

Gas Transport Across Hyperthin Membranes

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and poly(sodium 4-styrene sulfonate) (PSS) show very low H₂/CO₂ permeation selectivity (ca. 2) but exceptionally high CO₂/N₂ permeation selectivities (ca. 100). The H₂/CO₂ and CO₂/N₂ selectivity found with these LB bilayers is mainly due to differences in diffusivity, which reflect their kinetic diameters (H₂, 0.29 nm; CO₂, 0.33 nm; N₂, 0.36 nm), and also the tightness of the membrane. The very low H₂/CO₂ selectivity and high CO₂/N₂ selectivity associated with these PEMs is mainly the result of a high solubility of CO₂ relative to H₂ and N₂.

Progress Report

Two key requirements that must be met for a membrane to be considered as a candidate for gas separations are (i) that it exhibits high permeation selectivity and (ii) that it is capable of producing a high flux. In brief, the flux (J) of a gaseous permeant across a membrane is determined by a permeability coefficient (P), the pressure gradient (Δp) that is applied across the membrane, and the thickness (l) of that membrane, according to eq. 1. A normalized flux can also be expressed as a permeance, P/l , as shown in eq. 2. The ratio of the permeances for two gases, i and j , then represents the permeation selectivity, α , of the membrane (eq. 3). For nonporous membranes, the permeation selectivity is also related to diffusion and solubility coefficients, D and S , respectively according to eq. 4. Because of the inverse relationship that exists between J and l (eq. 1), creating membranes as thin as possible while maintaining permeation selectivity remains a primary goal.

$$J \text{ (cm}^3\text{/cm}^2\text{-sec)} = \frac{P \cdot \Delta p}{l} \quad (1)$$

$$\frac{P}{l} \text{ (cm}^3\text{/cm}^2 \cdot \text{s} \cdot \text{cm Hg)} = \frac{J}{\Delta p} \quad (2)$$

$$\alpha_{ij} = \frac{\left(\frac{P}{l}\right)_i}{\left(\frac{P}{l}\right)_j} \quad (3)$$

$$\alpha_{ij} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \quad (4)$$

Objectives

The objectives of this research are to learn how to synthesize “hyperthin” (<<100 nm) Langmuir-Blodgett films and polyelectrolyte multilayers having minimal film defects, and to use such knowledge in the design of novel permeation-selective membranes that have potential for separating gaseous mixtures; e.g., H₂/CO₂ and CO₂/N₂.

Technical Barriers

One main technical barrier in this area is preventing the formation of defects in membranes that are much thinner than ca. 100 nm. A second technical barrier is finding ways to exploit differences in solubility and diffusivity among gaseous permeants for their effective separation.

Abstract

Single Langmuir-Blodgett (LB) bilayers derived from a calix[6]arene-based surfactant and poly(acrylic acid) exhibit exceptional H₂/CO₂ permeation selectivities (ca. 75) and significant CO₂/N₂ selectivities (ca. 30). In sharp contrast, hyperthin polyelectrolyte multilayers (PEMs), formed from poly(diallyldimethylammonium chloride) (PDADMAC)

1. Unexpected Barrier Properties of Polyelectrolyte Multilayers.

Background and Hypothesis:

In previous work, we found that certain polyelectrolyte multilayers (PEMs) show CO₂/N₂ selectivities in excess of 100. [Wang, Y.; Stedronsky, E.; Regen, S. Defects in a Polyelectrolyte Multilayer: The Inside Story, *J. Am. Chem. Soc.*, **2008**, *130*, 16510-16511; (b) Wang, Y.; Janout, V.; Regen, S. L. Creating Poly(ethylene oxide)-based Polyelectrolytes for Thin Film Construction Using an Ionic Linker Strategy. *Chem. Mater.*, **2010**, *22*, 1285-12887]. Such CO₂/N₂ selectivity is exceptional and, therefore, warranted more detailed investigation. Since poly(allylamine hydrochloride) was common to the different PEMs showing this behavior, and since primary amine groups are capable of enhancing the permeation of CO₂ across polymeric membranes via a facilitated transport mechanism, we were led to hypothesize that these amine groups were playing a central role.

Results:

To test this hypothesis, we fabricated a series of analogous PEMs that were devoid of primary amine groups. Specifically, 14 nm-thick PEMs were prepared using **1** and **2** as complementary polyelectrolytes and an anchor layer that consisted of a Langmuir-Blodgett monolayer of **3**, which was stabilized with **2** (Figure 1). Table 1 shows typical permeance values across composite membranes made from these PEMs on supports made from poly[1-(trimethylsilyl)-1-propyne] (PTMSP). Also shown are typical permeances across the supports themselves. The high CO₂/N₂ selectivity of these membranes is in sharp contrast to their very low H₂/CO₂ selectivity. This fact, together with the fact that size difference between CO₂ (0.33 nm) and N₂ (0.36 nm) is similar to the size difference between H₂ (0.29 nm) and CO₂, implies that it is the *solubility* of CO₂ that is largely responsible for such selectivities. More specifically, the permeation of the smaller and more soluble CO₂ molecule is strongly favored

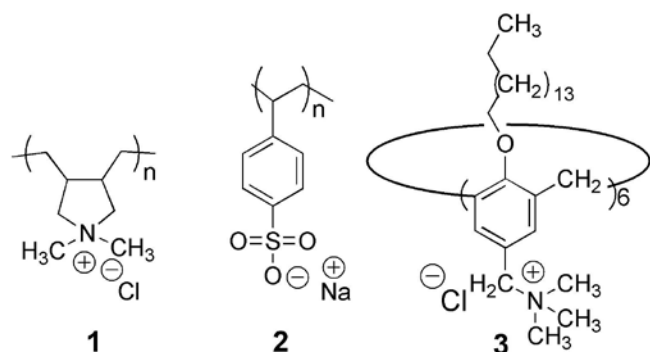


FIGURE 1. Structures of polymers and calix[6]arene-based surfactant used to fabricate PEMs and single LB bilayers.

over N₂ due to favorable differences in diffusivity and solubility. In contrast, a favored diffusivity of the smaller H₂ molecule is offset by the favored solubility of a larger CO₂ molecule, resulting in low H₂/CO₂ selectivity. These results further show that primary amine groups are not required for high CO₂/N₂ permeation selectivity.

TABLE 1. Barrier Properties of Polyelectrolyte Multilayers ($\Delta p=30$ psi, $10^6 P/l$ (cm³/cm²-s-cm Hg))

| PEM | H ₂ | CO ₂ | N ₂ | H ₂ /N ₂ | H ₂ /CO ₂ | CO ₂ /N ₂ |
|--------------|----------------|-----------------|----------------|--------------------------------|---------------------------------|---------------------------------|
| ----- | 620 | 1400 | 260 | 2.4 | 0.44 | 5.4 |
| ----- | 620 | 1500 | 260 | 2.4 | 0.41 | 5.8 |
| 1 + 2 | 48 | 28 | 0.25 | 190 | 1.7 | 110 |
| 1 + 2 | 45 | 19 | 0.18 | 250 | 2.4 | 110 |

2. Single Langmuir-Blodgett Bilayers Made from a Calix[6]arene-based Surfactant and Poly(acrylic acid).

Membrane design:

In Figure 2 is shown our experimental design for hyperthin membranes that were expected to exhibit exceptional permeation selectivity based on molecular sieving. Here, a “porous surfactant” is used to form a monolayer on the surface of an aqueous subphase containing a polymeric counterion. The purpose of the polymer is to stabilize the assembly in its monolayer state and also in a corresponding Langmuir-Blodgett bilayer. If the polymeric network is sufficiently loose, the main barrier for gas transport is then expected to be the pores within the surfactants that make up each monolayer—a situation that

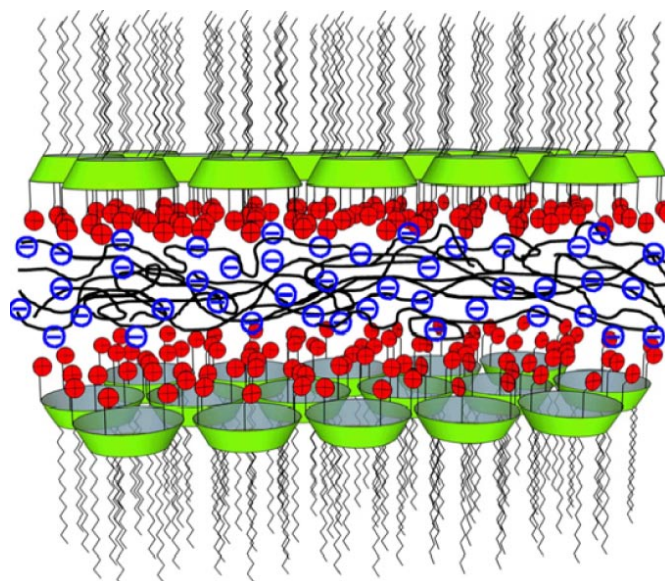


FIGURE 2. Stylized illustration of a perforated LB bilayer that has been stabilized with a polymeric counterion.

could result in molecular sieving action and exceptional size-selectivity.

Results:

Single Langmuir-Blodgett bilayers containing poly(acrylic acid) (PAA) were fabricated using a pH of 3.1 and conditions similar to those previously reported (see publication #4). Table 2 summarizes the barrier properties of these membranes. In brief, significant H₂/CO₂ and CO₂/N₂ permeation selectivities were observed. The fact that these selectivities are similar implies that the permeation of all three gases is dominated by diffusion and permeant size. The slightly greater H₂/CO₂ selectivity is also consistent with a slightly greater difference in kinetic diameters between H₂ and CO₂ compared with CO₂ and N₂.

Table 2. LB Bilayer of 3/poly(acrylic acid) ($\Delta p=30$ psi, $10^6 P/l$ (cm³/cm²-s-cm Hg))

| PEM | H ₂ | CO ₂ | N ₂ | H ₂ /N ₂ | H ₂ /CO ₂ | CO ₂ /N ₂ |
|-------|----------------|-----------------|----------------|--------------------------------|---------------------------------|---------------------------------|
| ----- | 620 | 1400 | 260 | 2.4 | 0.44 | 5.4 |
| ----- | 620 | 1500 | 260 | 2.4 | 0.41 | 5.8 |
| 3/PAA | 5.7 | 0.081 | 0.0024 | 2400 | 70 | 34 |
| 3/PAA | 4.0 | 0.054 | 0.0023 | 1700 | 74 | 23 |

Relationship to Existing Polymeric Membranes.

To judge the intrinsic permeability properties of these hyperthin membranes, we have employed the series resistance model. Thus, if one assumes that the resistance (i.e., the reciprocal of the permeance) of each composite membranes is equal to the sum of the resistances of the hyperthin membrane, itself, and that of the PTMSP support, then the permeance of the hyperthin membrane, $[P/l]_{ht}$, can be calculated from the equation, $1/[P/l]_{composite} = 1/[P/l]_{PTMSP} + 1/[P/l]_{ht}$. Based on the thicknesses of a given hyperthin membrane, one can then calculate its intrinsic permeability coefficient using the equation: $P_{ht} = [P/l]_{ht} \times l_{ht}$. To place these permeation properties into perspective, we have included them in “upper bound” plots for H₂/CO₂ and for CO₂/N₂ in which the permeation selectivity is plotted as a function of the permeability coefficient for the smaller gaseous permeant (not shown). Such plots have previously been constructed for a large series of polymeric membranes (Robeson,

L.M. The Upper Bound Revisited. *J. Membr. Sci.*, **2008**, 320, 390-400). A straight line that can be drawn from such data then defines the highest performing polymeric membranes, and the negative slope reflects a “trade-off” between permeability and permeation selectivity; i.e., the higher selectivity the lower permeability and *vice versa*. The fact that the intrinsic barrier properties of these PEMs and LB bilayers lie *beneath this upper bound* implies that a solution-diffusion mechanism of permeation is dominant in both cases (see publications #2 and #4 for these plots).

Future Directions

The barrier properties of these hyperthin PEMs and LB bilayers that we have investigated are fundamentally different. Studies currently in progress are aimed at obtaining a deeper understanding of these differences, and at exploiting membrane solubility as a means of enhancing H₂/CO₂ and CO₂/N₂ permeation selectivities.

Publications

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2. Wang, Minghui; Janout, Vaclav; Regen, Steven L. Unexpected Barrier Properties of Structurally Matched and Unmatched Polyelectrolyte Multilayers. *Chem. Commun.*, **2013**, 49, 3576-3578.
3. Wang, Minghui; Janout, Vaclav; Regen, Steven L. Minimizing Defects in Polymer-Based Langmuir-Blodgett Monolayers and Bilayers Via Gluing. *Langmuir*, **2012**, 28, 4614-4617.
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6. Wang, Yao; Janout, Vaclav; Regen, Steven L. Creating Poly(ethylene oxide)-based Polyelectrolytes for This Film Construction Using and Ionic Linker Strategy. *Chem. Mater.*, **2010**, 22, 1285-1287.