Exceptional Gas Permeation Selectivity of a Glued Langmuir−Blodgett Bilayer by pH Control

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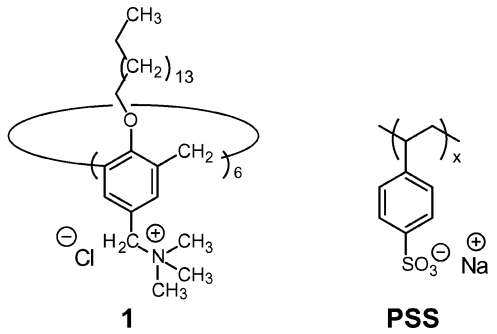
The monolayer properties of 5,11,17,23,29,35-hexakis[(*N*,*N*,*N*-trimethylamonium)-*N*-methyl-37,38,39,-40,41,42-hexakis-*n*-hexadecyloxy-calix[6]arene hexachloride (**1**) have been characterized over aqueous solutions of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) as a function of pH. At high pH values (e.g., pH 10), such monolayers show relatively low surface viscosities. At low pH (e.g., pH 4.4), these monolayers exhibit relatively high surface viscosities. The barrier properties of single Langmuir−Blodgett bilayers of **1**, which have been ionically cross-linked (i.e., "glued together") with PAA were found to correlate with changes in surface viscosity. Thus, bilayers that were fabricated under low pH conditions exhibited high permeation barriers and high permeation selectivity with respect to He and N_2. Given the extreme thinness of these glued bilayers (ca. 6 nm), the optimized He/N_2 selectivity of ca. 1000 is extraordinary. These results, taken together, demonstrate the feasibility of fine tuning the surface viscosity of monolayers of **1**, and also the barrier properties of corresponding glued bilayers, by adjusting the pH of an aqueous subphase that contains a weak polyacid.

Introduction

We have previously introduced a new class of Langmuir−Blodgett (LB) film in which water-soluble polyelectrolytes are used to ionically cross-link *multiply*-charged surfactants.[1] The fact that these "glued" bilayers can be prepared free of defects has allowed us to fabricate extremely thin membranes (ca. 6 nm in thickness) having gas permeation selectivities that lie well above the Knudsen diffusion limit.[2] For example, a *single* bilayer of calix[6]arene **1**, which was ionically cross-linked with poly-(4-styrenesulfonate) (PSS), exhibited a He/N_2 permeation selectivity of ca. 200 (Chart 1). In contrast, unglued analogues showed negligible He/N_2 selectivity, reflecting the presence of defects. We have also found that gluing efficiency has a strong dependency on the concentration of PSS that is present in the subphase.[3] Thus, whereas moderate concentrations (i.e., 5 mM in repeat unit) afford moderately viscous monolayers and high-quality LB film, the use of much lower concentrations (e.g., 0.1 mM in repeat unit) lead to highly viscous monolayers that are difficult to transfer in a defect-free form.

Recently, it occurred to us that the use of weak polyacids as cross-linking agents could lead to bilayers having even higher permeation selectivities. Specifically, we reasoned that by adjusting the pH of a subphase containing a weak polyacid, one should be able to modulate the overall hydrophobic−hydrophilic balance of the polymer, its interactions with multiply charged surfactants (i.e., gluing efficiency), LB transferability, and permeation selectivity. Thus, at lower pH values, one might expect that increased hydrophobicity of the polymer would enhance ionic association with the surfactant assembly through hydrophobic forces. The primary aim of the work that is reported herein was to demonstrate the feasibility of using pH to control gluing efficiency and film quality and also to gain fundamental insight into the interactions between weak polyacids and assemblies of multiply charged surfactants.

Chart 1



Experimental Section

Methods and Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. House-deionized water was purified using a Millipore Milli-Q-filtering system containing one carbon and two ion-exchange stages. The pH of a given subphase was adjusted by addition of either aqueous NaOH or HCl solutions. Chloroform/methanol (9/1,v/v) that was used as a spreading solvent was prepared from HPLC grade Burdick and Jackson solvents. Methods that were used to prepare 5,-11,17,23,29,35-hexakis[(*N*,*N*,*N*-trimethylamonium)-*N*-methyl-37,38,39,40,41,42-hexakis-*n*-hexamedecyloxy-calix[6]arene hexachloride (**1**) were similar to those previously described.[1] Experimental methods that were used to measure gas permeability

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and to fabricate LB films have been reported elsewhere.[4] All polymers that were investigated in this study were used as obtained: poly(acrylic acid), M_w 240 000, Aldrich Chem.; poly(acrylic acid), M_w 50 000, Polysciences Inc; poly(methyl acrylic acid), M_w 100 000, Polysciences, Inc.; poly(methyl acrylate), M_w 40 000, Aldrich Chem. Poly[1-(trimethylsilyl)-1-propyne, which was used as support material, was a gift from Air Products and Chemicals. With the exception of surface tension measurements that were made for 0.1 mM solutions of PAA and PMAA, all other monolayer measurements and LB film fabrications were made using a Lauda film balance.

Surface Pressure−Area Isotherms. Surface pressure−area isotherms were recorded using a MGW Lauda film balance, which was equipped with a computerized data acquisition station. All isotherms were measured at 25 °C. Water (ca. 1 L), which was used as a subphase, was purified via a Milli-Q filtration system and purged with nitrogen for 15 min. Before addition to the film balance, the surface of this degassed water was removed via aspiration in order to remove surface-active contaminants. All surfactant solutions were spread onto the aqueous subphase having a surface area of 600 cm^2, using a gastight, 50 μL Hamilton syringe. Surfactant solutions that were used were typically 1.0 mg/mL. Exact concentrations were determined by direct weighing of aliquots after evaporation of solvent using a Cahn 27 electrobalance. In all cases, spreading solvents were allowed to evaporate for at least 30 min prior to compression under a flow of nitrogen.

Surface Viscosity Measurements. For surface viscosity experiments, a home-built canal viscometer (192 mm × 40 mm solid Teflon block, having a centrally located 6.0 mm slit) was placed in front of the compressing barrier and the monolayer was compressed at a rate of 25 cm^2/min. When the surface pressure began to rise, the compression speed was decreased to 13 cm^2/min to allow for more precise control over the surface pressure. Compressions were stopped when a target pressure of 20 dyn/cm was reached. The resulting monolayer was then allowed to equilibrate at this pressure for 3 h. After this period of time, the moving barrier was expanded at the maximum speed of 120 cm^2/min, leaving the canal viscometer at its original position. The resulting surface pressure was then recorded as a function of time. The rate of surface pressure decrease was taken as a measure of the surface viscosity of the monolayer.

Results

Selection of Polymers. In this investigation, we chose poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) as weak polyacids to interact with monolayers and bilayers of **1**. Our reason for selecting these polymers was 3-fold. First, PAA and PMAA have pK_a values of 5.2 and 5.6, respectively.[5] Thus, their degree of ionization can be readily adjusted over a convenient pH range. Second, the conformational behavior of these polymers has already been defined as a function of pH. Specifically, at pH values less than 6.0, PAA and PMAA favor a hypercoiled conformation.[6−23] When the pH is increased beyond 6.0, deprotonation of the carboxylate groups starts to uncoil the polymers. At pH 8, they assume a "stretched out" conformation due to electrostatic repulsion between neighboring anionic groups. Third, PMAA is more hydrophobic than PAA due to the presence of a methyl substituent within each repeat unit. Thus, a comparison of the two polymers should provide insight into the contributions that hydrophobic forces make to gluing efficiency. Finally, we chose to examine the interactions of a nonionizable analogue (i.e., poly(methyl acrylate), PMA) with **1** since associative interactions can only occur in this case through hydrophobic forces.

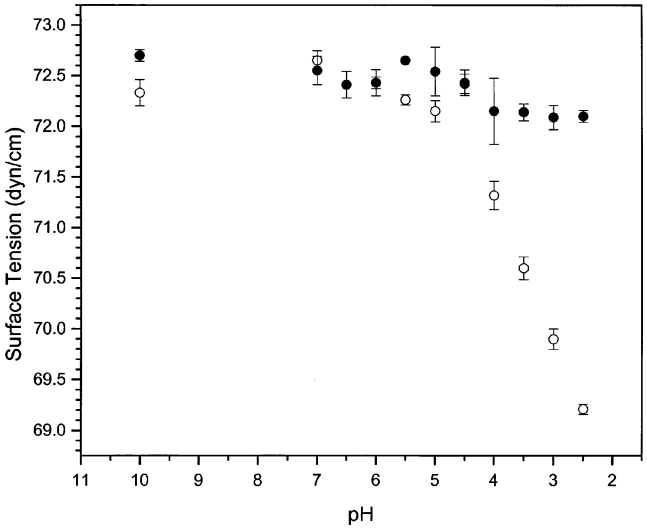
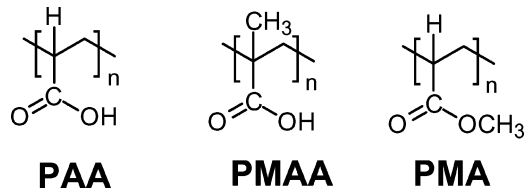


Figure 1. Surface tension over aqeous solutions of (○) PAA (M_w = 240 000) and PMAA (●) (M_w = 100 000) at 22 °C, using 0.1 mM repeat unit concentrations.

Chart 2



Surface Activity of the Polyacids. Before examing the effects of PAA and PMAA on the monolayer properties of **1**, we first examined the surface activity of both polyelectroyltes as a function of pH. Figure 1 summarizes the results that we obtained using 0.1 mM solutions of PAA and PMAA. Here, surface activities were determined by tension measurements. In contrast to PMAA, which showed only a slight lowering of the surface tension of water (ca. 1 dyn/cm) on going from a pH of 10.0 to 2.5, PAA showed significanlty greater surface activity (ca. 3 dyn/cm) below a pH 4.0.

Effects of Polymers on The Surface Pressure−Area Isotherm Behavior of 1. Surface pressure−area

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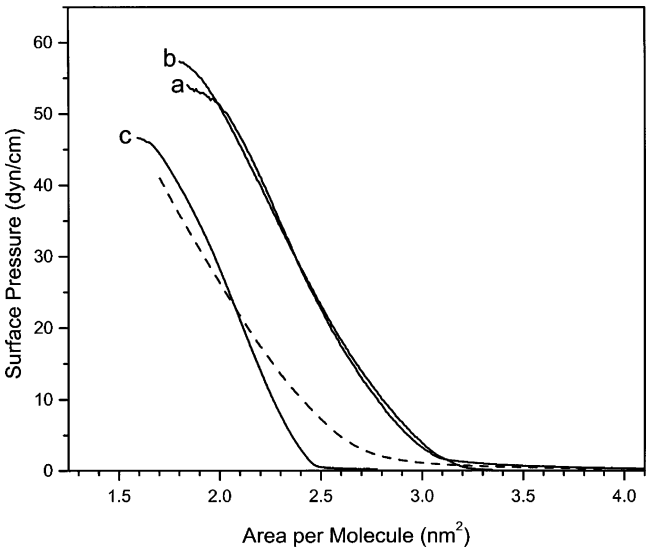

Figure 2. Surface pressure–area isotherms for **1** over a PAA subphase (0.1 mM repeat units, M_w 240 000) adjusted to a pH of (a) 4.4, (b) 5.2, and (c) 10.0 at 25 °C. Dash plot is the isotherm of **1** over pure water.

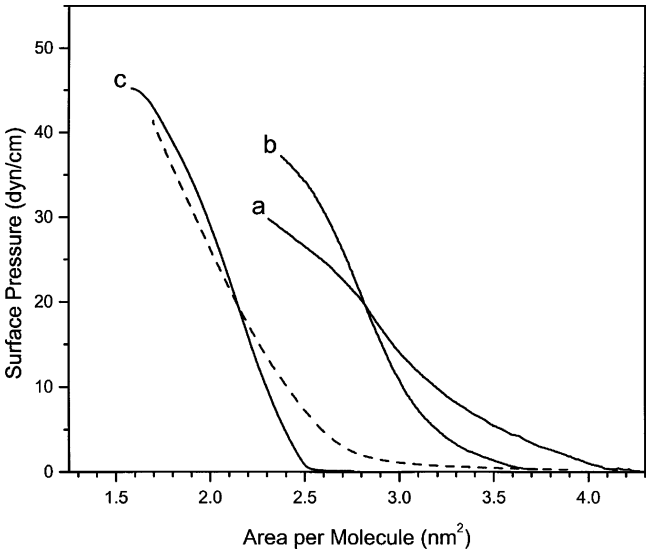

Figure 3. Surface pressure–area isotherms for **1** over a PMAA subphase (0.1 mM repeat units, M_w 100 000) adjusted to a pH of (a) 4.4, (b) 5.2, and (c) 10.0 at 25 °C. Dash plot is the isotherm of **1** over pure water.

isotherms that were then measured for **1** over an aqueous subphase containing PAA (0.1 mM repeat units, M_w 240 000). Figure 2 shows how the surface pressure–area isotherm was influenced by changes in pH. At pH 10.0, the isotherm was characterized by a limiting area of ca. 2.45 nm^2/molecule. This value is slightly less than that found for **1** over pure water (i.e., 2.60 nm^2/molecule). In addition, the monolayer over the polelectrolytes was found to be less compressible, suggesting a transition from a liquid-condensed to a solidlike state. On lowering the pH of the subphase, the isotherm tended to shift "toward the right" to higher limiting areas.

Figure 3 shows related surface pressure–area isotherms that were obtained for **1** over an aqueous PMAA subphase as a function of pH. Qualitatively, the dependency of the monolayer properties of **1** was similar to that found with PAA, except the shifts were significantly greater. In addition, when the pH was lowered to 5.2, and also to 4.4, the isotherm shifted strongly "to the right" and became much more compressible.

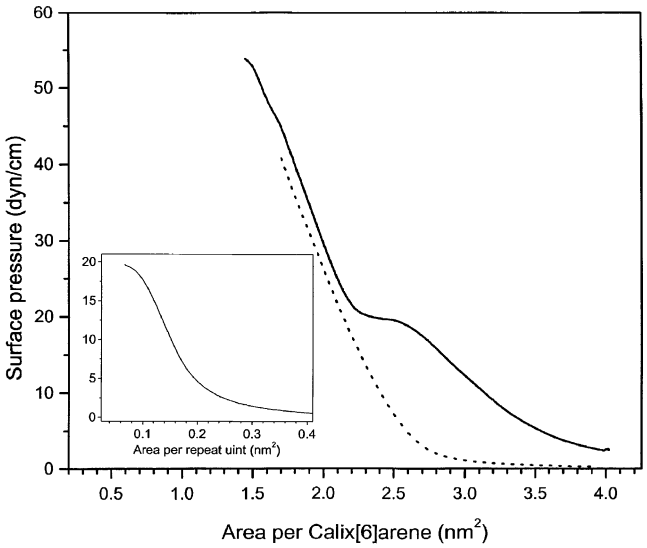

Figure 4. Surface pressure area isotherms for (· · ·) **1** and (—) **1** plus an equimolar quantity of repeat units of poly(methyl acrylate) (M_w 40 000) over a pure water subphase (pH = 6.0). The inset shows the surface pressure–area isotherm for PMA over a pure water subphase.

In a separate experiment, we measured the surface pressure–area isotherm of **1** in the presence of an equimolar amount of repeat units of poly(methyl acrylate) (PMA) over a pure water subphase at pH 6.0. Figure 4 shows the resulting isotherm. It should be noted that the area occupied per calix[6]arene has been plotted as a function of surface pressure. In other words, the presence of the polymer is ignored in defining the *x*-axis. Also included in this figure is the surface pressure–area isotherm for PMA, itself. Similar to what has previously been reported, PMA is characterized by high compressibility, a collapse pressure of ca. 20 dyn/cm, and a limiting area of ca. 0.23 nm^2/repeat unit.[18] Compression of the monolayer composed of **1** and PMA showed a collapse pressure that was identical to that of PMA. In addition, further compression beyond this collapse point generated a surface pressure–area isotherm that traced the same isotherm that was found for the pure calix[6]arene.

Effects of the Polymers on the Surface Viscosity of 1. To probe the influence that PAA and PMAA have on the surface viscosity of **1**, monolayers of the calix[6]arene were compressed to 20 dyn/cm over aqueous solutions of each polyacid at different pH values. After this surface pressure was maintained for 30 min, the film was then exposed to a slit opening (6 mm) of a canal viscometer, and the decrease in surface pressure then monitored as a function of time. In each experiment, the area that was occupied by the monolayer at the start of the surface viscosity measurement was ca. 300 cm^2.

Figure 5 summarizes the principal results that were obtained with PAA. In essence, when the pH of the subphase was lowered from 10.0 to 3.0, a steady increase in surface viscosity was observed. Replacing PAA with a lower molecular weight form (i.e., M_w 50 000) resulted in a moderate decrease in the monolayer's surface viscosity. Figure 6 shows the corresponding effects that pH had on the surface viscosity of **1** over a PMAA subphase. In this case, an abrupt increase in surface viscosity was noted as the pH was lowered beyond a value of 6.5. This abrupt change mirrors the abrupt change in ionization and conformation that is characteristic of PMAA within this pH region.[17] Finally, examination of a monolayer composed of equimolar mixtures of **1** and poly(methyl acrylate)

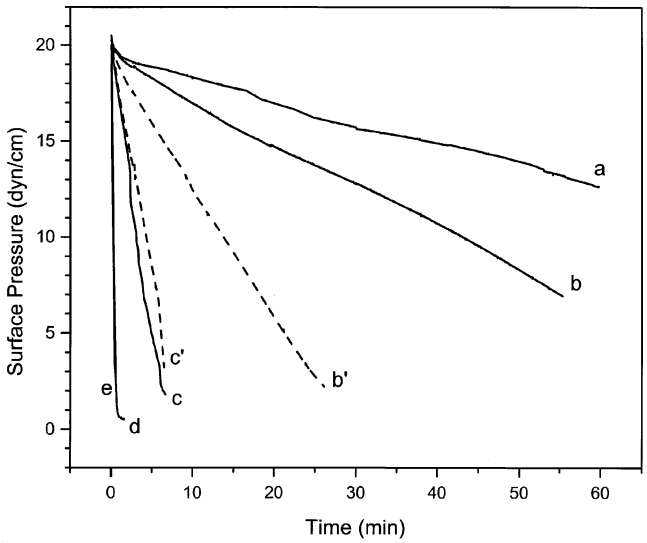

Figure 5. Surface viscosity of monolayers of **1** over PAA (0.1 mM of repeat units, M_w = 240 000), where the pH of the subphase was adjusted to (a) 3.5, (b) 4.4, (c) 5.2, (d) 6.0, and (e) 10.0 at 25 °C. Note: (b′) is similar to (b) except that PAA having a M_w of 50 000 was used; (c′) is similar to (c) except that the surface pressure was maintained for 120 min instead of the standard 30 min at 20 dyn/cm prior to exposure to the slit opening.

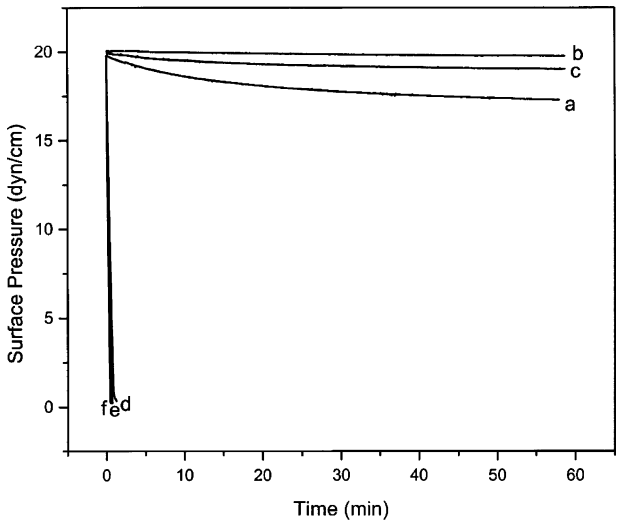

Figure 6. Surface viscosity of monolayers of **1** over PMAA (0.1 mM of repeat units; M_w = 100 000), where the pH of the subphase was adjusted to (a) 4.4, (b) 5.2, (c) 6.0, (d) 6.5, (e) 7.0, and (f) 10.0 at 25 °C.

showed no signficant surface viscosity over a pure water supbhase (pH 6.0) (Figure 7).

Barrier Properties of Glued LB Bilayers Derived from 1. Using conventional LB dipping methods, a series of glued LB bilayers of **1** were prepared from aqueous subphases containing 0.1 mM repeat units of either PAA or PMA at various pH values. For permeability measurements, poly(1-(trimethylsilyl)-1-propyne) (PTMSP) was used as support material.[4] The transfer ratio, which is defined as the decrease in monolayer area at the air–water interface divided by the geometrical surface area of the substrate passing through the interface, for all down- and upstrokes was 1.0 ± 0.1. A summary of the barrier properties of the resulting films, with respect to He and N_2 gaseous permeants, is presented in Table 1. With PAA as a cross-linking agent, the barrier for permeation, and also the permeation selectivity, of the bilayer increased with decreasing pH. It should be noted that the very high

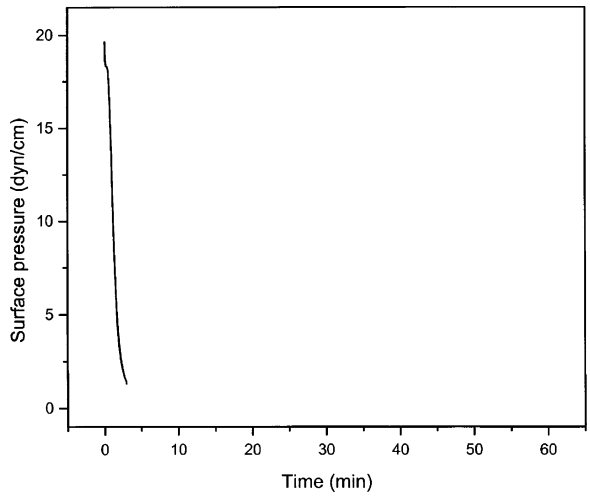

Figure 7. Surface viscosity of a monolayer of **1** plus an equimolar quantity of poly(methacrylate) repeat units over a pure water subphase (pH = 6.0) at 25 °C.

Table 1. Flux of He and N_2 across Glued Langmuir–Blodgett Bilayers of 1[a]

polymer[b]	pH	$10^6P/l$ (cm^3/cm^2 s cm Hg) He	N_2	He/N_2 (α)
none	6.0	513	504	1.0
PAA	10.0	264	2.5	110
	6.0	232	1.5	160
	5.2	135	0.49	280
	5.2	178	0.57	310
	4.4	98	0.1	980
	4.4	71	<0.1	>710
PAA[c]	10.0	280	3.9	71
	4.4	83	0.07	1180
PMAA	10.0	332	9.5	35
	7.0	271	4.1	66

[a] All LB films were fabricated using a constant surface pressure of 30 dyn/cm and a dipping speed of 2 mm/min; the transfer ratio in all cases was 1.0 ± 0.1. Unless noted otherwise, the molecular weights of PAA, PMAA, and PMA were 240 000, 100 000, and 40 000, respectively. Normalized flux (P/l) equals the observed flow rate, divided by the effective area of the membrane (9.36 cm^2) and by the pressure gradient (10 psi) employed. Each set of data corresponds to a separate composite membrane made using an ca. 15 μm thick PTMSP support plus a single glued bilayer of **1**. All measurements were made at ambient temperatures. Values were obtained from 5 to 10 independent measurements; the error in each case was ±5%. [b] The polymer concentrations in the subphase was 0.1 mM of repeat units. [c] M_w 50 000.

He/N_2 selectivities that are reported in this table are without precedent for organic membranes that are as thin as ca. 6 nm.[24] On the basis of their extreme thinness, He/N_2 selectivities of ca. 1000 are truly extraordinary. Replacement of PAA with a lower molecular weight form (i.e., 50 000) afforded glued bilayers with similar barrier properties (Table 1). Because of the very high surface viscosities that were found with monolayers of **1**, which were formed over PMAA subphases at pH values less than 6.5, efficient LB transfers were not possible. For this reason, LB bilayers that were glued with PMAA were fabricated only at pH 7.0 and 10.0. Compared with PAA, glued bilayers that were made from PMAA showed reduced barrier properties and reduced permeation selectivity.

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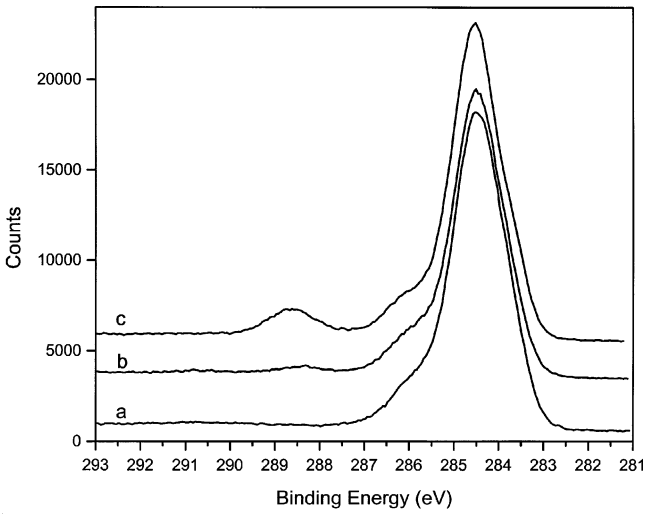

Figure 8. C 1s spectra of LB bilayers of **1** that were deposited onto PTMSP-coated silicon wafers; XPS analyses were made using a takeoff angle of 75°. Bilayers were fabricated using (a) a pure water subphase (pH 6.0), (b) a PAA subphase (0.1 mM repeat units) at pH 10.0, and (c) a PAA subphase (0.1 mM repeat units) at pH 4.4.

Incorporation of PAA into LB Bilayers of 1. To gain insight into the quantity of PAA that is incorporated into bilayers of **1** at low and at high pH, we examined two samples by X-ray photoelectron spectroscopy (XPS). In Figure 8 are shown the C 1s spectra for three LB bilayers: one that was prepared over a pure water subphase (pH 6.0), one that was fabricated over a 0.1 mM PAA solution (pH 10), and one that was made over a 0.1 mM PAA solution (pH 4.4). In each case, the bilayers were deposited onto silicon wafers that were coated with a ca. 100 nm thick layer of PTMSP. What is readily apparent from the carboxyl carbon (288.8 eV) in these spectra is that considerably more PAA is incorporated at pH 4.4 as compared with 10.0. On the basis of the atomic compositions for the carboxyl carbon and nitrogen (N 1s), the molar ratio of repeat unit to quaternary ammonium group is estimated to be 3.3 for the bilayer that was fabricated at pH 4.4. At pH 10.0, this ratio is reduced to ca. 0.4. Analysis of the ellipsometric film thickness of a glued bilayer that was made from **1** plus PAA (pH 4.4), deposited onto a silylated silicon wafer, gave a value of 5.4 ± 0.10 nm.[25] A similar glued bilayer that was prepared at pH 10.0 gave a film thickness of 4.9 ± 0.19 nm. In the absence of PAA (pH 6.0), a bilayer of **1** yielded an ellipsometric film thickness of 4.6 ± 0.14 nm.

Discussion

Control over Gluing by pH Adjustment. The results of this investigation clearly demonstrate the feasibility of controlling the packing properties and the surface viscosity of monolayers of **1** by adjustment of the pH of an aqueous subphase that contains a weak polyacid. They also demonstrate the ability to control the barrier properties of corresponding glued bilayers by such pH adjustment.

How does pH control the gluing efficiency? The answer appears to lie in a *combination* of changes that occur in the degree of ionization, the hydrophobic−hydrophilic balance, and the chain conformation of these polyacids. Thus, at high pH, deprotonation of the polyacid affords a "stretched out" conformation and there is only partial uptake by the surfactant monolayer (Figure 9A). That the uptake of the polyanion by the monolayer is relatively low is clearly evident from the XPS results. Apparently, the *low density* of polymer chains at the air−water interface are insufficient to affect the surface viscosity of the monolayer. In contrast, at low pH, the polyacid is less ionized, more hydrophobic, and favors a coiled conformation. Here, associative interactions with the calix[6]arene monolayer occur through a combination of ionic and hydrophobic forces, and the quantity of polyelectrolyte that is associated with the monolayer is much greater; that is, there are a relatively large number of ionic and hydrophobic interactions (Figure 9B). Since the viscosity of PAA in the bulk aqueous phase is known to decrease as the pH is lowered, the observed increase in surface viscosity at low pH cannot be attributed to changes in the bulk aqueous phase. Instead, they must reflect direct interactions between the polymer and the surfactant monolayer.

That hydrophobic forces, alone, are insufficient in promoting gluing is indicated by the lack of significant interaction between poly(methyl acrylate) and **1** at the air−water interface. In fact, the inability of PMA to influence the surface viscosity of **1**, the retention of the collapse point of PMA in mixed monolayers of PMA and **1**, and the retention of the calix[6]arene's surface pressure−area isotherm beyond the collapse point of the polymer provide strong evidence that **1** and PMA are completely immiscible. Thus, the formation of highly viscous monolayers appears to require a combination of ionic and hydrophobic interactions.

The monolayer properties of **1** over aqueous PAA and PMA solutions as a function of pH are also consistent with our model. Thus, at pH 10, the shift toward a relatively low limiting area (Figures 1 and 2) and the

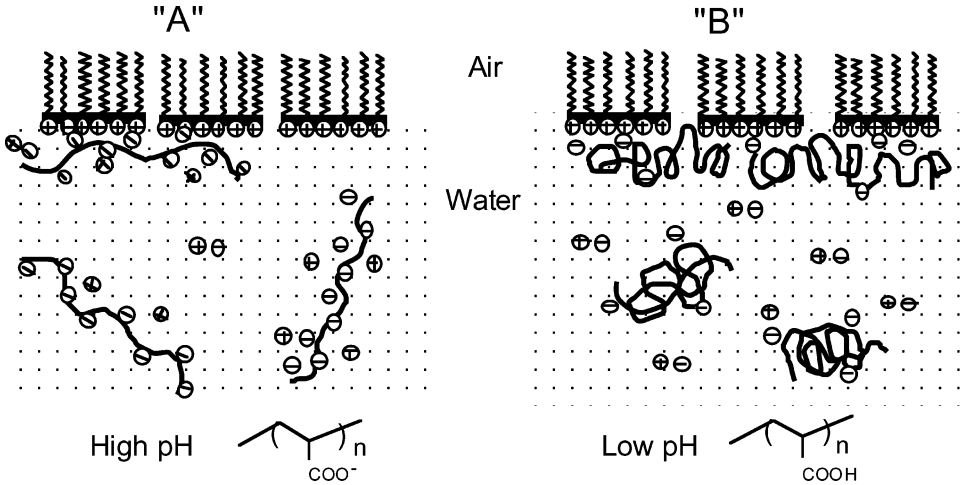

Figure 9. Stylized illustration of ionically cross-linked monolayers formed at (A) high and (B) low pH, respectively.

negligible surface viscosity (Figure 4) point toward only partial ion pairing and partial cross-linking. The apparent change from a liquid-condensed-like to a solidlike state is also consistent with ion pairing, where reduced repulsive interactions between neighboring quaternary ammnonium groups exists. The observed shift toward relatively high limiting areas is a likely consequence of partial insertion of the polymer chains into the monolayer, being driven by hydrophobic forces. The fact that the effects of PMAA are much greater than that found with PAA also indicates that hydrophobic interactions play a significant role at low pH.

In the absence of **1**, surface tension measurements have revealed that PMAA is less surface active than PAA at low pH, despite the fact that the former has a more hydrophobic backbone. The reason for this difference, we believe, is that the methyl groups of PMAA are buried within coiled conformations of the polymer. Specifically, we suggest that intrapolymer chain aggregation of the methyl groups promotes the exposure of the pendant carboxylic acid groups to the aqueous phase, which results in micelle-like structures being formed, and a relatively strong preference for residing in the bulk aqueous phase over the air−water interface. When **1** is present at the air−water interface, however, PMAA can be more strongly drawn into the calix[6]arene monolayer at low pH. In this case, intrapolymer chain aggregation is apparently reduced in favor of methyl−calix[6]arene hydrophobic interactions.

Barrier Properties of Glued LB Bilayers. The pH dependency of the barrier properites of bilayers of **1**, which have been glued together with PAA, correlate with changes in surface viscosity. Thus, relatively low pH values result in highly viscous monolayers, high permeation barriers, and high permeation selectivity. Three separate factors may be contributing to the formation of high-quality bilayers under low pH conditions conditions: (i) the greater cohesiveness of the monolayers that undergo LB transfer, (ii) the additional mass that is added to the bilayer by the inclusion of the polyelectrolyte, and (iii) tighter packing within the surfactant assembly. In principle, an increase in film cohesiveness (reflected by an increase in surface viscosity) should help to minimize the formation of defects during the LB dipping process. Also, the incorporation of polyelectrolyte into the LB bilayer provides additional mass to the membrane that can help "patch up" defects by filling in void space. Finally, a more tightly packed assembly of calix[6]arenes (indicated by less compressible isotherms) should reduce the contributions of permeation between (as opposed to through) neighboring calix[6]-arenes. At the present time, we suspect that all of these factors are important in producing high-quality glued bilayers, but we are unable to quantify the actual contributions made by each one.

(25) Silylation was performed using *n*-octadecyltrichlorosilane: Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465.

Conclusions

The efficiency of poly(acrylic acid) and poly(methacrylic acid) in gluing monolayers of calix[6]arene **1**, and in controlling the barrier properties of resulting LB films, has been found to be very sensitive to pH. Thus, low pH favors the formation of highly viscous monolayers, a high density of polymer chains associated with the glued bilayer, relatively high barrier properties, and relatively high permeation selectivity. When surface viscosities are too high, however, effective LB transfer tends to be difficult. Thus, the use of moderate surface viscosities have been found to provide maximum permeation selectivity. At high pH, fewer polymer chains become incorporated into the glued bilayer, and the barrier properties and permeation selectivity are relatively low. A model that is consistent with these features, which is based on a combination of ionic and hydrophobic interactions, has been proposed.

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