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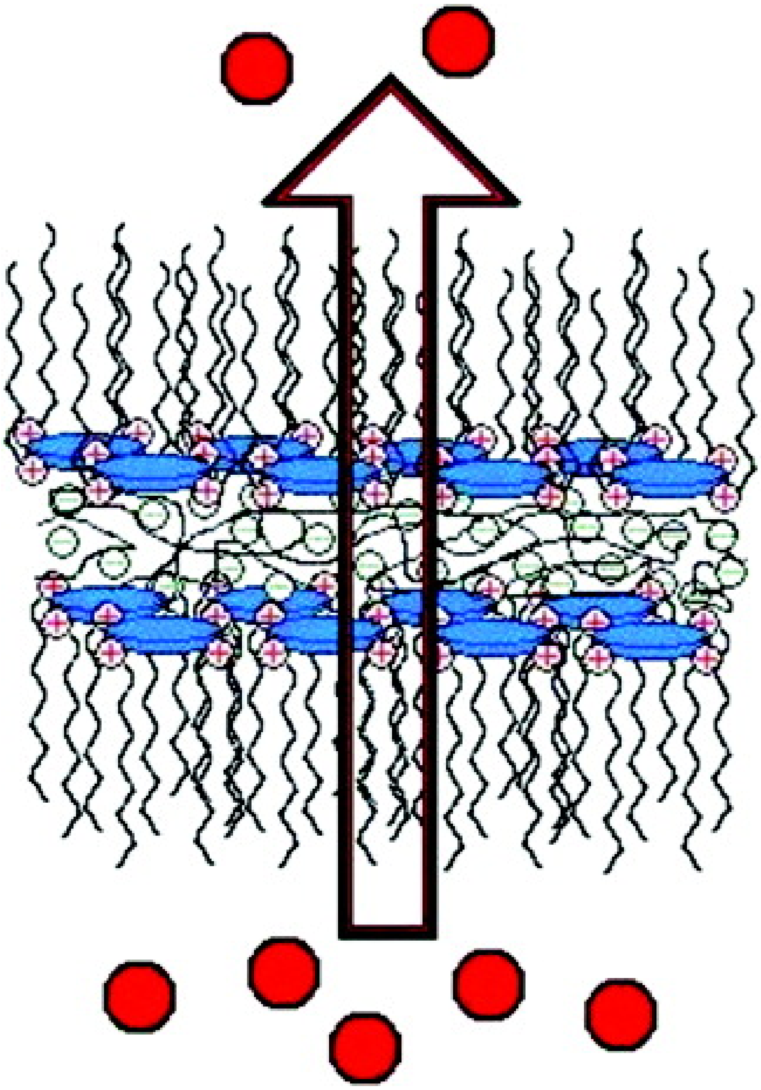

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Insight into the Permeation Barrier of Glued Langmuir−Blodgett Bilayers

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Abstract: Permeation measurements have been made for He, CO_2, and N_2 across single Langmuir−Blodgett (LB) bilayers derived from 1,2,4,5-tetrakis[(*N*-(undecanoamidoethyl)-*N*,*N*-dimethyl ammonium) methyl]benzene tetrabromide (**2**) and 1,2,4,5-tetrakis[(*N*-(perfluoroundecanoamidoethyl)-*N*,*N*-dimethyl ammonium)methyl]benzene tetrabromide (**3**) in the absence and in the presence of entrapped poly(acrylic acid) (PAA). In the absence of PAA, single LB bilayers of **3** show a higher permeance for He and N_2 but a lower permeation rate of CO_2, as compared with analogous LB bilayers made from **2**. The relatively low permeation rate of CO_2 for the former has been attributed to reduced associative interactions with the fluorocarbon-rich bilayer. The same behavior has also been observed for LB bilayers containing PAA, formed under conditions that yield glued bilayers of **2** and **3** having similar diffusional pathways, as judged by He/N_2 selectivities. These results, together with the fact that glued bilayers of **2** (having a *thinner* PAA layer as compared with those made from **3**) exhibit *lower* He and N_2 permeances, provide compelling evidence that the main barrier for gas transport is the combination of surfactant plus PAA and not simply a thin PAA layer that is encased within the surfactant bilayer.

Introduction

Langmuir−Blodgett (LB) films have been the subject of considerable interest for more than 70 years.[1−5] Despite this interest, problems associated with film quality have limited their practical development. One classic example can be traced to pioneering studies by Katherine Blodgett, herself, where she first suggested that LB films could find use as filters for molecular separations.[6] Since that time, many attempts have been made to reduce this concept to practice in the area of gas separations. Unfortunately, in nearly all studies reported to date, LB films have been found to exhibit gas permeation selectivities that follow Graham's law. Such a finding, in and of itself, indicates that diffusion is occurring through defects in the membrane.[7−17]

In an effort to improve the cohesiveness of surfactant monolayers, and to eliminate defects in LB films, we have introduced the concept of "gluing".[18] In essence, a glued monolayer is one that is made from a *multiply charged* surfactant that has been ionically cross-linked using a water-soluble, polymeric counterion. For example, we have shown that monolayers derived from calix[6]arene **1** can be ionically cross-linked with poly(4-styrenesulfonate) (PSS) and that such cross-linking is reflected by a substantial increase in their surface viscosity at the air/water interface (Chart 1).[18a] We have also shown that single LB bilayers of **1** exhibit He/N_2 gas permeation selectivities that lie well above the Graham's law value of 2.6. For example, using PSS as the cross-linking agent, a He/N_2 selectivity of ca. 200 was observed;[18a] when poly(acrylic acid) (PAA) was used for cross-linking, this selectivity increased to ca. 1000.[18c]

[†] Department of Chemical Engineering.

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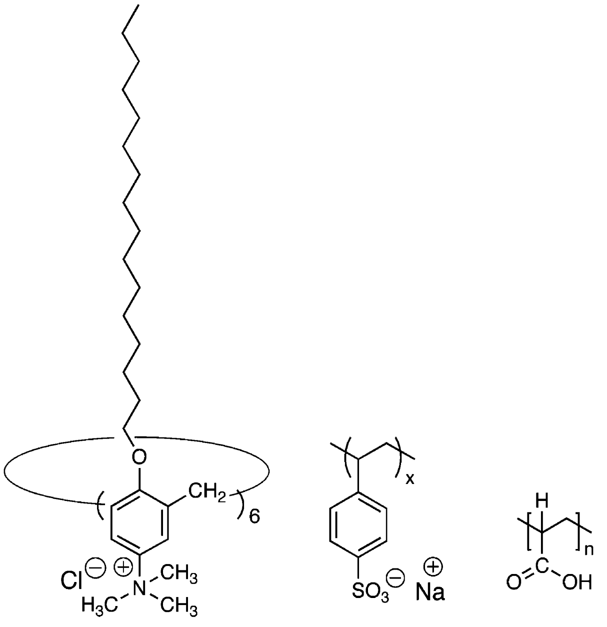
Chart 1



1 **PSS** **PAA**

In the work that is reported herein, our primary aim was to gain a deeper understanding of the permeation barrier of a typical glued LB bilayer. Specifically, we sought to clarify whether it is the *combination of the surfactants plus polymer* that serves as the main barrier for gas transport or whether the main barrier is simply a thin layer of pure polymer that is encased by the lipids. This fundamental question is of particular importance since it bears, directly, on the rational design of new classes of glued LB films, that is, whether the structure and composition of the lipids play an important role in the barrier properties of such membranes. This question also has relevance for the potential use of glued LB films as ultrathin sensors, transducers, and protective coatings.

Results

Experimental Design. The experimental approach that we have used in this work has been to compare the permeances of He, N_2, and CO_2 across glued LB bilayers made from a hydrocarbon surfactant with ones made from a fluorocarbon-rich analog. Although the permeation of gases across single surfactant monolayers has previously been described by an activation energy barrier model (i.e., a single-step permeation process), in the case of glued bilayers, where a polymeric layer is present as a major component, the classic solution−diffusion model can be considered.[19,20] According to this model, the permeability (P) of a gaseous permeant crossing a membrane is the product of diffusivity (D) and solubility (S); that is, $P = DS$. Since the solubility of CO_2 in organic membranes is known to have a greater influence on its overall permeation, as compared with He and N_2, the possibility exists that one may be able to use this difference as a diagnostic tool for determining whether the lipid portion of the assembly contributes to the main barrier for transport.[19]

Consider two hypothetical glued LB bilayers, one made from a hydrocarbon surfactant and the second from a fluorocarbon-rich analog. On the basis of diffusivity alone, permeation rates across both membranes are expected to decrease as the size of a gaseous permeant increases. Thus, for He, CO_2, and N_2, which have kinetic diameters of 0.260, 0.330, and 0.363 nm, respectively, the relative permeances should be He > CO_2 > N_2.[21] In principle, if permeation across the surfactant portion of the membrane contributes to the rate-limiting step, then the substitution of hydrogen with fluorine atoms could affect the permeance of CO_2 to a greater extent than for He and N_2, due to differences in solubility. Since previous studies indicate that CO_2 has a stronger association with hydrocarbons than with fluorocarbons, one might expect that fluorination could lower the permeation of CO_2 to a greater extent than that of He and N_2, based on solubility considerations.[22]

Synthesis of a Cross-Linkable Surfactant and a Fluorocarbon-Rich Analog. To explore this experimental approach, two cross-linkable surfactants that were chosen for study, that is, **2** and **3** (Chart 2). The tetracationic surfactant **2** bears a close resemblance to one that we previously used in preparing nonporous glued LB bilayers.[18d] In Scheme 1, we outline a two-step synthesis that was used to prepare **3**. Thus, direct condensation of methyl perfluoroundecanoate with *N*,*N*-dimethylethylenediamine, followed by quaternization with 1,2,4,5-tetrakis(bromomethyl)benzene afforded **3**. To our knowledge, **3** is the first example of a surfactant molecule bearing multiple fluorinated chains and multiple charges. Surfactant **2** was prepared in a similar way. In this work, PAA was chosen as a cross-linking agent, because of its ability to form glued LB bilayers from **1** having high gas permeation selectivities.[18c]

Monolayer Properties. Surface pressure−area isotherms that were recorded for **2** over a pure water subphase, and over a subphase containing PAA at different pH values, are shown in Figure 1. Similar to what we have observed for **1**, the presence of PAA shifts the isotherms "to the right", especially as the pH of the subphase is lowered.[18c] In Figure 2, we show related isotherms that were obtained for **3** under similar conditions. Qualitatively, the results were similar to those found with **2**, except that the molecular areas occupied by **3** were less than those of **2** and the collapse pressures were higher. In the absence of surfactant, no significant surface pressure was detected as the compressing barrier was swept across the surface of an aqueous subphase containing PAA at pH 4.2.

To test for enhanced cohesiveness due to gluing, the relative surface viscosities on monolayers made from **2** and **3** were measured using a canal viscometer. As shown in Figures 3 and 4, surface viscosities were found to increase as the pH of the subphase was lowered.

Barrier Properties of Glued and Unglued Langmuir−Blodgett Bilayers Derived From 2 and 3. With the use of experimental procedures similar to those previously described, *single* glued LB bilayers of **2** and **3** were deposited onto poly-

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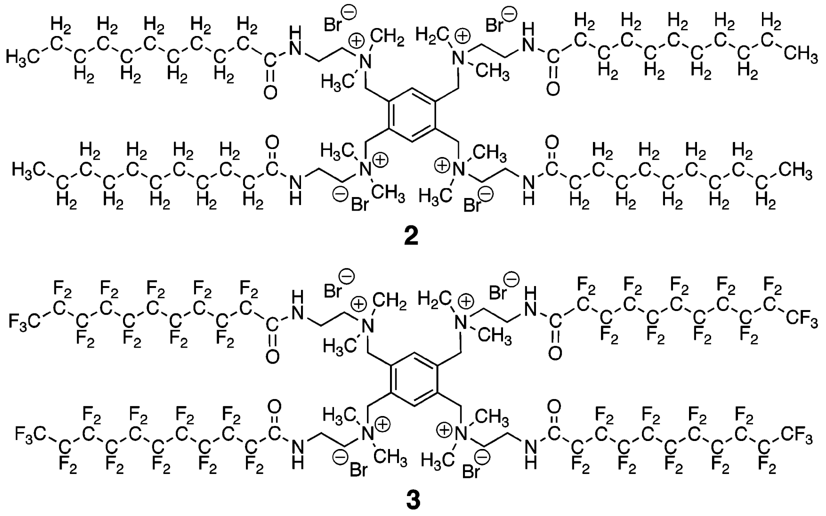
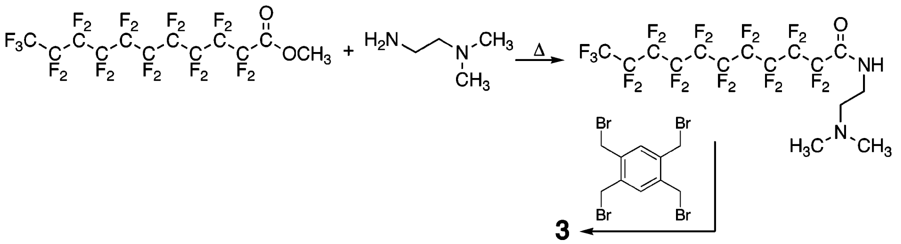
Chart 2



Scheme 1



[1-(trimethylsilyl)-1-propyne] (PTMSP) by one vertical down-trip into, and one vertical up-trip out of, a PAA subphase at pH 4.2.[18c] For **2**, two different surface pressures were used for LB transfer; one was slightly below the collapse pressure of 32 dyn/cm (i.e., 25 dyn/cm), and the second was considerably lower in pressure (i.e., 17 dyn/cm). Similarly, two different surface pressures (30 and 45 dyn/cm) were used in the fabrication of glued bilayers derived from **3**; both were below the collapse pressure of 50 dyn/cm. In all cases, the transfer ratios were 1.0 ± 0.1. Glued bilayers were prepared in triplicate, and their pemeabilities were measured with respect to He, CO_2, and N_2 at ambient temperature. Table 1 summarizes the principal results obtained. All values that are listed in the table refer to permeances (i.e., normalized flux), which were calculated by dividing the observed flux by the area of the membrane and the pressure gradient employed.

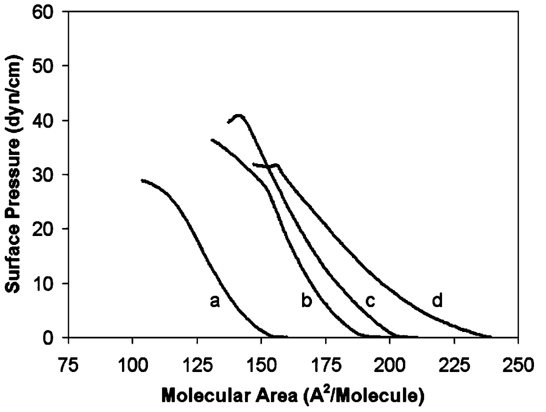


Figure 1. Surface pressure−area isotherms for **2** over (a) water and over subphases containing PAA (5 mM repeat units, M_w 240 000) that were adjusted to pH (b) 10.2, (c) 7.0, and (d) 4.2 at 25 °C.

In the absence of surfactant and PAA, bare PTMSP exhibited a high flux for all of the gases, little He/N_2 selectivity, and a modest preference for the permeation by CO_2; that is, the He/N_2 and He/CO_2 selectivities were 0.9 and 0.3, respectively. Deposition of a single *unglued* LB bilayer of **2** (25 dyn/cm) resulted in a modest reduction in the permeance of each gas, with similar permeation selectivities. When a single unglued bilayer of **3** (30 dyn/cm) was deposited onto PTMSP, a lower permeance for CO_2 and higher permeances for He and N_2 were observed relative to bilayers of **2**. Increasing the surface pressure of **3** to 45 dyn/cm resulted only in a modest reduction (ca. 10%) of the flux of each gas, with no significant change in He/N_2 and He/CO_2 selectivities.

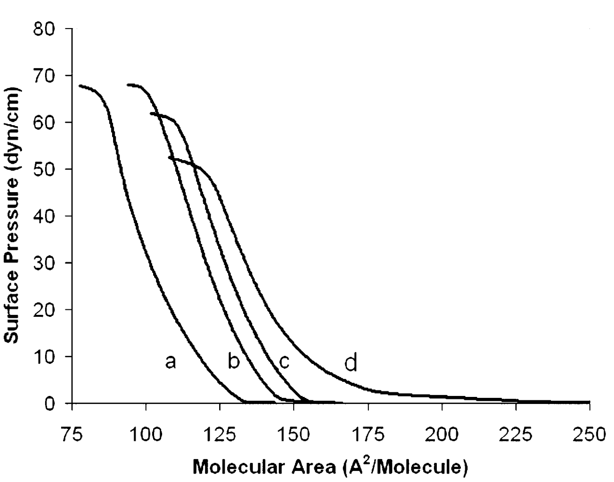


Figure 2. Surface pressure−area isotherms for **3** over (a) water and over subphases containing PAA (5 mM repeat units, M_w 240 000) that were adjusted to pH (b) 10.2, (c) 7.0, and (d) 4.2 at 25 °C.

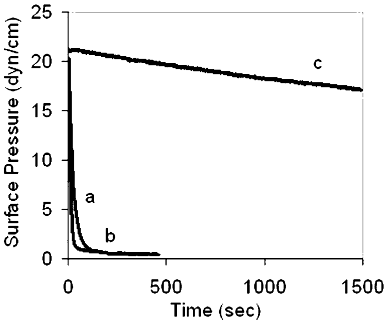


Figure 3. Relative surface viscosities of monolayers of **2** over (a) water and over subphases containing PAA (5 mM repeat units, M_w 240 000) that were adjusted to pH (b) 10.2 and (c) 4.2. An initial surface pressure of 20 dyn/cm was maintained for 60 min prior to exposure of the monolayer to the slit opening of 6 mm.

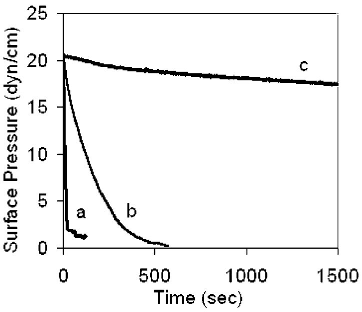


Figure 4. Relative surface viscosities of monolayers of **3** over (a) water and over subphases containing PAA (5 mM repeat units, M_w 240 000) that were adjusted to pH (b) 10.2 and (c) 4.2. An initial surface pressure of 20 dyn/cm was maintained for 60 min prior to exposure of the monolayer to the slit opening of 6 mm.

Table 1. Permeances of Gases Across Langmuir−Blodgett Bilayers[a]

LB bilayer	surface pressure (dyn/cm)	10^6 *P*/*l* (cm^3/cm^2·s·cm Hg) He	N_2	CO_2	$\alpha_{He/N2}$	$\alpha_{He/CO2}$
		481	521	1400	0.9	0.3
2	25	256	265	1100	1.0	0.2
		245	246	1210	1.0	0.2
3	30	324	339	878	1.0	0.4
		420	438	1050	1.0	0.4
	45	375	391	975	1.0	0.4
2/PAA	17	72	0.5	13	144	5.7
		75	0.5	12.7	151	5.9
		79	0.6	14.6	141	5.4
	25	65	0.4	10	170	6.7
		69	0.4	10.1	168	6.8
		65	0.4	9.2	177	7.1
3/PAA	30	56	1.4	14	40	4.2
		63	1.3	16.1	49	3.9
		61	1.5	15	42	4.1
	45	74	0.8	4.2	93	17.6
		67	0.6	4.0	107	16.6
		80	0.8	4.9	97	16.4

[a] Permeance values at ambient temperature, (*P*/*l*), were calculated by dividing the observed flow rate by the area of the membrane (9.36 cm^2) and by the pressure gradient (10 psi) employed, using ca. 30 μm thick PTMSP.

All of the glued bilayers that were examined showed a substantial reduction in gas permeation and He/N_2 permeation selectivities that were well in excess of the Graham's law value of 2.6; the He/CO_2 permeations selectivities were also in excess of the Graham's law value of 3.3. For glued bilayers that were prepared from **2**, an increase in the surface pressure from 17 to 25 dyn/cm resulted in a modest increase in He/N_2 and He/CO_2 permeation selectivities. For ones that were derived from **3**, a more dramatic increase in the He/N_2 and He/CO_2 permeation selectivities was observed on going from 30 to 45 dyn/cm for LB deposition. In addition, for all glued bilayers, the He permeation was greater than that found for CO_2, which was opposite to that observed for the unglued bilayers. Comparison of glued bilayers of **3** (fabricated at 45 dyn/cm) with analogs made from **2** (fabricated at 25 dyn/cm) showed He permeances that were slightly higher with the former. The permeance that was observed for N_2 across the glued bilayer of **3** was ca. 2 times greater than that of **2**, but the CO_2 permeance was ca. 2 times *lower*.

To judge relative thicknesses of the PAA layers in glued LB bilayers of **2** (25 dyn/cm) and **3** (45 dyn/cm), we deposited corresponding bilayers onto silicon wafers that were silylated with *n*-octadecyltrichlorosilane and measured their film thicknesses by ellipsometry. In the absence of PAA, a single LB bilayer of **2** showed an apparent film thickness of 2.6 ± 0.1 nm. When PAA was included, the total thickness was 5.3 ± 0.1 nm, corresponding to a PAA thickness of 2.7 nm. For **3**, the film thicknesses that were found in the absence and in the presence of PAA were 1.9 ± 0.1 and 7.9 ± 0.3 nm, corresponding to a PAA thickness of 6 nm.

Discussion

Effects of Gluing on Monolayer Properties. Monolayers that were formed from **2** and **3** showed, qualitatively, similar behavior over an aqueous subphase containing PAA. Thus, as the pH was lowered, both monolayers showed an increase in the area occupied per surfactant molecule and a significant increase in surface viscosity. This behavior is exactly analogous to what we have previously observed for the action of PAA on monolayers of **1**.[18c] As discussed elsewhere, such pH control over gluing appears to be the result of changes in (i) the degree of ionization, (ii) the hydrophobic−hydrophilic balance, and (iii) the conformation of the polymer. Specifically, as the pH is lowered, the polyacid becomes less ionized, more hydrophobic, and coiled. Under these conditions, associative interactions with the surfactant monolayer appear to involve a combination of ionic and hydrophobic interactions.

In the absence of PAA, the larger area that is occupied by **2** can be accounted for in terms of a greater degree of hydration of the first few carbons of the aliphatic chain relative **3**. On the basis of previous experimental and theoretical studies, indicating that water has a greater ability to hydrate $-CH_2-$ groups relative to $-CF_2-$ groups, one may expect that water molecules are more likely to intercalate between the acyl chains of **2**, as compared with those of **3**, resulting in a larger head group area for **2**.[22] In the absence of intercalated water, the chains of **3** should then stack more cleanly, resulting in a higher collapse pressure.

Influence of Surfactant Density, Surface Pressure, and Polymer Thickness on the Barrier Properties of Glued Bilayers of 2 and 3: Evidence for a Lipid/PAA Permeation Barrier. Permeation measurements that were made for He, CO_2, and N_2 across bare PTMSP showed a distinct preference for CO_2 permeation. Because CO_2 is larger in size than He, this can only be accounted for in terms of enhanced solubility of the former in the membrane. The modest reduction in the permeances observed for all three gases upon deposition of unglued LB bilayers of **2** and **3** indicates that these bilayers make a contribution to the barrier properties of PTMSP but that permeation is dominated by the support and by defects within the LB film. Nonetheless, the fact that unglued bilayers of **3** on PTMSP show *higher* permeances for He and N_2 and a *lower* permeance for CO_2, as compared with bilayers of **2**, supports the hypothesis that CO_2 has a stronger association with this hydrocarbon-based surfactant than the fluorocarbon analog. This difference in selectivity also serves as a “fingerprint” for these surfactants. Thus, if the surfactant portion of glued bilayers of **2** and **3** contributed, significantly, to their overall barrier properties, one would expect to observe similar differences in selectivity; that is, the fluorocarbon-rich membrane should exhibit a low CO_2 permeance relative to the hydrocarbon-rich analog.

For all of the glued LB bilayers that were investigated, the relative permeances were He > CO_2 > N_2. This indicates that diffusivity plays a dominant role in their permeation, since the larger gases cross these membranes more slowly. The reversal of the He and CO_2 permeances, upon gluing, further indicates that the barrier contributions from the PTMSP support is negligible. In addition, the fact that the He/N_2 selectivities are well in excess of the Graham’s law value of 2.6 demonstrates that the main pathway for diffusion of these gases is not through defects, but through an intact membrane.

Glued bilayers of **2** and **3** that were fabricated using similar surface pressures (i.e., 25 dyn/cm and 30 dyn/cm, respectively) showed a similar permeance for He but higher permeances of N_2 and CO_2 in the case of **3**. Thus, glued bilayers of **3** exhibited lower He/N_2 and He/CO_2 permeation selectivities. On the basis of the surface pressure−area isotherms that were recorded for **2** and **3** over PAA, under the same conditions that were used for these LB depositions, the density of the fluorocarbon chains is greater than that of the hydrocarbon chains in these assemblies. We tentatively attribute the lower He/N_2 and He/CO_2 selectivities associated with glued bilayers of **3** to weaker van der Waals forces between the fluorocarbon chains of neighboring surfactants, which results in a looser pathway through which the gases travel. A looser pathway across unglued bilayers of **3** relative to those of **2** can also account for the higher He and N_2 permeances found with the former. It should be noted, however, that the fact that both the alkyl and fluoroalkyl chains have the potential for folding into the void space that is created above the aromatic framework makes an assessment of the relative intermolecular van der Waals forces more complex.

When a higher surface pressure is used to fabricate glued bilayers of **3** (i.e., 45 dyn/cm), the permeance for N_2 now becomes closer (as does the He/N_2 selectivity) to that found for glued bilayers of **2** fabricated at 25 dyn/cm, indicating that the diffusional pathway is closer in character. This allows for a clearer assessment to be made of differences in permeation that are due to differences in solubility contributions. The fact that these glued bilayers of **3** exhibit a lower He/N_2 selectivity, and a higher He/CO_2 selectivity, relative to glued bilayers of **2**, is fully consistent with the results obtained with unglued bilayers; that is, both systems have the same “fingerprint”.[23] This fact implies that the lipids contribute in a significant way to the main barrier for gas transport and that *the main barrier is not simply the thin layer of PAA that is encased in the lipid bilayer*. At the same time, these results lend support for our use of the solution−diffusion model in describing gas permeation across glued LB films. The fact that glued bilayers of **2** (25 dyn/cm), containing a *thinner* PAA layer, exhibit *lower* He and N_2 permeances relative to glued bilayers of **3** (45 dyn/cm) provides further confirmation that pure PAA is not the main barrier for gas transport.[24]

One last issue that deserves comment is the structure of these surfactant/PAA bilayers. Specifically, does the PAA layer simply function as an ionic cross-linker, or does it also penetrate into the monolayers filling in defects like “caulking” material. On the basis of the significant “shift to the right” that has been observed for the surface pressure−area isotherms in the presence of PAA for both **2** and **3**, it would appear that there is significant polymer penetration into these monolayers. We cannot judge from such experiments, however, the depth at which these polymer penetrate each monolayer. Nonetheless, these results suggest that caulking may be an important factor in removing defects within glued LB bilayers. Finally, the greater sensitivity of the permeation selectivity of glued bilayers of **3** toward surface pressure, relative to unglued analogs, is a likely consequence of the lower fluorocarbon density and the presence of polymer that has penetrated the surfactant assembly. How much of this greater sensitivity is due to changes in (i) the surfactant density, (ii) the extent of polymer penetration, and (iii) depth of polymer penetration upon compression, however, remains to be determined.

Conclusions

Permeation measurements that have been made for He, CO_2, and N_2 across LB bilayers derived from **2** and **3**, in the absence and in the presence of a polymeric cross-linking agent (PAA), in combination with film thickness measurements have provided strong evidence that it is *the surfactants plus polymer* that serves as the main barrier for gas transport and not simply a thin layer of pure polymer that is encased within the lipid bilayer. These findings are significant because they raise the possibility of designing new classes of glued LB films that can discriminate among permeants on the basis of their size, shape, hydrophobicity, and polarity by molecular design.

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Supporting Information Available: Methods used to synthesize **2** and **3**, to measure surface pressure−area isotherms, surface viscosity, and film thicknesses, and to prepare silylated silicon wafers and glued Langmuiur−Blodgett bilayers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Due to the lower collapse pressure of **2** over PAA, we were not able to fabricate glued bilayers from this lipid at 45 dyn/cm.

(24) The reason why a thicker layer of PAA is taken up by glued bilayers of **3** is not presently clear. We believe, however, that it is related to the higher surfactant density of **3** and the corresponding higher charge density within the monolayer; that is, it is a consequence electrostatic interactions between PAA and the surfactants.