

Glued Langmuir–Blodgett Bilayers from Porous versus Nonporous Surfactants

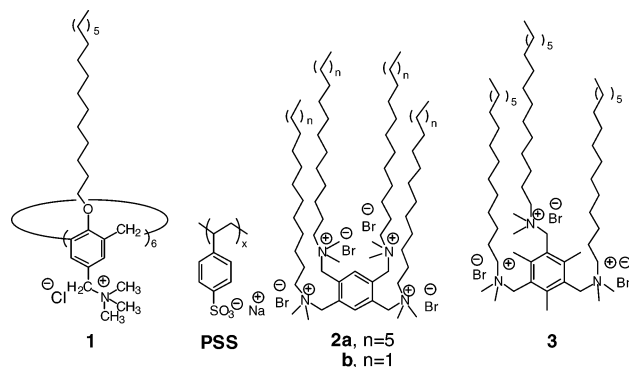
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We have recently introduced the concept of “glued” Langmuir–Blodgett (LB) film in which polyelectrolytes are used to ionically cross-link multiply charged surfactants.¹ In the first such example, we showed that single LB bilayers made from calix[6]arene **1** (a porous surfactant) plus poly(4-styrenesulfonate) [PSS] exhibit a He/N₂ permeation selectivity of ca. 200 (Chart 1). This value, which lies well above the Knudsen diffusion limit of 2.6, indicates that these assemblies are of high quality and free of defects.^{1–3} In the absence of PSS, no significant selectivity was observed. One issue that has proven extremely difficult for us to assess is whether the “molecular pore” of the calix[6]arene contributes to the film’s overall permeation selectivity. In this communication, we address a question that is of equal importance, but one that is far more tractable: Can glued LB bilayers derived from *nonporous* analogues exhibit permeation selectivities that are comparable?

Chart 1



To probe this question, we synthesized a series of aromatic surfactants, **2a**, **2b**, and **3** by quaternization reactions using commercially available starting material (Chart 1). Thus, reaction of 1,2,4,5-tetrakis(bromomethyl)benzene with excess *N,N*-dimethyl-*N*-hexadecylamine and *N,N*-dimethyl-*N*-dodecylamine afforded **2a** and **2b**, respectively. Similar reaction of 2,4,6-tris(bromomethyl)-mesitylene with *N,N*-dimethyl-*N*-hexadecylamine afforded **3**.

Surface pressure–area isotherms that were recorded for **2a**, **2b**, and **3** are presented in Figure 1. Also shown in this figure is the surface pressure–area isotherm for **1**. Within this series of compounds, **2a** exhibits the lowest compressibility. Reducing the *n*-hexadecyl chains by four methylene units, to give **2b**, resulted in greater compressibility and a lower collapse pressure. When the number of pendant *N,N*-dimethyl-*N*-*n*-hexadecylmethylene ammonium groups surrounding the central benzene moiety was reduced from four to three (i.e., **3**), a modest increase in compress-

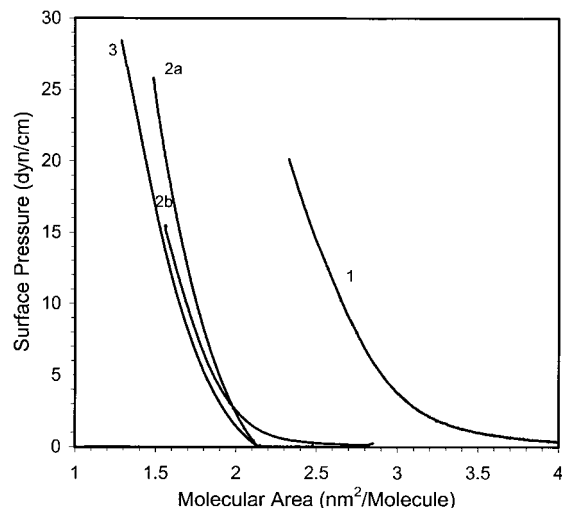


Figure 1. Surface pressure–area isotherms for **1**, **2a**, **2b**, and **3** over an aqueous subphase maintained at 25 °C.

ibility was detected. The limiting areas for **2a**, **2b**, and **3** were found to be 1.82, 1.95, and 1.80 nm²/molecule, respectively. The corresponding collapse pressures were ca. 34, 15, and 33 dyn/cm, respectively. Because monolayers of **2b** collapsed at a relatively low surface pressure, they were not used in further experiments. The fact that **2a** and **2b** have similar limiting areas, however, supports a classic “Langmuir argument” that the alkyl chains of both surfactants extend into air upon compression.

Similar to what has been found with **1**, the effect of gluing on monolayers of **2a** was readily apparent from surface viscosity measurements.^{1,4} Thus, after being compressed over an aqueous subphase that was 5 mM in PSS (*M_w* 70 000), subsequent exposure to a 6-mm slit opening of a canal viscometer resulted in a very slow decrease in surface pressure (Figure 2). In contrast, the effect of PSS on the surface viscosity of **3** could not be detected. Apparently, the degree of ionic cross-linking is a sensitive function of the number of ionic sites that are present in the surfactant.

To confirm that PSS can be incorporated into LB bilayers of **2a** and **3**, we compared thicknesses of films that were prepared in the absence and in the presence of PSS. For these experiments, silylated silicon wafers were used as substrates.⁵ Thus, using a constant surface pressure of 30 dyn/cm, the transfer ratio for the down-trip and the up-trip for both monolayers was 1.0 ± 0.1.^{4,5} Subsequent analysis by ellipsometry indicated apparent film thicknesses of 4.12 ± 0.04 nm and 6.30 ± 0.31 nm for **2a**, when pure water and 5 mM PSS were used as the subphase, respectively. With **3**, the corresponding ellipsometric film thicknesses for unglued and glued bilayers were 2.30 ± 0.2 and 5.3 ± 0.06 nm, respectively.

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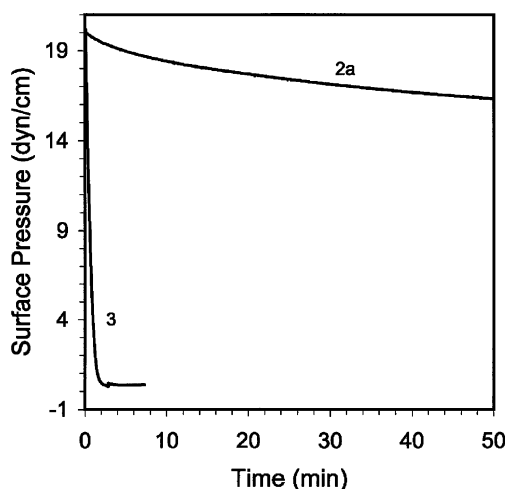


Figure 2. Surface viscosity of monolayers of **2a** and **3** over an aqueous subphase containing 5.0 mM PSS. Monolayers were maintained at 20 dyn/cm for 60 min prior to exposure to a slit opening of 6 mm, and the decrease in surface pressure was then recorded as a function of time. The area occupied by each monolayer at the start of the measurement was ca. 300 cm²; the subphase temperature was 25 °C. In the absence of PSS, **2a** and **3** showed profiles that were similar to that of **3** over a PSS subphase (not shown).

Table 1. Permeation Across LB Bilayer/PTMSP Composite Membranes^a

bilayer	10 ⁶ P/l (cm ³ /cm ² -s-cm Hg)		α _{He/N₂} (P/l) _{He} /(P/l) _{N₂}
	He	N ₂	
—	481	521	0.9
2a	445	326	1.4
	422	264	1.6
2a/PSS	260	2.9	90
	230	1.7	140
3	548	564	1.0
	507	560	0.9
3/PSS	210	2.6	81
	220	2.6	85
1	513	504	1.0
	460	400	1.2
1/PSS	200	1.2	170
	210	1.0	210

^a Normalized fluxes were calculated by dividing the observed flux by the area of the membrane and the pressure gradient used (10 psig). Here, *P* is the permeability coefficient that characterizes the membrane/permeant combination, and *l* is the thickness of the composite membrane. Transfers were made using a surface pressure of 30 dyn/cm (25 °C). In all cases, 15 μm PTMSP films were used as support material.

Single glued LB bilayers of **2a** and **3** were then deposited onto poly[1-(trimethylsilyl)-1-propyne] (PTMSP) supports and their barrier properties measured with respect to He and N₂.⁴ As shown in Table 1, glued bilayers of **2a** and **3** had He/N₂ permeation selectivities approaching that which was found for glued bilayers of **1**.

Given the absence of pores in **2a** and **3**, the pathway for diffusion across these glued bilayers must lie *between neighboring surfactants*. Thus, the permeation selectivity that is observed is a likely consequence of a solution–diffusion mechanism, whereby He and N₂ diffuse through transient gaps that develop as the result of thermal motion.⁶ Because He is much smaller than N₂ (the kinetic

diameters for He and N₂ are 0.260 and 0.364 Å nm, respectively), it can diffuse through such gaps at a faster rate.⁷ How much of a contribution the PSS makes to the overall barrier properties of these membranes, however, remains to be established.

The present findings are significant because they show that porous surfactants are not essential for creating permeation-selective glued bilayers. In a broader context, these results add “new life” to an old technology, which has suffered from problems relating to film quality for almost 70 years.^{2,3,8} Specifically, they show how gluing allows one to use unexceptional, multiply charged surfactants (e.g., **2a** and **3**) to construct ultrathin, permeation-selective barriers. Although self-assembly methods have evolved as a modern alternative to the LB technique, to our knowledge, they have not been successfully applied to the preparation of gas permeation-selective barriers down to 6-nm thicknesses.⁹ Thus, glued LB technology provides a means for preparing novel materials that are not accessible by any other means. Efforts aimed at exploring the full scope of glued LB bilayers, with a view toward the fabrication of new materials and devices, are currently in progress.

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Supporting Information Available: Synthesis of **2a**, **2b**, and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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