BARRIER MEMBRANES WITH HIGH CONCENTRATIONS OF ALIGNED IMPERMEABLE FLAKES

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We have been developing barrier membranes containing aligned mineral flakes [1-5]. Because these mineral flakes are crystalline, their very low permeabilities can reduce the permeability of the composite film. However, the mechanism of reduction remains controversial. Many expect that the permeability change will vary linearly with the volume fraction of flakes; others, including us, think that it will vary more nearly with the square of this volume fraction. There are similar disagreements about how the permeability will vary with flake shape, usually expressed as an aspect ratio.

In this paper, we want to begin to resolve these ambiguities, primarily by measuring diffusion of gases or aqueous acids and bases across rubbery polymer membranes containing flakes of mica, vermiculite, and montmorillonite. We begin by reviewing past theories which predict these effects, and then describe how our measurements are made. We conclude by reporting the measurements themselves, and by discussing their implications for practical barrier coatings.

The prediction of relative permeability for periodically aligned impermeable flakes depends on the direction of alignment. If the flakes are aligned perpendicular to the barrier surface, they have a minor effect; if they are aligned parallel to the surface, their effect is much larger. We are interested in the latter case, when the flakes are parallel to the membrane's surface. We are also interested in a dilute suspension of flakes, where the volume fraction is small ($\phi << 1$). There are two dilute limits which depend on the aspect ratio α, defined as half the flake width divided by its thickness [6]. When $\phi << 1$ and $\alpha\phi < 1$, the suspension's permeability is predicted to be [7]:

$$\frac{P_o}{P} = 1 + \alpha\phi \tag{1}$$

However, when $\phi << 1$ but $\alpha\phi > 1$, the suspension, now termed "semi-dilute," has a relative permeability equal to [1,8]

$$\frac{P_o}{P} = 1 + \mu\frac{\alpha^2\phi^2}{1-\phi} \tag{2}$$

where μ is a geometric parameter. The dependence on the square of volume fraction ϕ and aspect ratio α is a consequence of the increased tortuosity and of the reduced area available for diffusion.

We will use Equations 1-2 to analyze the measurements in this paper. We are particularly interested in the prediction of these equations that the relative permeability (P_o/P) is independent of the continuum permeability P_o and of the flake size. We want to test whether the relative permeability varies with the volume fraction to the first or second power. These comparisons of theory and experiment should improve the rationale for developing better barrier membranes.

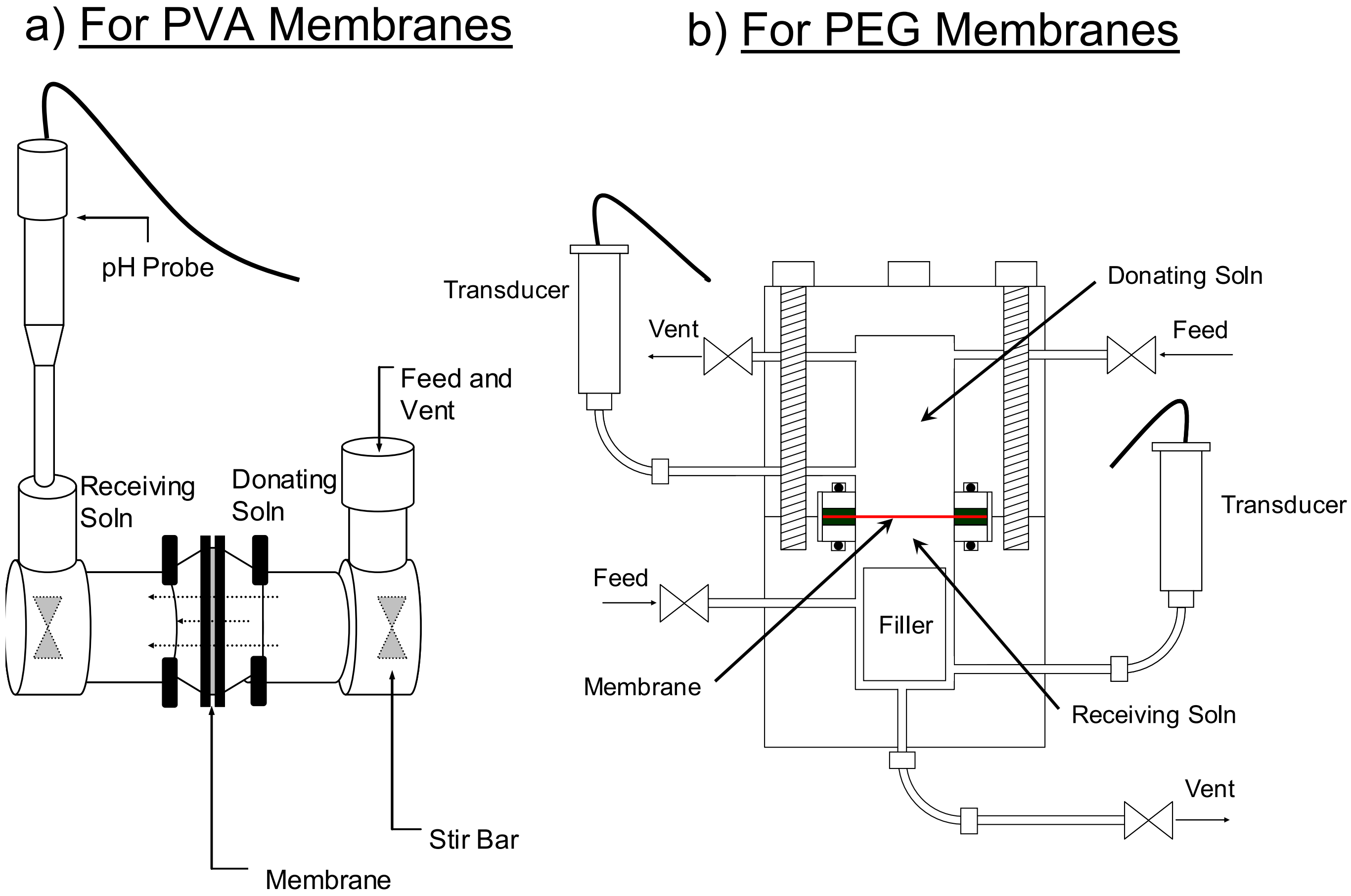
Transport across the PVA and PEG membranes was measured in a diaphragm cell [9]. The PVA liquid transport measurements used a cell with a membrane separating two stirred compartments, as shown in Figure 1a. The "donating" compartment normally contained 0.1 M HCl but occasionally

0.1 M NaOH. The "receiving" compartment initially contained pure water and a pH probe, used to calculate the acid or base concentration.

Because measurements were made at short times when the concentration in the receiving compartment was less than five percent of that initially in the donating compartment c_{10}, this receiving concentration varied linearly with time, with slope *m*. This linearity was observed after a lag time t_L. The membrane's permeability *P* was found from the relation

$$P = \frac{mV\ell}{c_{10}A} \tag{3}$$

where *V* is the volume of the receiving compartment; and *A* and ℓ are the membrane's area and thickness, respectively.


a) For PVA Membranes

b) For PEG Membranes

Fig. 1. Diaphragm cells. For PVA membranes, acid and base diffusion is measured with a pH meter as shown in (a). For PEG membranes, gas transport is recorded as pressure changes illustrated in (b).

Transport measurements in gases across the PEG membranes used a different diaphragm cell, which is shown in Figure 1b. This cell used a membrane clamped between donating and receiving compartments. Occasionally, a brass plug was added to reduce the volume of the receiving compartment and thus allow a shorter experiment. After flushing, approximately 100 kPa of helium was added to the donating compartment, and the pressure difference between the compartments was measured with two pressure transducers as a function of time. The permeability P was calculated from these differences by means of the equation [9]

$$P = \frac{\ell}{At\ \frac{1}{V'}+\frac{1}{V''}} \ln\frac{\Delta p_o}{\Delta p} \tag{4}$$

where Δp_o and Δp are the pressure differences initially and at time t, respectively; and V' and V'' are the volumes of the two compartments.

The measurements of flake alignment depend on micrographs and X-ray scattering. The SEM pictures show that vermiculite and mica are well dispersed in PVA, with flakes aligned parallel to the membrane surface. In these cases, the alignment is probably largely due to evaporation, although the shear in casting the membrane may also have an effect [4]. X-ray scattering data give a measure of alignment over a larger sample than that covered by the micrographs. As a result, they are a more effective test. Data for mica and vermiculite in PVA show the sharp spots characteristic of good alignment.

Equation 2 is tested by the correlation given in Figure 2a. The open symbols, which are results of this work, include the two polymers PVA and PEG; the three flakes mica, vermiculite, and montmorillonite; and the three solutes HCl, NaOH, and helium. The closed symbols, which are the results of others [1-3,10,11], include flakes of mica, nylon, and clay, and the polymers polydimethylsiloxane and polycarbonate. The correlation with $(1 + \alpha^2\phi^2 / (1 - \phi))$ is successful.

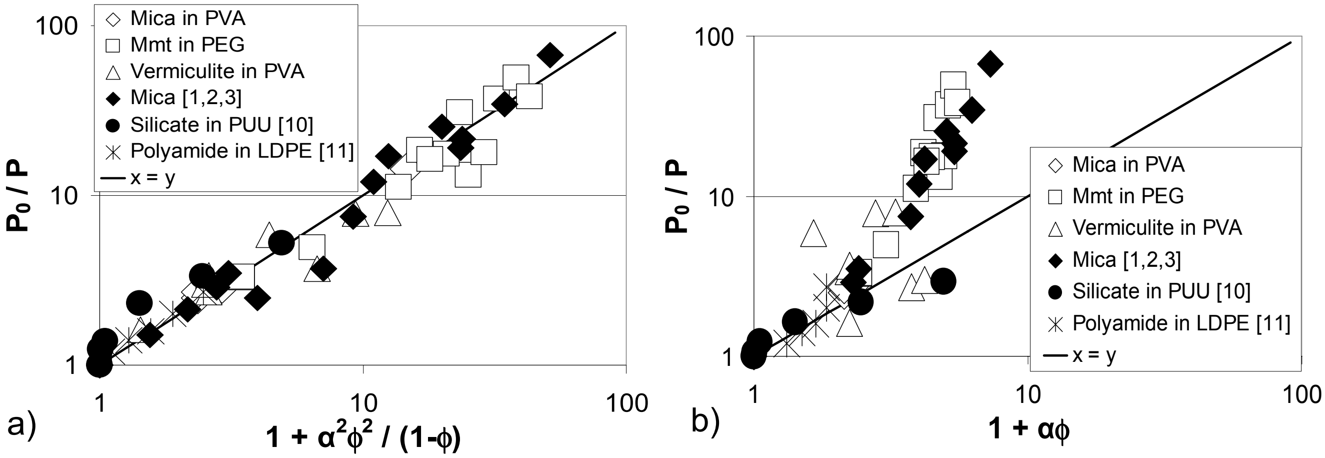


Fig. 2. Permeability vs. flake concentration and aspect ratio. The results in part (a) are consistent with the semi-dilute limit in Equation 2. The results in part (b) show that the data are not described as well by the dilute limit in Equation 1. Data from References [1-3, 10, 11] are included.

We expect that the permeabilities in Figure 2 will be correlated by Equation 2 because we are in the semi-dilute region, when $\alpha\phi > 1$. We would not expect Equation 1 to apply because we are not in the dilute region, when both $\phi << 1$ and $\alpha\phi < 1$. The data in Figure 2b, which are the same as those in Figure 2a, show that Equation 1 is less successful. Thus the change in permeability does seem to vary with ϕ^2 for the cases considered here. However, we recognize that this may not be true if the flakes are not well aligned or periodically arrayed. For example, if the flakes settle, the permeability change may vary with the apparent ϕ even in the semi-dilute case [12].

The prediction that permeability varies with the square of $(\alpha\phi)$ is also true for other, older data also plotted in Figure 2. These results on different chemical systems reinforce the argument that good barriers should be semi-dilute solutions, not dilute solutions. In a semi-dilute solution the flakes overlap: while $\phi << 1$, $\alpha\phi > 1$. Thus diffusion through the composite film involves a lot of wiggles, which increase the path length for diffusion by a factor proportional to $(\alpha\phi)$. Diffusion is also through a reduced cross sectional area, which is proportional to $\alpha\phi / (1 - \phi)$. It is this combination of increased path length and reduced area which is responsible for the variation predicted by Equation 2.

Finally, we want to discuss the changes in permeability vs. changes in mechanical properties. We are getting smaller permeabilities by means of a composite material. But we recognize that it is less flexible. To see how much the flexibility is compromised, we turn to Halpin-Tsai equations [13]. Two limits of these equations are interesting. First, when the flakes have an extremely large aspect ratio, we have

$$\frac{E}{E_o} = 1 + \frac{E_F\phi}{E_o} \tag{5}$$

This says that the composite is very brittle indeed, with a Young's modulus closely related to that of the flakes themselves. Second, when the aspect ratio is more modest but the flakes themselves are still brittle, we have

$$\frac{E}{E_o} = 1 + \frac{4\alpha\phi}{1-\phi} \tag{6}$$

This relation says that the composite is certainly less elastic than the continuum, but not dramatically so.

We can now compare the result for permeability in Equation 2 with that expected for Young's modulus from Equations 5-6. Equation 2 says that we want the aspect ratio α to be as big as possible. However, Equations 5-6 imply that we want α to be smaller than (E_F / E_o). We must compromise. For the systems we are studying here, (E_F / E_o) is about 10^4 [14], so α should be less than perhaps 10^3. This is still much larger than the value for α of around 30 typical of our experiments. Thus we should be able to get still less permeable films without seriously compromising their mechanical properties. We plan to continue experiments which seek this goal.

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