by simple immersion of a suitable support into a solution containing an excess of monomer. Common examples of monomers and supports that have been used in forming self-assembled monolayers include: organic amines + Pt,[5] organosilanes + silica,[6] and organic thiols + Au.[7,8] The formation of multilayer arrays *via* self-assembly has also become popular. Most commonly, a charged surface is dipped into a solution containing a polyionic species, followed by dipping into a second solution that contains a polymeric counterion. Repetition of such dipping then produces the desired material in a layer-by-layer manner.[9,10]

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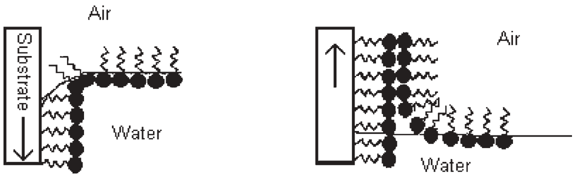

**Fig. 1** A stylized illustration showing a single surfactant monolayer being transferred to a hydrophobic support on a down-trip, followed by the transfer of a second monolayer on the up-trip, to form a bilayer.

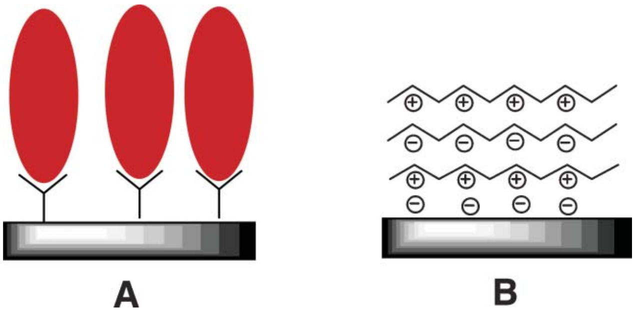

**Fig. 2** Illustrations showing (A) a self-assembled monolayer and (B) an alternating array of polycations and polyanions supported on a negatively-charged substrate.

The primary aim of this Feature Article is to highlight one recent advance in the LB area, which promises to provide new opportunities for LB-based materials. Specifically, we show how ionic cross-linking of multiply-charged surfactants (a process that we have termed, "gluing") can yield LB films having extraordinary barrier properties and stability.

## Langmuir–Blodgett films as permeation-selective membranes

The possibility of utilizing LB films as membranes for molecular separations was first recognized by Katherine Blodgett, herself. Thus, in an early patent, Blodgett noted that, "Skeleton films…may be employed as sieves or filters for the segregation of previously non-filterable substances of molecular magnitudes".[11]

Before discussing the barrier properties of a few representative

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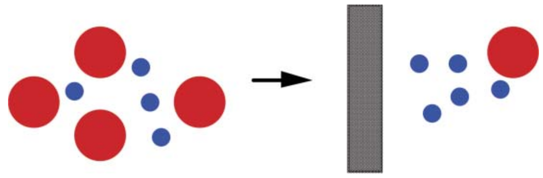


**Fig. 3** Gaseous permeants, *i* (blue) and *j* (red) diffusing across a hypothetical membrane. Eqn. (1) shows the relationship between the flux (***F***), permeation coefficient (*P*), surface area of the membrane (*A*), pressure gradient used ($\Delta P$) and membrane thickness (*l*). Eqns. (2) and (3) define the normalized flux (*P*/*l*) and the permeation selectivity ($\alpha$), respectively.

LB films, we first review some of the general principles governing membrane permeation. An illustration of two gaseous molecules (*i* and *j*) diffusing across a hypothetical membrane is shown in Fig. 3. Also shown are three equations (1-3) that characterize gas permeation. Thus, eqn. (1) shows how the flux (***F***) of each permeant is related to the membrane's surface area (*A*), the pressure gradient ($\Delta P$) that is applied, the permeability coefficient (*P*) that characterizes the membrane/permeant combination, and the thickness (*l*) of the membrane. A normalized flux (*P*/*l*), often referred to as the permeance, is given by eqn. (2). Finally, the permeation selectivity ($\alpha$) of the membrane, with respect to *i* and *j*, is given by the ratio of the permeances of the two gases (eqn. (3)). The inverse relationship that exists between the flux of a gas and the thickness of the membrane has an important practical consequence. Specifically, thin membranes favor a high flux and high membrane productivity. The higher the permeation selectivity, the more efficient the membrane as a separating medium. Thus, two key factors defining the utility of a membrane are the flux and the permeation selectivity. From an industrial standpoint, membrane thicknesses of *ca.* 100 nm are generally regarded as being very thin. The challenge of creating thinner membranes, without introducing defects, is significant.

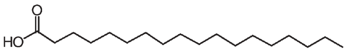
$$F(\mathrm{cm^3\,s^{-1}}) = \frac{PA\Delta p}{l} \tag{1}$$

$$\frac{P}{l}\left(\mathrm{cm^3\,cm^{-2}s\,cm\,Hg}\right) = \frac{F}{A\Delta p} \tag{2}$$

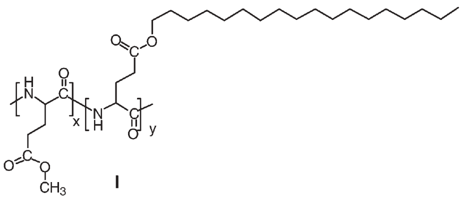
$$\alpha = \frac{\left(\frac{P}{l}\right)_i}{\left(\frac{P}{l}\right)_j} \tag{3}$$

Because the permeation selectivity of a membrane is highly sensitive to the presence of defects, it can be a useful criterion to judge the quality of an LB film. Consider, for example, the permeation of helium and nitrogen across a hypothetical membrane. If this membrane were to contain defects, then the observed He/$N_2$ permeation selectivity is expected to approach the Knudsen diffusion limit—a value that is defined by Graham's law, whereby the rate of diffusion of each gas is inversely proportional to the square root of its molecular weight; that is a He/$N_2$ selectivity of 2.6. In such a case, the size of the defects is larger than the effective diameter of the permeant gases, but smaller than their mean free path. A permeation selectivity that exceeds the Knudsen diffusion limit indicates that any pores that are present are comparable in size to He and $N_2$.

Until recently, the permeation properties of nearly all LB films that have been investigated have been found to obey Knudsen diffusion. For example, multilayers of stearic acid that were deposited onto a silicone copolymer showed Knudsen diffusion characteristics even with films as thick as 48 layers, corresponding to a thickness of *ca.* 120 nm.[12,13] In one rare example in which the permeation selectivity was found to exceed the Knudsen diffusion limit, an LB film that was constructed from 40 monolayers (60 nm) of a polymeric surfactant, **I** ($X$ = 70% and $Y$ = 30%), showed a He/$N_2$ selectivity of *ca.* 8.[14]



**stearic acid**



**I**

## Perforated Langmuir–Blodgett films

Our own efforts in the LB film area have focused sharply on the concept of "perforated monolayers" (Fig. 4).[15–17] In brief, a monolayer of "porous" surfactants is formed at the air–water interface. Subsequent LB-deposition onto a support that is sufficiently permeable, such that gas permeation through the LB film is rate-limiting, affords the desired composite membrane. Because of their microporous structure, these perforated monolayers are expected to provide unusually high permeation selectivity due to molecular sieving.

In most of our studies, the calix[6]arene framework has been used as starting material due to its ready availability, and its ease of modification.[15–19] For example, in one previous report, a calix[6]arene-based surfactant (**II**) was synthesized in which amidoxime moieties were used as polar head groups and *n*-octyl chains served as the hydrocarbon tails (Fig. 5).[15] The fact that the limiting area of this surfactant was nearly identical to an analog having *n*-hexadecyl tails provided strong support for orientation at the air–water interface; that is, where the tails of both compounds extend into air and the amidoxime groups are in intimate contact with water. Fig. 6 shows a side view and a top view of space filling models of a similar calix[6]arene having *n*-butyl groups as tails. In these models, the alkyl chains have been placed in an all-*anti* conformation and the calix[6]arene in a "open" conformation to give a *maximum* internal pore diameter of *ca.* 0.48 nm. Because of its conformational flexibility, the effective pore diameter is likely to be smaller, approaching that of He and $N_2$, which are 0.26 and 0.36 nm, respectively. Single LB bilayers of **II**, which were transferred to cast films made from poly[1-(trimethylsilyl)-1-propyne] (PTMSP), were found to exhibit a He/$N_2$ permeation selectivity of *ca.* 18 (Fig. 7).

Subsequent gas permeation measurements of LB bilayers of **II**, which were carried out in the presence of water vapor, have

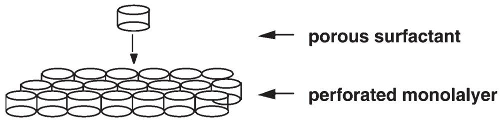


**Fig. 4** An illustration of a perforated monolayer formed from a porous surfactant.

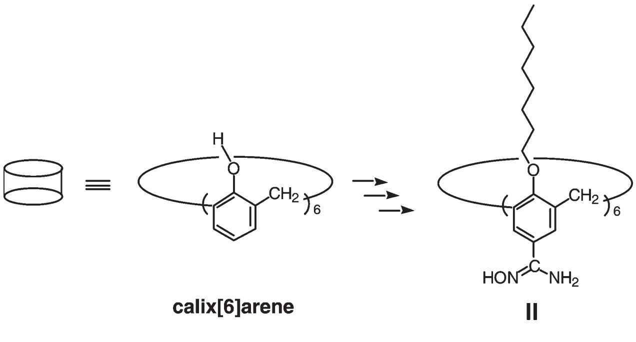


**Fig. 5** The calix[6]arene framework used to prepare a surfactant derivative, **II**, bearing *n*-octyl and amidoxime groups.

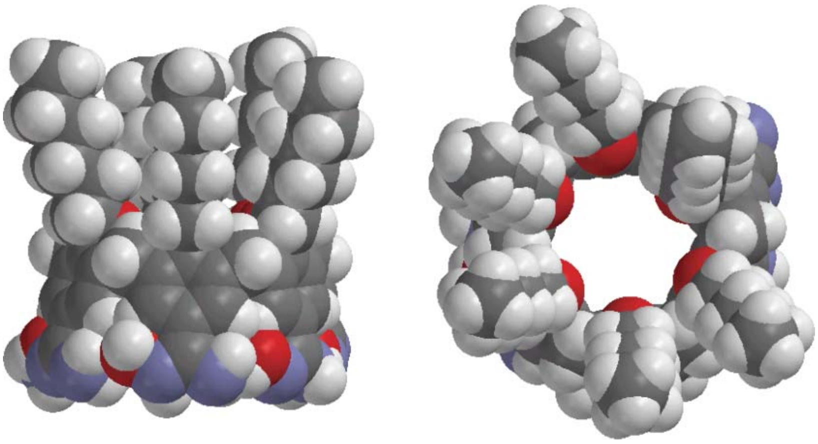


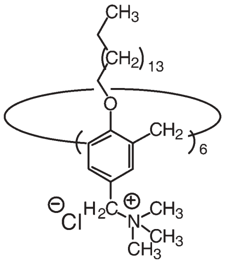
**Fig. 6** Space filling models of an analog of **II** having *n*-butyl "tails"; sideview (left) and topview (right).

provided strong inferential evidence for two distinct pathways for diffusion.[18] Specifically, the permeability of helium (but not nitrogen) across these films was significantly reduced when the film was hydrated. These results, together with normalized fluxes that were observed for He and $N_2$ as a function of the pressure gradient, provided support for a model in which He (but not $N_2$) diffuses through individual calix[6]arenes. Nitrogen is presumed to diffuse through transient gaps that develop between neighboring calix[6]arenes as a result of thermal motion.

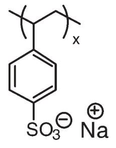
## Glued Langmuir–Blodgett film

In an effort to improve the cohesiveness of calix[6]arene-based LB film, and also their barrier properties, we synthesized ionically-cross-linkable analogs. Our presumption was that ionic cross-linking of a cationic calix[6]arene-based LB film by use of a water-soluble polyanion, would produce a two-dimensional network with enhanced stability. We further reasoned that by filling in void space (defects), the polymeric counterion would result in enhanced permeation selectivity (Fig. 8). 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.[20–23]

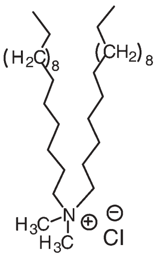
To demonstrate the feasibility of this concept, we used calix[6]arene **III** as a bilayer-forming amphiphile and poly(4-styrenesulfonate) (PSS) as the glue.[18] Compression of **III** on the surface of pure water yielded stable monolayers having a limiting area of *ca.* 2.71 ± 0.07 $nm^2$/molecule. Compression over an aqueous subphase containing 5.0 mM of repeat units of PSS (average $M_W$ ca. 70 000) generated a similar surface pressure–area curve. To confirm the existence of ionic cross-linking, we measured the surface viscosity of monolayers of **III** in the absence and in the presence of PSS in the subphase. As expected, the presence of PSS dramatically increased the surface viscosity of the monolayer.



**III**



**PSS**



**IV**

That PSS was incorporated into the LB bilayer was firmly established by a combination of X-ray photoelectron (XPS) and ellipsometric measurements. Thus, after depositing a single bilayer of **III** onto a silylated silicon wafer, subsequent analysis by ellipsometry revealed a film thickness of 5.64 ± 0.04 nm. A similar bilayer that was prepared in the absence of PSS showed a thickness of 4.80 ± 0.16 nm. In essence, therefore, 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 of ion exchange

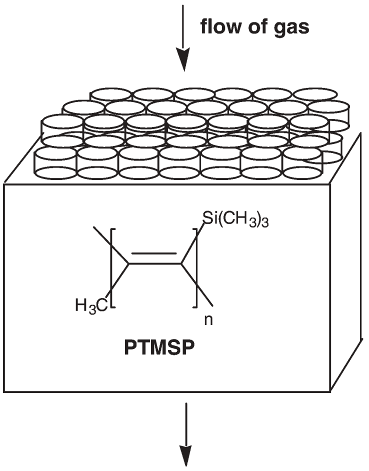


**Fig. 7** Composite membrane formed from a bilayer of **II** and poly[1-(trimethylsilyl)-1-propyne] (PTMSP).

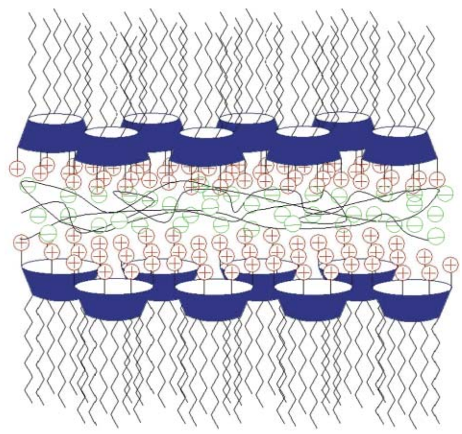


**Fig. 8** An illustration of a LB bilayer, made from a multiply charged calix[6]arene that has been glued together through the use of a polymeric counteron.

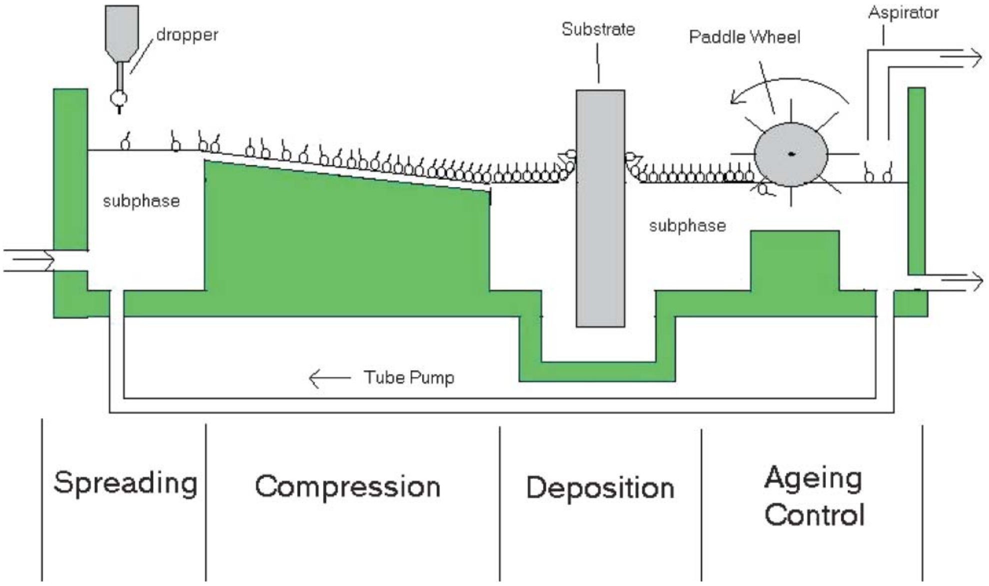


**Fig. 9** Experimental design of a continuous LB film deposition apparatus.

between PSS and the calix[6]arenes. By using various "take-off" angles, we were able to assess the atomic compositions at different depths. On the basis of a plot of nitrogen (N) and sulfur (S) content *versus* take-off angle, we were able to establish that both of these elements were buried within the LB film. In addition, the fact that the N/S atomic ratio (0.38 ± 0.09) showed little dependency over the entire range of take-off angles, implied that both of these atoms were located at similar depths. Since no chlorine could be detected by XPS, and since the atomic percentage for Na (1.23%) plus N (1.58%) was very close to the atomic percentage of S (3.16%, 90° take-off angle), we concluded that ion exchange is essentially complete, and that the glued film contains *ca.* a two-fold excess of sodium 4-styrenesulfonate groups. That gluing afforded a substantial improvement in stability of the assembly was demonstrated by exposing the film to chloroform. Thus, whereas the unglued bilayer was readily removed by rinsing with chloroform, the PSS-glued analog remained fully intact, as judged by ellipsometry.

To probe the quality of glued LB bilayers of PSS and **III**, we measured their permeation selectivity with respect to He and $N_2$, using cast films of PTMSP as support material. In contrast to unglued bilayers of **III**, which exhibited a He/$N_2$ selectivity of 1.02, the glued film showed a significant decrease in the normalized flux for He, and a very dramatic decrease in the normalized flux for $N_2$; the net result being a permeation selectivity of *ca.* 240. Such selectivity, for an organic membrane that is less than 6 nm in thickness, is without precedent. In control experiments, we found that analogous LB films that were fabricated using *N,N*-dimethyl-*N,N*-dihexadecylammonium chloride (**IV**) in place **III** showed negligible surface viscosity and negligible He/$N_2$ permeation selectivity. It should be noted that a combination of a *singly*-charged surfactant and a multiply-charged counterion (*i.e.*, **IV** + PSS) is not capable of producing a cross-linked network. Finally, in preliminary studies, we have found that the use of certain other polyanions can produce analogous bilayers with even higher permeation selectivities. For example, replacement of PSS with poly(acrylic acid) has yielded a bilayer having a He/$N_2$ permeation selectivity of *ca.* 1000. Such selectivity is remarkable for a membrane that is less than 6 nm in thickness.

## Large-scale Langmuir–Blodgett film synthesis

Most film balances that are commercially available can be used for fabricating LB films on a small-scale. None are well-suited for large-scale manufacturing, where a continuous film deposition process would be desired. Fig. 9 shows a recent design of a continuous LB deposition device that could be used for the large-scale production of LB films.[24] In essence, the trough consists of four stages: (i) a spreading area, (ii) a compression stage, (iii) a deposition stage, and (iv) an ageing control stage. After spreading on the water surface, the surfactant molecules are carried along with a circulating subphase to a compression stage, where they flow down a slope to combine with a compressed layer at the bottom. Two experimental variables that control the surface pressure of the film are the angle of the slope and the flow rate of the subphase. At the third stage, the compressed monolayer is then deposited onto the desired substrate. Finally, a fourth stage (the ageing control stage) removes unused surfactant at a constant rate from the deposition area. Thus, such a trough can self-replenish the surfactant, maintain a constant surface pressure, and remove aged film from the dipping area. The main issue that has hampered the practical development of LB films has been the properties of the films, themselves, not manufacturing. From this standpoint, glued LB films open new avenues for exploration.

## Prospectus

Single glued LB bilayers that have been prepared to date have exhibited a combination of permeation selectivity, extreme thinness and stability, which is without precedent. These properties, alone, should provide ample stimulus for new creative synthetic organic and polymer chemistry with a view towards practical LB-based devices. Given the likelihood of significant increased energy costs in the future, and the fact that membrane-based methods of gas separations are energy-efficient relative to conventional cryogenic and sorption methods, the application of glued LB films for gas separations at the industrial level may be on the horizon.[25] Although it is likely that the use of self-assembly methods, for the fabrication of monolayer and multilayer arrays, will continue to grow in the future, our success to date with glued LB bilayers should serve as as an ample reminder not to forget Langmuir–Blodgett films.

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