

SHORT COMMUNICATIONS

**Efficient Oxygen Enrichment by a Langmuir–Blodgett Film of the Polyion Complex of a Double-Chain Fluorocarbon Amphiphile**

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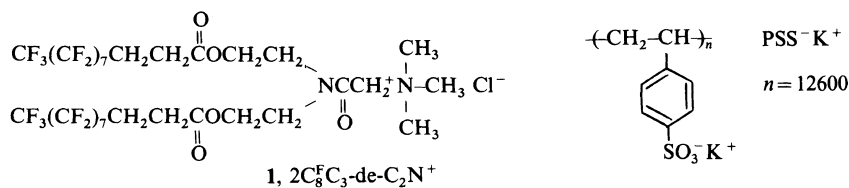
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We have shown that bilayer-forming fluorocarbon amphiphiles can be immobilized with and without poly(vinyl alcohol) in the form of cast films in which the ordered multilayer structure is maintained.<sup>1</sup> Oxygen gas permeates these films better than nitrogen. When a cast film is made of hydrocarbon and fluorocarbon components, the fluorocarbon component is concentrated near the film surface and the permeation rate is enhanced in the presence of the liquid crystalline hydrocarbon layers.<sup>2</sup>

The Langmuir–Blodgett technique<sup>3</sup> can prepare ultra-thin multilayers and should

be useful for obtaining permselective, high flux films. Reduced gas permeation due to Langmuir–Blodgett films has been reported by Rose and Quinn,<sup>4</sup> by Gaines and Ward<sup>5</sup> and by Albrecht *et al.*<sup>6</sup> However, effective gas separation was not achieved. We describe here selective permeation of oxygen by a built-up multilayer of a polyion complex<sup>7</sup> of a double-chain fluorocarbon amphiphile and poly(styrenesulfonate). Oxygen enrichment by simple Langmuir–Blodgett films containing fluorocarbon amphiphiles is reported elsewhere.<sup>8</sup>



The surface pressure-area behavior of **1** with and without PSS<sup>-</sup>K<sup>+</sup> in the subphase was reported before.<sup>7</sup> Deposition onto a porous polycarbonate film (Nuclepore NP-300, pore

size 0.03 μm, Nomura Micro Science Co., Ltd.) was performed at a surface pressure of 35 mN·m<sup>-1</sup> where the monolayer was in the condensed phase. The substrate was supported

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by a Teflon plate and thus the transfer ratio could not be determined. The formation of a Y-type multilayer was evident, however, since the decrease in the surface area was the same during the upward and downward strokes. The surface elemental analysis by X-ray photoelectron spectroscopy (instrument, ESCA 750, Shimadzu & Co.) indicated that an equimolar complex of **1** and  $\text{PSS}^-$  is deposited, on the basis of the relative intensity of the corrected  $\text{N}_{1s}$  and  $\text{S}_{2p}$  peaks. The relative existing ratio of elements was detected up to a depth of about 5 nm from the film surface. A schematic

illustration of the multilayer is given in Figure 1.

A Langmuir-Blodgett film with 76 layers thus obtained was used for the permeation experiment. The permeation rate,  $R$  ( $\text{cm}^3$  (STP)  $\text{cm}^{-2} \text{s}^{-1} \text{cm Hg}^{-1}$ ) of oxygen and nitrogen was measured by the high vacuum method. The upstream pressure was maintained at 15 mmHg. Figure 2 demonstrates the temperature dependence of permeation rates ( $R_{\text{O}_2}$  and  $R_{\text{N}_2}$ ) and their ratio  $\alpha(R_{\text{O}_2}/R_{\text{N}_2})$ . The  $R_{\text{O}_2}$  value was enhanced only slightly with temperature (16.5 to 75°C), being in the range

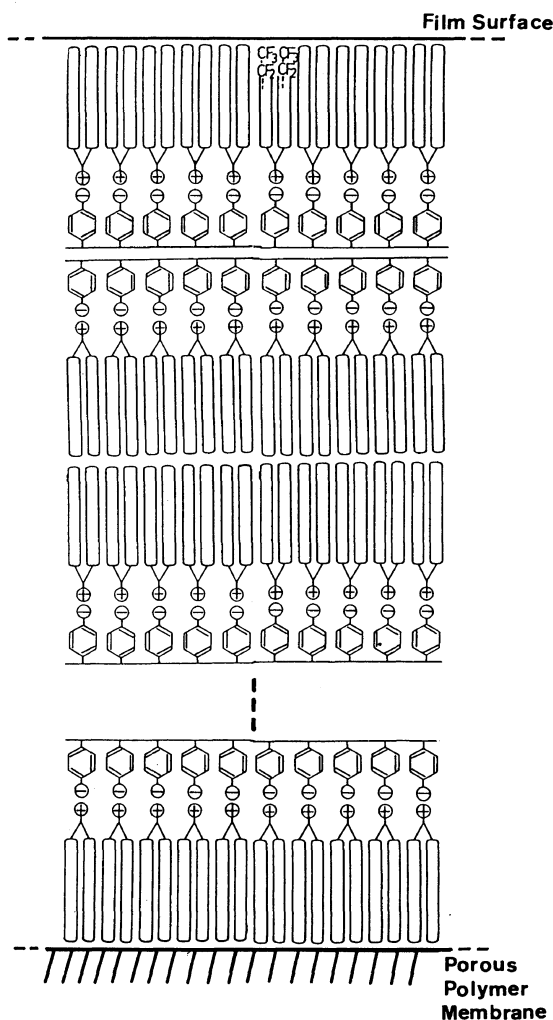
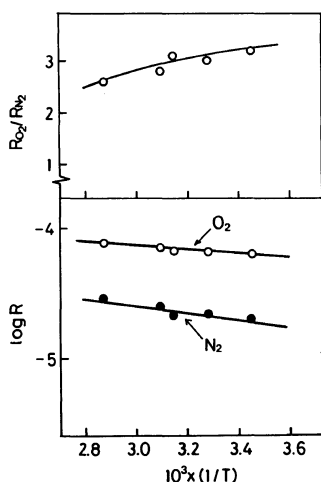


Figure 1. Schematic illustration of LB film.



**Figure 2.** Temperature dependence of the permeation characteristics of oxygen and nitrogen.

of  $6.3 \times 10^{-5} \sim 7.7 \times 10^{-5}$ . Its apparent activation energy was  $2.9 \text{ kJ mol}^{-1}$ . The permeation rate of nitrogen was smaller and the apparent activation energy was  $5.3 \text{ kJ mol}^{-1}$ . The magnitude of  $\alpha$  was 3.2 at  $16.5^\circ\text{C}$  and slightly decreased with temperature (2.6 at  $75^\circ\text{C}$ ). The apparent activation energy for  $R_{O_2}$  was much larger ( $52 \text{ kJ mol}^{-1}$ ) in a mixed cast film of **1** and poly(vinyl alcohol): **1**, 70 wt%, film thickness,  $40 \mu\text{m}$ . The smaller value observed in the present system suggests that thermal motion of the molecular chain is effectively suppressed by polyion complex formation. This effect may also be responsible for the enhanced  $\alpha$  value in the multilayer relative to those of the mixed cast film ( $\alpha=2.3$ ) and a single-component (without poly(vinyl alcohol)) cast film ( $\alpha=2.3$ ).<sup>9</sup>

It is interesting to compare the permea-

tion characteristics observed here with those of plasma-polymerized thin films. A plasma-polymerized film of hexamethyldisiloxane (thickness,  $1500 \text{ \AA}$ ) gives  $R_{O_2} = 4 \times 10^{-5}$  and  $\alpha=2.9$ ,<sup>10</sup> and that of perfluorobenzene (thickness,  $4000 \text{ \AA}$ ) gives  $R_{O_2} = 2 \times 10^{-5}$  and  $\alpha=2.9$ .<sup>11</sup> A crude estimate of the multilayer thickness is *ca.*  $2000 \text{ \AA}$ . Therefore, the multilayer film displays permeation characteristics ( $R_{O_2}$  and  $\alpha$ ) somewhat better than the plasma-polymerized membranes.

In conclusion, the present data indicate that a LB multilayer stabilized by polyion complex formation acts as an effective permselective membrane for oxygen.

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