V.N.3 Gas Transport Across Hyperthin Membranes

Principal Investigator: Professor Steven L. Regen
Department of Chemistry
Lehigh University
Bethlehem, Pennsylvania
Phone: (610) 758-4842
Email: slr0@lehigh.edu

Mr. Minghui Wang
Department of Chemistry
Lehigh University
Bethlehem, Pennsylvania
Phone: (610) 758-3482
Email: miw308@lehigh.edu

Dr. Vaclav Janout
Department of Chemistry
Lehigh University
Bethlehem, Pennsylvania
Phone: (610) 758-3482
Email: vaj2@lehigh.edu

DOE Program Manager: Larry A. Rahn
Phone: (301) 903-2508
Email: Larry.Rahn@science.doe.gov

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., H_2/CO_2 and CO_2/N_2.

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 H_2/CO_2 permeation selectivities (ca. 75) and significant CO_2/N_2 selectivities (ca. 30). In sharp contrast, hyperthin polyelectrolyte multilayers (PEMs), formed from poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrene sulfonate) (PSS) show very low H_2/CO_2 permeation selectivity (ca. 2) but exceptionally high CO_2/N_2 permeation selectivities (ca. 100). The H_2/CO_2 and CO_2/N_2 selectivity found with these LB bilayers is mainly due to differences in diffusivity, which reflect their kinetic diameters (H_2, 0.29 nm; CO_2, 0.33 nm; N_2, 0.36 nm), and also the tightness of the membrane. The very low H_2/CO_2 selectivity and high CO_2/N_2 selectivity associated with these PEMs is mainly the result of a high solubility of CO_2 relative to H_2 and N_2.

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.

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

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

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

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

1. Unexpected Barrier Properties of Polyelectrolyte Multilayers.

Background and Hypothesis

In previous work, we found that certain polyelectrolyte multilayers (PEMs) show CO_2/N_2 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 CO_2/N_2 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 CO_2 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 CO_2/N_2 selectivity of these membranes is in sharp contrast to their very low H_2/CO_2 selectivity. This fact, together with the fact that size difference between CO_2 (0.33 nm) and N_2 (0.36 nm) is similar to the size difference between H_2 (0.29 nm) and CO_2, implies that it is the *solubility* of CO_2 that is largely responsible for such selectivities. More specifically, the permeation of the smaller and more soluble CO_2 molecule is strongly favored
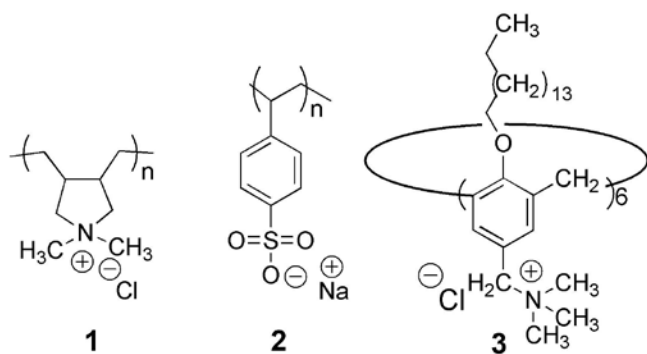
over N_2 due to favorable differences in diffusivity and solubility. In contrast, a favored diffusivity of the smaller H_2 molecule is offset by the favored solubility of a larger CO_2 molecule, resulting in low H_2/CO_2 selectivity. These results further show that primary amine groups are not required for high CO_2/N_2 permeation selectivity.

TABLE 1. Barrier Properties of Polyelectrolyte Multilayers (Δp=30 psi, $10^6 P/l$) (cm^3/cm^2-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
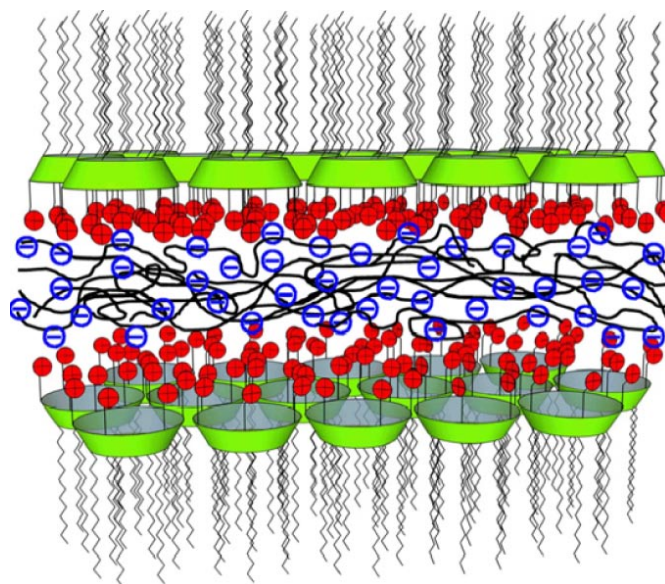

FIGURE 1. Structures of polymers and calix[6]arene-based surfactant used to fabricate PEMs and single LB bilayers.

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 H_2/CO_2 and CO_2/N_2 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 H_2/CO_2 selectivity is also consistent with a slightly greater difference in kinetic diameters between H_2 and CO_2 compared with CO_2 and N_2.

Table 2. LB Bilayer of 3/poly(acrylic acid) (Δp=30 psi, $10^6 P/l$) (cm^3/cm^2-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 H_2/CO_2 and for CO_2/N_2 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 mechansim 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 H_2/CO_2 and CO_2/N_2 permeation selectivities.

Publications

1. Wang, Minghui; Janout, Vaclav; Regen, Steven L. Gas Transport Across Hyperthin Membranes. *Accounts of Chemical Research,* **2013,** DOI: 10.1021/ar3002624.

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.

4. Wang, Minghui; Janout, Vaclav; Regen, Steven L. Hyperthin Organic Membranes with Exceptional H_2/CO_2 Permeation Selectivity: Importance of Ionic Crosslinking and Self-Healing. *Chem Commun.* **2011**, *47*, 2387-2389.

5. Wang, Minghui; Janout, Vaclav; Regen, Steven L. Glued Langmuir-Blodgett Bilayers From Calix[n]arenes: Influence of Calix[n]arene Size on Ionic Crosslinking, Film Thickness and Permeation Selectivity. *Langmuir*, **2010**, *26*, 12988-12993.

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.