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Membrane Composites Derived from Porous versus Nonporous Surfactants: Evidence for Uniqueness of Calix[6]arene-Based Surfactants

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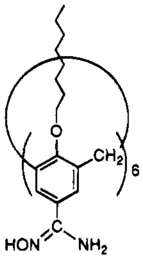
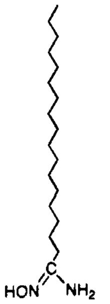
We have previously outlined a strategy for the synthesis of ultrathin membranes that possess size selectivity toward permeants.[1,2] In essence, it involves the deposition of monolayers or multilayers of "porous" surfactants onto highly permeable supports. When defects within the surfactant assembly are negligible, diffusion across the composite is expected to be governed by pores that exist within and between the surfactants. Recently, we have demonstrated the feasibility of this approach by showing that composites made from Langmuir−Blodgett (LB) multilayers of calix[6]arene-based surfactants plus poly[1-(trimethylsilyl)-1-propyne] (PTMSP) supports discriminate between He and N_2 on the basis of their size.[2,3] While this work showed the uniqueness of PTMSP as support material, as compared with commonly-used polymers such as Celgard (stretched forms of polypropylene) and Nuclepore membranes (track-etched polycarbonate film), the uniqueness of the calix[6]arene surfactants, themselves, was not firmly established.[4]

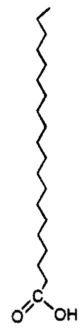
In this paper we provide evidence for uniqueness of calix[6]arene surfactants as building blocks for the construction of permeation-selective composites.[5] Specifically, we show that membranes made from PTMSP plus multilayers of calix[6]arene **I** exhibit significant permeation selectivity toward He and N_2, but that those based on arachidic acid (**AA**), cadmium arachidate (**AA**/Cd^{2+}), a polyion complex of **AA** plus poly(ethyleneimine) (**AA-PEI**), and stearamide oxime (**SA**) *show no permeation selectivity and no alteration in the barrier properties of the support.* We also report results of surface analyses of PTMSP/**I** and PTMSP/**SA** by X-ray photoelectron spectroscopy (XPS) that offer insight into the origin of these striking differences.



I



SA



AA

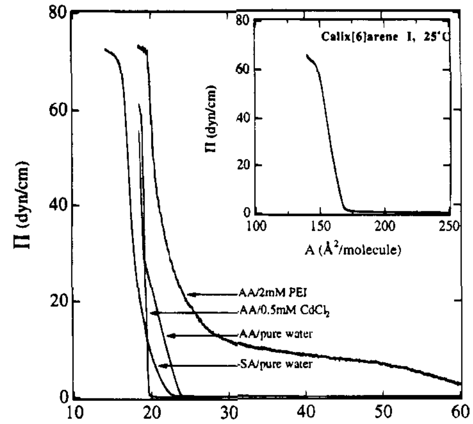


Figure 1. Surface pressure−area isotherms for **I**, **AA**, and **SA** over a pure water subphase and for **AA** over 2 mM PEI and over 0.5 mM $CdCl_2$ at 25 °C.

Calix[6]arene **I** was designed in our laboratory on the basis of the belief that it would form robust LB film. Specifically, we envisioned that cross-linking would take place within each monolayer due to intermolecular hydrogen bonding. Surface viscosity measurements at the air−water interface (to be reported elsewhere) do, in fact, support such a hypothesis. Calix[6]arene **I** was synthesized via bromination of 37,38,39,40,41,42-hexakis-(*n*-octyloxy)calix[6]arene, followed by cyanation and addition of hydroxylamine; **SA** was prepared by a similar addition of hydroxylamine to stearonitrile.[6] Calix[6]arene **I** produced stable monolayers having low compressibility and a limiting area of ca. 170 Å^2/molecule, a value that is consistent with a tightly packed monolayer in which all of the amide oxime moieties are in contact with the water surface and where the calix[6]arene framework adopts a near-cylindrical geometry (Figure 1). Monolayers prepared from **SA** were very similar to those of **AA**, except that they were slightly less compressible. When **AA** was spread over 0.5 mM $CdCl_2$, a "solid-like" film resulted.[7] In sharp contrast, monolayers of **AA** that were spread over a subphase containing 2 mM poly(ethyleneimine) (repeat unit concentration) were highly compressible.

Composite membranes were fabricated by standard LB-vertical dipping of PTMSP through monolayers of **I**, **SA**, **AA**, **AA**/Cd^{2+}, and **AA-PEI** at the air−water interface; in each case, a total of four monolayers were transferred beginning with the first "down-trip" (air into water). Transfers were carried out with a dipping speed of 4 mm/min, a subphase temperature of 25 °C, and surface pressures of 40, 40, 30, 30, and 30 dyn/cm for **I**, **SA**, **AA**, **AA**/Cd^{2+}, and **AA-PEI**, respectively. Films were allowed to dry under a stream of N_2 for 30 min (**SA**, **AA**, **AA**/Cd^{2+}, and **AA-PEI**) or 60 min (**I**) between dipping cycles. A longer drying time for **I** was necessary in order to have an effective monolayer transfer on the down-trip.

Permeation properties that were measured for each of the composites were determined using methods similar to those previously described and are shown in Table 1.[3] In the absence of a surfactant overlayer, bare PTMSP showed negligible selectivity toward He and N_2. Within experimental error,

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[1] Markowitz, M. A.; Bielski, R.; Regen, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 7545.

[2] Conner, M. D.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 1178.

[3] Conner, M. D.; Janout, V.; Kudelka, I.; Dedek, P.; Zhu, J.; Regen, S. L. *Langmuir* **1993**, *9*, 2389.

[4] Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473.

[5] For general features of calixarenes, see: (a) Gutsche, C. D. *Calixarenes*; The Royal Society of Chemistry: Thomas Graham House, Science Park, Cambridge, 1989. (b) Vicens, J.; Bohmer, V. *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer Academic Publishers: Boston, 1991.

[6] Bromination was carried out using 2 equiv of NBS in 2-butanone for 40 h at room temperature; subsequent cyanation with 10 equiv of CuCN in refluxing *N*-methylpyrrolidone for 5 h afforded the corresponding nitrile. Addition of hydroxylamine (10 equiv) in aqueous *tert*-butyl alcohol/ethanol (1/7, v,v) at 70 °C for 48 h afforded, after workup, **I** in 10% overall yield. Compounds **I** and **SA** exhibited satisfactory spectral and exact mass data.

[7] Ulman, A. *An Introduction To Ultrathin Organic Films: From Langmuir-Blodgett To Self-Assembly*; Academic Press: New York, 1991.

[8] A silicon wafer was coated with a thin (ca. 20 μm) film of PTMSP for XPS studies.

[9] Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165.

[10] PTMSP used in this work was found to have a slightly higher permeability and lower permeation selectivity than that previously reported: Takada, K.; Matsuya, H.; Masuda, T.; Higashimura, T. *J. Appl. Polym. Sci.* **1985**, *30*, 1605. Nonetheless, our values, and those previously reported, both lie on the upper bound.

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Table 1. Flux of He and N_2 across PTMSP/Surfactant Composites[a]

surfactant	monolayers	He 10^6**F** (cm^3/cm^2-s-cmHg)	N_2	He/N_2 (flux ratio)
none	0	560	633	0.88
	0	560	621	0.90
AA	4	519	592	0.88
	4	537	592	0.91
AA/Cd^{2+}	4	532	603	0.88
	4	528	586	0.90
SA	4	541	592	0.91
	4	499	571	0.88
AA-PEI	4	560	646	0.84
	4	503	571	0.88
I	2	466	18	25
	2	503	23	22
	4	160	3.7	43
	4	150	3.6	42
	4	147	2.6	56
	6	55	0.61	90
	6	66	0.90	73
	8	64	0.43	150
	10	49	0.55	89

[a] Normalized flux (**F**) equals the observed flow rate, divided by the area of the membrane (9.36 cm^2) and by the pressure gradient (0.7 atm) employed. Each set of data corresponds to a separate composite membrane made using a ca. 25 μm thick PTMPS support plus multiple layers of surfactant. All measurements were made at ambient temperatures. Values were obtained from 5−10 independent measurements; the error in each case was ±5%. Transfer ratios, δ, defined as the decrease in monolayer area at the gas−water interface divided by the geometrical surface area of the substrate passing through the interface were, typically, as follows. **AA**: 1.2 (1st-down), 0.7 (1st-up), 1.2 (2nd-down), 0.7 (2nd-up). **AA**/Cd^{2+}: 1.2 (1st-down), 1.2 (1st-up), 1.1 (2nd-down), 1.2 (2nd-up). **AA-PEI**: 0.7 (1st-down), 1.2 (1st-up), 0.7 (2nd-down), 1.2 (2nd-up). **SA**: 0.9 (1st-down), 1.1 (1st-up), 0.9 (2nd-down), 1.2 (2nd-up). **I**: 1.0 (1st-down), 1.2 (1st-up), 1.0 (2nd-down), 1.2 (2nd-up). Additional monolayers of **I** transferred, similarly.

deposition of four layers of **AA**, **AA**/Cd^{2+}, **AA-PEI**, and **SA** did not alter the barrier properties of the support. In sharp contrast, deposition of four monolayers of **I** resulted in a less permeable composite, having significant permeation selectivity with respect to He and N_2. Additional monolayers of **I** that were deposited onto PTMSP led to a maximization in the He/N_2 selectivity in the range 90−150; six monolayers appeared to be sufficient for producing a relatively defect-free LB overlayer. Although the stability of each composite was excellent throughout the course of the permeation measurements, some variability in film quality (i.e., presence of defects) was apparent, especially with thicker LB films. This variability appeared to be dependent upon the transfer ratio; i.e., higher permeation selectivity was observed when transfer ratios were closer to 1.0 on the down-trip.

Analysis of PTMSP/**I** (four monolayers) by XPS (Scienta ESCA-310), using a takeoff angle of 15°, revealed a calix[6]arene-coated surface as indicated by the presence of C, N, and O and by the absence of Si.[8] In sharp contrast, similar analysis of PTMSP/**SA** (four monolayers) showed no evidence of the surfactant on the polymer's surface; only the carbon and silicon atoms of PTMSP were detected. That **SA** was, in fact, transferred to the PTMSP support was confirmed by transmission FTIR spectroscopy, which showed the C−H bands of the **SA** at 2926 and 2855 cm^{-1} and a broad N−H/O−H band at 3244 cm^{-1}; each of these bands was absent in bare PTMSP prior to transfer.

The dramatic difference in the permeation properties between composites made from **I** and **SA** correlates, directly, with the surfactant's ability to be retained on the surface of the support; i.e., only **I** remains on the surface, and only **I** leads to permeation selectivity. The stability of monolayers of **I** on the surface of PTMSP is, we believe, a consequence of its large size (limiting area of 170 Å^2/molecule), which prevents its penetration into the polymer. In contrast, the much smaller, single-chain **SA** (having a limiting area of ca. 20 Å^2/molecule) is able to "slither" through micropores on the polymer's surface, resulting in the disassembly and loss of the surfactant to the polymer's bulk phase. The fact that monolayers of **SA** have a greater hydrocarbon density than those of **I**, together with the fact that **SA** does not alter the permeation characteristics of bare PTMSP, in and of itself, provides compelling evidence for disassembly of the LB film. On the basis of the permeation properties of each of the **AA** composites, we infer that a similar disassembly has occurred.

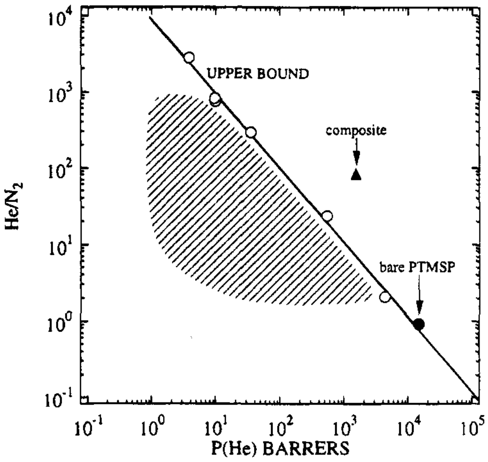

Figure 2. Plot of He/N_2 selectivity as a function of helium permeability for polymers with maximum permeation selectivity and helium permeability (○);[9] bare PTMSP (●) and PTMSP/**I** (▲) are also included. The shaded region represents more than 90% of ca. 300 polymers tested; *none* lie above the upper bound. 1 barrer = 1 × 10^{-10} (cm^3-cm/cm^2-s-cmHg). Values that are shown for bare PTMSP and PTMSP/**I** (6 monolayers) represent permeability coefficients that are based on a PTMSP film thickness of 25 μm; here, P(He) = **F** × membrane thickness.

In order to put the permeation properties of PTMSP/**I** into perspective, we show the helium permeability, P(He), and He/N_2-permeation selectivity of a 6-monolayer composite in relation to the "upper bound" for He/N_2 (Figure 2), i.e., an empirical limit for He/N_2 that has been defined by six polymers having the highest permeability *and* the highest selectivity out of more than 300 tested.[9,10] The fact that PTMSP/**I** has permeation characteristics that place it *above* this upper bound is particularly significant. To the best of our knowledge, *this is the first instance in which an LB-based composite has crossed an upper bound.* The ultrathinness of the calix[6]arene LB overlayer, together with its intact structure, is undoubtedly responsible for such behavior.

Although the unusually high permeability of PTMSP makes it particularly attractive as support material for LB films, its usefulness in fabricating permeation-selective composites is critically dependent upon the specific structure of the surfactant that is used. In this regard, calix[6]arenes such as **I** clearly show unique features relative to conventional LB film-forming surfactants.

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