Unusual Pressure Effects on the Permeation Properties of a Langmuir−Blodgett Composite Membrane

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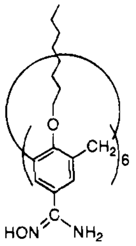
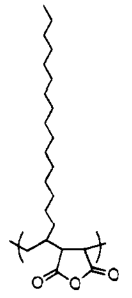
In this paper, we document our discovery of extraordinary permeation properties of composite membranes derived from Langmuir−Blodgett (LB) multilayers of calix[6]arene **I** plus poly[1-(trimethylsilyl)-1-propyne] (PTMSP) film. Specifically, we show that the intrinsic permeability and selectivity of such composites toward He and N_2 increase with increasing permeant pressures. In striking contrast, analogous composites prepared with a "conventional" polymeric surfactant, poly(1-octadecene-*co*-maleic anhydride) (**II**) show unexceptional behavior, i.e., permeation characteristics that are independent of pressure. The theoretical and practical implications of these findings are briefly discussed.



I



II

Surfactants **I** and **II** form stable monolayers at the air−water interface having low compressibility, collapse points that are in excess of 40 dyn/cm, and limiting areas of 170 Å²/molecule and 36 Å²/repeat unit, respectively.[1] Using procedures similar to those that have previously been described, composite membranes were fabricated via vertical dipping of 25-μm-thick PTMSP film through monolayers of **I** and **II**, respectively.[2,3] Transfers were carried out with a dipping speed of 4 mm/min, a pure water subphase (25 °C), and constant surface pressures of 40 and 30 dyn/cm for **I** and **II**, respectively; in all cases, the first monolayer was deposited on a "down-trip". Films were allowed to dry under a stream of N_2 for 30 min (**II**) and 60 min (**I**) between dipping cycles. A longer drying time for **I** was necessary in order to have an effective monolayer transfer on the second down-trip. Transfer ratios were 1.0 ± 0.2 in all cases.

Helium and nitrogen were chosen as permeants in order to define the permeation properties of each of the composites, PTMSP/**I** and PTMSP/**II**.[4,5] In all cases, normalized fluxes (P/l) were determined by experimentally measuring the volumetric flow rate (F) of the permeant gas through the membrane and dividing this quantity by the membrane's cross-sectional area (A) and by the pressure gradient (Δp) employed (eq 1); P represents an intrinsic permeability coefficient that characterizes the specific membrane-permeant combination, and l corresponds to the membrane thickness; permeation selectivities were calculated from the ratio $(P/l)_{He}/(P/l)_{N2}$.[6]

$$P/l = F/(A\Delta p) \qquad (1)$$

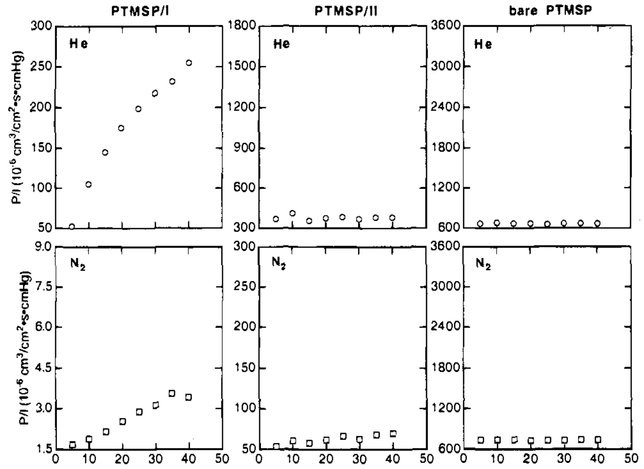


Figure 1. Plot of normalized flux (P/l) for He and N_2 through PTMSP/**I**, PTMSP/**II**, and bare PTMSP as a function of Δp.

All of the data reported in Figure 1 were obtained using single membranes; all of the composites contained four monolayers of surfactant.[7] Normalized fluxes that were observed as Δp was systematically increased were reversible; i.e., returning Δp to lower pressures afforded the original values. Similar data were obtained from a series of individually-prepared composites in which the permeation properties of each membrane were measured at a single applied pressure gradient. In the case of PTMSP/**I**, the N_2-normalized fluxes were found to increase linearly with Δp; such linearity for He, however, was only apparent at higher pressures. In the lower pressure regime, an incremental increase in Δp resulted in a relatively large increase in the normalized He fluxes. In sharp contrast, P/l values for He and N_2 for PTMSP/**II** and for bare PTMSP were constant over this same pressure range.

A comparison of the He/N_2 selectivities, $(P/l)_{He}/(P/l)_{N2}$, for the two LB composites and bare PTMSP are shown in Figure 2 as a function of Δp. When an applied pressure gradient of 5 psi was employed, PTMSP/**I** exhibited significantly greater permeation selectivity than PTMSP/**II**; no selectivity was observed with the bare PTMSP support. As Δp increased to 20 psi, the permeation selectivities of PTMSP/**I** significantly increased; the selectivities of PTMSP/**II** and bare PTMSP, however, remained unchanged.

In related experiments, composites made with two and six monolayers of **II** gave normalized fluxes and permeation selectivities that were also independent of Δp. In contrast, composites made from six monolayers of **I** showed a pressure dependence similar to those made using four monolayers;

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(1) Surfactant **II** was obtained from commercial sources (Polysciences, MW 30 000 to 50 000) and used as obtained. The synthesis and monolayer properties of **I** have been reported previously: Lee, W.; Hendel, R. A.; Dedek, P.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1995**, *117*, 6793.

(2) (a) Markowitz, M. A.; Janout, V.; Castner, D. G.; Regen, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8192. (b) Conner, M. D.; Janout, V.; Kudelka, I.; Dedek, P.; Zhu, J.; Regen, S. L. *Langmuir* **1993**, *9*, 2389. (c) Lee, W.; Hendel, R. A.; Dedek, P.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1995**, *117*, 6793.

(3) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473.

(4) Solubility contributions to the He/N_2 permeation selectivity of organic polymeric membranes is very modest, compared with most other gas combinations that have been used in fundamental studies: Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165.

(5) The kinetic diameters of He and N_2 are 2.3 and 3.6 Å, respectively: Breck, D. W. *Zeolite Molecular Sieves*; John Wiley: New York, 1974.

(6) Hwang, S. T.; Choi, C. K.; Kammermeyer, K. *Sep. Sci.* **1974**, *9*, 461.

(7) All measurements were made at ambient temperatures. Values were obtained from 5−10 independent measurements; the error in each case was ±5%.

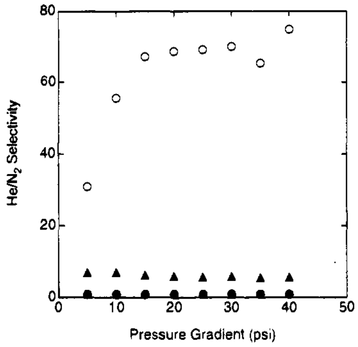

Figure 2. Plot of He/N_2 selectivity for PTMSP/**I** (○), PTMPS/**II** (▲), and bare PTMSP (●) as a function of Δp.

membranes made with only two layers, however, had permeation properties that were independent of pressure. Preliminary transmission FTIR measurements that have been made for two monolayers of **I** on PTMSP indicate an asymmetric C−H band for the CH_2 group at 2929 cm^{-1}; with six monolayers, this band shifts to 2918 cm^{-1}. These results imply that a more crystalline-like assembly is formed after deposition of the second complete bilayer.[8]

In principle, the permeability characteristics of a polymeric membrane should be independent of Δp; i.e., as Δp increases for a given permeant, a proportional increase in F is expected. Thus, the constancy of P/l observed for He and N_2 for PTMSP/**II** and bare PTMSP as a function of Δp is unexceptional. However, the increase in P/l for both gases for PTMSP/**I**, *coupled with an increase in the He/N_2 selectivity*, is extraordinary. The standard interpretation for an increase in P/l with increasing Δp is that the higher pressure gradient leads to an increase in film defects. In the present instance, such an interpretation cannot be correct since an increase in film defects must be accompanied by a *decrease* in permeation selectivity; i.e., our results are just the opposite.

The increase in the permeability and the permeation selectivity of PTMSP/**I** with increasing Δp clearly reflects a structural change within the LB composite. The fact that this process is reversible further indicates that the change is dynamic in character. Although we do not yet understand the nature of this alteration in membrane structure, the fact that PTMSP/**II** (an LB assembly having no permanent "molecular pores") does not exhibit such behavior leads us to believe that "molecular channels" are involved. In particular, we presently favor a model in which the flux of the gases induces an alignment of the calix[6]arene pores in the direction of the permeant flow, thereby creating channels that can more effectively discriminate between He and N_2 on the basis of their size.

The pressure effects on the permeation properties of PTMSP/**I** that are reported herein are remarkable. The fact that both the permeability and permeation selectivity increase with increasing pressure gradients indicates that "porous" surfactants can lead to truly novel membranes, which have the potential for separation efficiencies that have not previously been possible. Efforts aimed at exploring and exploiting this new phenomenon are continuing in our laboratories.

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[8] Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.