Barrier Membranes with Tipped Impermeable Flakes

Diana M. Eitzman, R. R. Melkote, and E. L. Cussler
Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

Diffusion of carbon dioxide through silicone-polycarbonate membranes containing oriented mica flakes is proportional to the square of the volume fraction of the flakes, to the square of the aspect ratio, and to the square of the cosine of the angle at which the flakes are oriented. These experiments are consistent with Monte Carlo simulations. The simulations allow investigation of more complex geometries, including other flake orientations and polydisperse flake sizes.

Introduction

Diffusion coefficients are often described with simple models. Perhaps the simplest is the Stokes-Einstein equation, which gives the diffusion coefficient D_o for a solute sphere of radius a diffusing in a continuum of viscosity μ (Einstein, 1905):

$$D_o = \frac{k_B T}{6\pi\mu a} \tag{1}$$

Another common model (Maxwell, 1881) describes the diffusion coefficient D of a small solute through a continuum partly filled with a suspension of impermeable spheres:

$$\frac{D}{D_o} = \frac{1-\phi}{1+\phi/2} \tag{2}$$

where D_o is the diffusion coefficient in the absence of the spheres and ϕ is the "loading," that is, the volume fraction of the spheres. This is a small effect: if ϕ equals 0.1, the diffusion drops about 15%.

This article is concerned with the diffusion of a small solute through a continuum partly filled with a periodic suspension of impermeable flakes. The flakes, as shown in Figure 1, are assumed very long normal to the figure, so that the diffusion is essentially two-dimensional. This diffusion depends strongly on the orientation of the flakes. If the flakes are all oriented parallel to the direction of the diffusion, as shown in Figure 1a, the result is approximately:

$$\frac{D}{D_o} = 1-\phi \tag{3}$$

where D_o is again the diffusion coefficient in the absence of flakes and the loading ϕ is now the volume fraction of the flakes. This is similar to Maxwell's result for spheres; like that result, it predicts that D is only slightly different than D_o. Again, if ϕ equals 0.1, the diffusion drops 10%.

The result is very different when the impermeable flakes are oriented perpendicular to the direction of diffusion, as shown in Figure 1b. In this case, the result depends strongly on the microstructure of the flakes, and more specifically on the location of the slits between adjacent flakes. When these

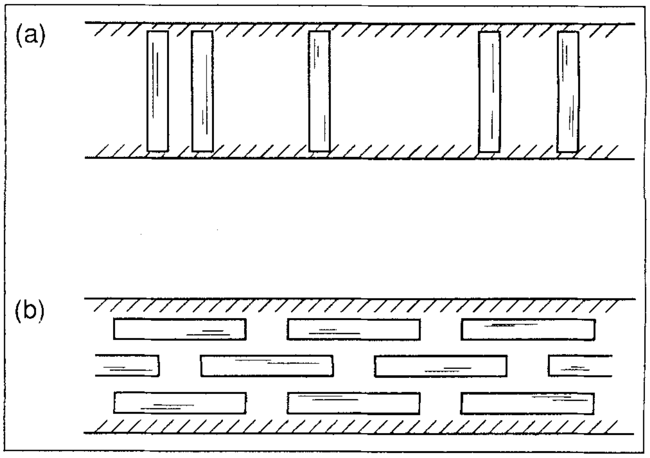

Figure 1. Flake-filled films.

Diffusion across these films is changed only slightly when the flakes are parallel to the diffusion (a), but can be reduced dramatically when the flakes are normal to the diffusion (b).

slits are oriented on top of one another, diffusion takes place quickly across the flake-filled film. When the slits between the flakes are staggered, as shown in Figure 1b, diffusion is greatly retarded by three factors: the tortuous wiggles to get around the flakes, the tight slits between the flakes, and the uncertain resistance of turning the corner to go from the wiggle into the slit.

This article focuses on the case where diffusion is most retarded by the wiggles, because this case is shown experimentally to be the most significant (Ramal and Jinnah, 1984; Cussler et al., 1988). The article deliberately focuses on limits where the slits and the turning have relatively little effect. It recognizes that the wiggles both increase the length for diffusion through the composite, and decrease the cross-sectional area through which the diffusion can occur. While past studies have always included the effect of the increased length, some (Barrer, 1968; Michaels et al., 1975) appear to have neglected the reduced cross-sectional area.

When the diffusion is dominated by wiggles around the flakes, the result is (Cussler et al., 1988)

$$\frac{D}{D_o} = \frac{1}{1 + \alpha^2\phi^2/(1-\phi)} \tag{4}$$

where α is the aspect ratio of the flakes. Flakes have one small dimension and two much larger dimensions; here, the aspect ratio is defined as half the second largest dimension divided by the smallest dimension. Now D can be very different than D_o. For example, when the aspect ratio equals thirty and ϕ equals 0.1, D is a tenth of D_o.

However, while the effect of flakes is larger, the equation for flakes in Eq. 4 still has strong parallels with the result for spheres in Eq. 2. In both cases, the altered diffusion depends not on the size of the impermeable material, but only on its volume fraction. It does not matter if the flakes are mica chips or pages of a lab notebook: if the flakes have equal aspect ratios, equal volume fractions, and equal spacing, then their effect on diffusion is the same. Equation 2 and Eq. 4 also predict that the ratio D/D_o is independent of D_o. It does not matter if the impermeable material is put into wax or into polyvinylchloride; the ratio D/D_o depends only on the shape and the volume fraction.

The result for flakes given in Eq. 4 does depend on serious assumptions which appear to be experimentally justified. One assumption, that the flakes are oriented like bricks in a wall (cf. Figure 1b), was discussed earlier (Cussler et al., 1988). A second assumption that the flakes are oriented perpendicular to the diffusion is explored in this article in two ways. First, the changes of solute movement through arrays of flakes which are perfectly and imperfectly oriented are explored with Monte Carlo simulations. Second, carbon dioxide transport measurements are reported across silicone rubber membranes containing flakes which are either perfectly oriented or disoriented by known amounts. Comparing the simulations and the experiments tests the validity of Eq. 4.

Theory

Presently, there is no general analytical model which can accurately predict the rate of solute transport through a composite of arbitrarily oriented flakes. The models developed in our laboratory (Cussler et al., 1988; Perry et al., 1989) are experimentally supported, yet rely on many approximations and idealizations. A more flexible model for predicting transport in less idealized composites begins with the ideas of Reyes and Iglesia (1991), as applied by Melkote and Jensen (1990, 1992) to gas diffusion in fibrous materials. A composite medium is constructed in a unit simulation volume. Monte Carlo simulations of molecular trajectories through this medium are interpreted via a mean-square displacement technique based on Brownian motion. In the case of diffusion in dense fluids where the mean free path is much smaller than the distance between flakes, an enormous amount of computational time would be required to probe the structure completely. Instead, a hybrid technique is used which averages the Brownian motion when far away from any flake and which follows a discrete step-by-step technique when near a flake. In particular, when a solute particle is away from any solid surface, it is allowed to advance a significantly longer distance than one mean free path. This large step is then converted to the distance that would have been traveled if the molecule were following a random walk.

The specific two-dimensional system for study is a rectangular cross section of impermeable flakes in a solvent continuum. The flakes are modeled as rectangles of equal size, always oriented so that the flake centers of one course are directly above the slits in the courses above and below (cf. Figure 1b). The size of the slits is taken as equal to the average distance between the flakes. The loading of the flakes, the maximum number of flakes, and their orientation serve to define the cross section of a unit cell. For example, for a membrane containing flakes of identical size and aspect ratio, positioned perpendicular to the direction of diffusion, the resulting cross section is shown in Figure 2a. As a second example, for random orientations, one resulting cross section is shown in Figure 2b. A third example for the case where the fillers are all positioned at a single orientation other than zero degrees is shown in Figure 2c.

The trajectories for the diffusing solute particles can then be calculated in this unit cell. The start for each particle trajectory is a randomly picked point near the center of the cross section. If the location picked falls outside of a flake, it is kept as an initial starting point; if it falls inside a flake, it is discarded but used to check the calculated value for the loading. The distance from this starting point to the surface of the nearest flake is then determined. If this distance is large compared to the mean free path, the particle is allowed to advance to a random point on the circumference of an imaginary circle of which the radius is equal to the distance to the

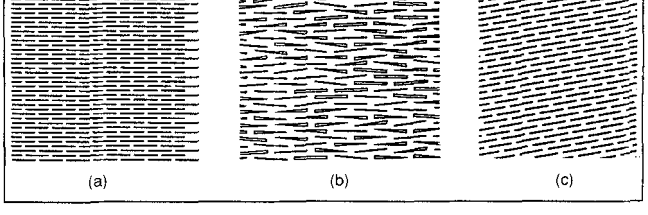

Figure 2. Typical cross sections of flake-filled films.

The flakes in (a) are regularly spaced perpendicular to the diffusion; those in (b) are randomly oriented; those in (c) are all at a fixed angle not perpendicular to diffusion.

nearest flake. The time it would take a trajectory to reach this position R for the first time, if it were following a random walk, is approximated as $R^2/4D_o$ (Siegel and Langer, 1986; Zheng and Chiew, 1989; Eitzman, 1992). This relation is valid only if the trajectory is large compared to the mean free path, and is not valid at regions close to the surface of a flake.

The region around the surface of each flake where the particle moves by taking steps equivalent to a mean free path implies an imaginary boundary layer. In our calculations, the boundary layer thickness is assumed equal to five mean free paths. When the advancing trajectory is this close to a flake, the particle is advanced in a random direction, a distance equivalent to the mean free path. In these calculations, the mean free path is taken from an exponential distribution of molecular mean free paths (Loeb, 1934; Eitzman, 1992). When this distance intersects a flake, the particle stops at the surface.

After the surface is hit, the particle moves a mean free path away from the flake in a random direction. It is then advanced a mean free path in a random direction until it again hits a flake or until it leaves the boundary layer. After it advances out of the boundary layer, its path is calculated as above. The resulting trajectory, exemplified by Figure 3, makes it possible for a trajectory to probe many layers of flakes in a reasonable time.

Calculating the ratio of actual to effective diffusion coefficients requires estimating the mean-square displacement as a function of time. The mean-square displacement in the x-direction is simply the square of the x-distance from the initial starting point. The time is proportional to the total distance traveled. When we plot the mean-square displacement vs. the total distance traveled, the slope of the plot is proportional to the diffusion coefficient. For one trajectory, the data scatter widely (cf. Figure 4a); however, for many trajectories, the data show reliable slopes with a correlation coefficient routinely above 0.995 (cf. Figure 4b). The slope of this plot yields the desired ratio (Eitzman, 1992):

$$\frac{D_o}{D} = \frac{2\lambda}{3(\text{slope})} \tag{5}$$

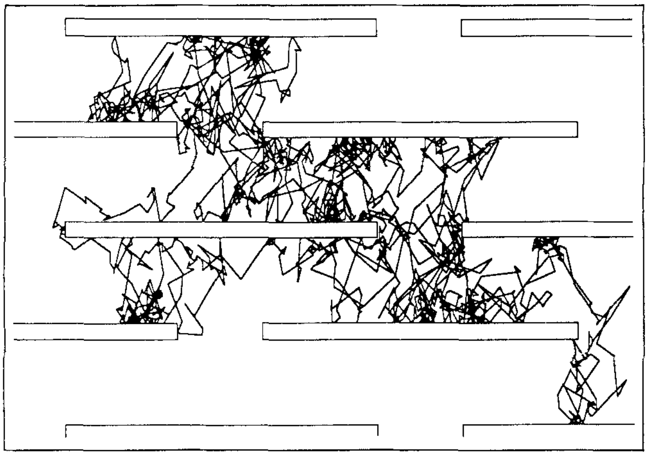

Figure 3. Typical path in a flake-filled film.

The displacement and the total distance traveled give a measure of diffusion.

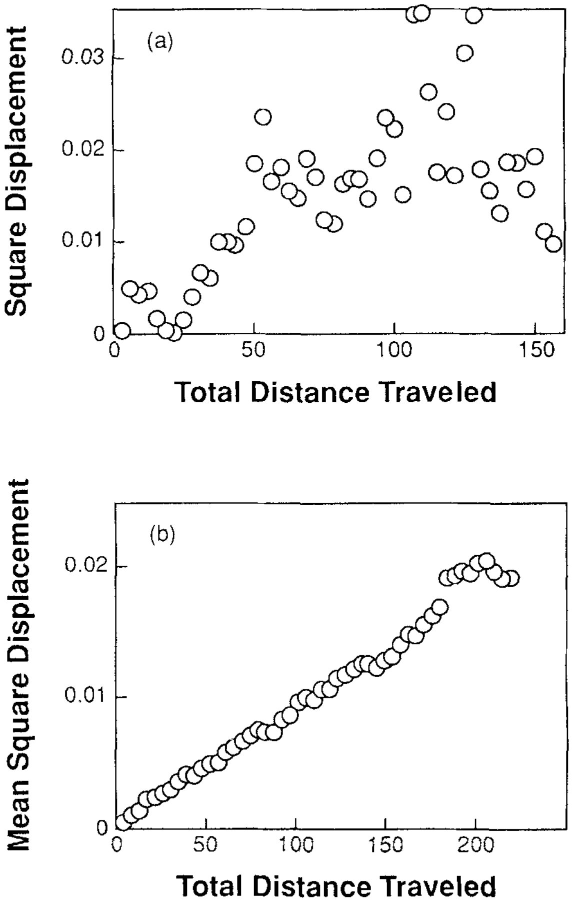

Figure 4. Calculating the diffusion coefficient.

Since the total distance traveled is proportional to the time, the slope on these graphs is proportional to the ratio of diffusion coefficients. For one trajectory (a), the slope is uncertain; for many (b), it is well-known.

where D_o and D are again the diffusion coefficients without and with flakes, respectively; and λ is the mean free path used in the calculation.

Two tangential but important aspects of the calculation merit mention. The first of these is the Knudsen number, the ratio of the mean free path to the distance between the flakes. This number must be less than one in order to use the method described above; at the same time, this number must be as large as possible to minimize the computational time. Experiments at different Knudsen numbers show that the answers are constant when this number is less than 0.1, so this value was used in the calculations.

The second important aspect of the calculation is the number of layers of flakes traversed. The results become independent of the number of layers only after five or more layers are probed so this value was used in the simulations. Probing five layers increases the probability that some solute particles escape from the unit cell. If a trajectory reaches the edge of the unit cell, the particle escapes if the flakes are oriented in any direction other than zero degrees. If the flakes are all at zero degrees, the trajectory is allowed to reenter the original structure in the location where it would be if the structure repeated itself. In every case, the unit cells are large enough so that fewer than five percent of particles escape.

Experimental

Materials

The experiments require choosing a diffusing solute, a polymer continuum, and an impermeable flake. The diffusing solute was chosen as reagent grade carbon dioxide (Praxair, Somerset, NJ), because it is highly permeable, nontoxic, and easy to analyze. The polymer continuum was a block copolymer of silicone and polycarbonate (Membrane #213, Oxygen Enrichment Co., Troy, NY). This polymer's high permeability for carbon dioxide (10^{-5} cm^2/s) allowed quick experiments and was easily made into sturdy membranes.

The impermeable flakes were chosen as mica and vermiculite clay. The surfactant treated mica (Ward et al., 1991) was readily dispersed in organic solvents. These mica particles were separated into 38, 53, 105, 150 and 300 μm samples with a sonic sifter (model L4P, ATM Corp., Milwaukee, WI). Vermiculite (W. R. Grace, Columbia, MD) was treated to separate the layers and make it dispersible in organic solvents. The procedure, suggested by Gaines (1990), closely follows that described by Ballard and Rideal (1983). These particles were separated into 105, 225, and 500 μm sizes with polyethylene sieves (Spectrum Medical, Los Angeles, CA).

Membranes

The membranes used in this work were made by casting polymer solutions containing dispersed flakes onto glass plates. To facilitate removing each membrane, the plate was first coated with an 0.1% polyisoprene (Aldrich) solution in chloroform cast at a thickness of 3 mil with a casting blade (Model AG-4302, Gardner-Neotec, Silver Spring, MD). The plate was then coated with a 10% silicone-polycarbonate solution cast at a thickness of 5 mil. The plate was covered with a dish and the solvent from the film allowed to evaporate for at least 6 h. The suspension containing the flakes was cast as a third layer 10 mil thick. Once the solvent had evaporated, at least two more flake-filled layers were added. The final layer of the membrane was cast from the flake-free silicone-polycarbonate solution. The membrane was removed from the glass plate by placing it in water, using a razor blade to release the upper edge and then gently pulling up from the released edge.

Many of the membranes studied in this work used this preparation, for it gives flakes which are oriented parallel to the membrane surface, as shown in Figure 5a. These give the greatest reduction in diffusion, and hence the best barrier properties. Membranes with tipped flakes were also prepared, as follows. A "membrane" of the same solutions used above with 20 or more 0.1 cm layers was cast in a Teflon mold 6.5×5.0×2.5 cm. Each chloroform solution was carefully degassed before casting; each layer was dried by placing the mold in a partially covered desiccator for at least one day. This procedure avoided bubble formation during drying and prevented the polymer composite from pulling away from the sides of the mold. Micrographs of these membrane blocks showed flakes oriented parallel to the block's surface (Eitzman, 1992).

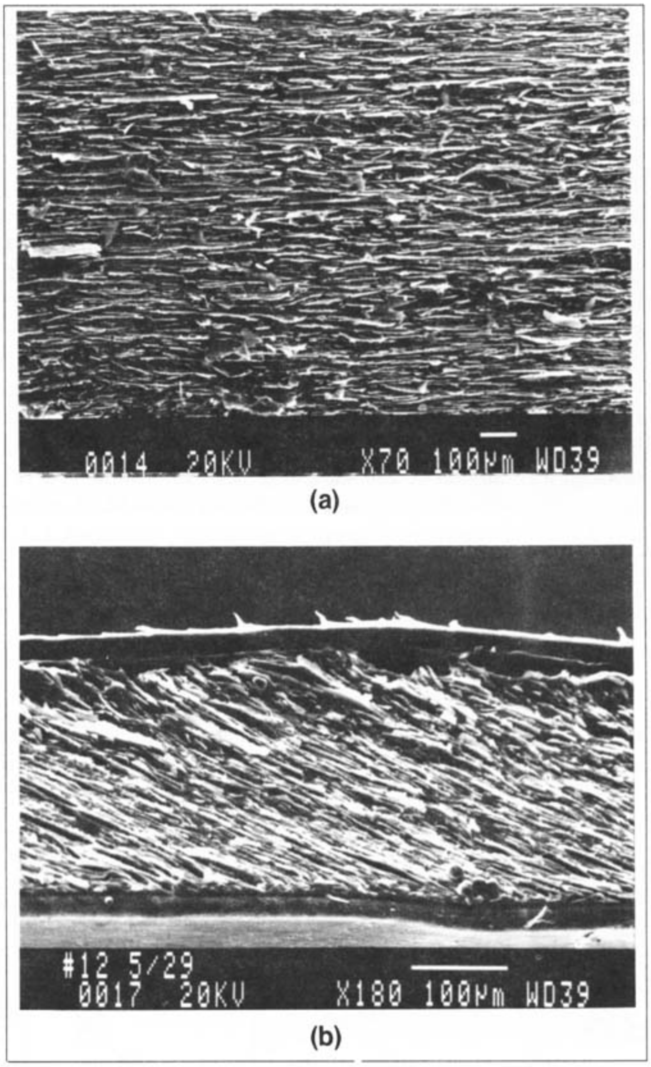

Figure 5. Micrographs of mica-filled silicone polycarbonate films.

The film in (a) has flakes perpendicular to the diffusion; (b) has flakes tipped at a fixed angle.

Preliminary 0.2 cm slices were then cut out of these blocks at 0°, 30°, 45°, 60°, and 90° with a jeweler's saw. These slices were attached with cyanoacrylate adhesive (Carl Goldberg, Chicago, IL) to a specially constructed aluminum stage, cooled with a dry ice-isopropanol bath. With this stage mounted in a freezing microtone, 120–150 μm membranes with flakes oriented at a known angle were cut. Micrographs showed that this cutting procedure did not disrupt the flakes' orientation. However, in some cases, surface cracks developed between the polymer and the flakes. Dip coating the membrane slices with additional polymer solution did not fill these cracks. Instead, the slice was clamped between two pieces of microporous polypropylene film (Celgard, Hoechst-Celanese, Charlotte, NC) coated with incompletely dried silicone-polycarbonate solution. The orientation of the flakes was uniform, as exemplified by the membrane shown in Figure 5b.

Apparatus and procedure

The permeability of the membranes was measured with a flow diffusion cell. The membrane was mechanically stabilized in the cell by placing it between two Teflon coated 4.7

cm metal support screens (250 μm pores, XX4404702, Millipore, Bedford, MA). The edge of the screens was sealed with high vacuum grease. This sandwich structure was mounted with greased O-rings in a stainless steel filter holder (XX4404700, Millipore, Bedford, MA) modified by drilling taps to give an inlet and an outlet on each side of the cell. The exposed area of the membrane was 11.6 cm^2; the chamber on each side of the membrane had a volume of approximately 2.0 cm^3. Gases of known concentration flowed at 23.5°C past each side of the membrane. The gas fed to the feed side of the cell was pure carbon dioxide at 5 L/min or more. The pressure of this stream was controlled with a regulator (Veriflow, Richmond, CA) and monitored with a gauge (model 12728-1, Victor, San Francisco, CA). The gas fed to the permeate side at 20 cm^3/min was 0.25% carbon dioxide in helium (Praxair, Somerset, NJ). The permeate gas flowed through a rotameter to the sample port of a continuous thermal conductivity detector (model 20-260, Gow-Mac) monitored with a transducer (Omega Engineering, Stamford, CT). The membrane permeability P is calculated from:

$$P = \frac{(c_{\text{out}} - c_{\text{in}}) Q \ell}{A(c_{\text{feed}} - c_{\text{in}})} \tag{6}$$

where c_{feed}, c_{in}, and c_{out} are the concentrations in the feed and in the permeate inlet and outlet, respectively; Q is the volumetric flow rate of the permeate stream; ℓ is the membrane thickness; and A is the exposed area of the membrane. The ratio of measured permeabilities with and without flakes is assumed equal to the ratio (D_o/D).

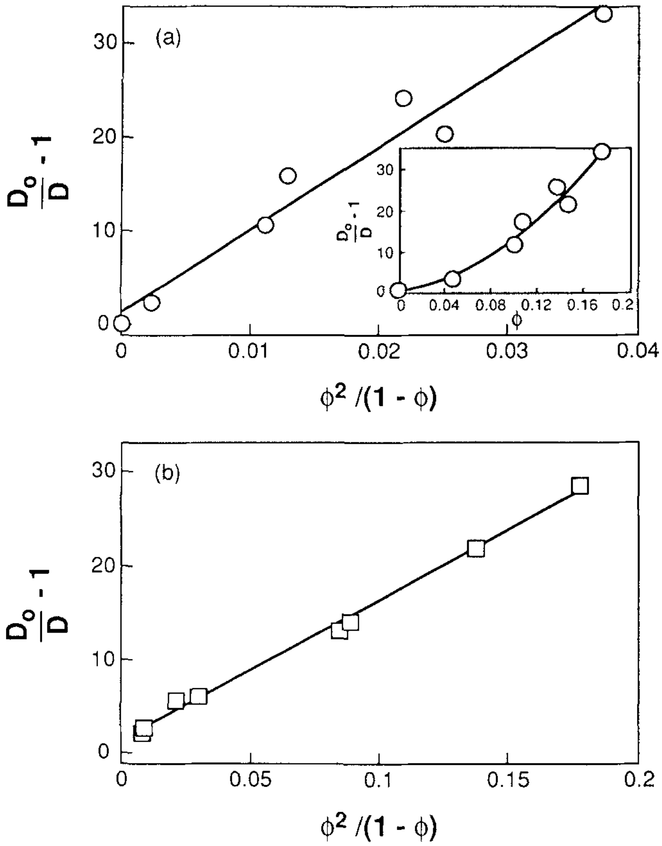

Figure 6. Diffusion vs. loading.

Carbon dioxide transport in (a) and Monte Carlo simulations in (b) vary linearly with $\phi^2/(1-\phi)$, but not with ϕ as shown in the inset. This is consistent with analytical models.

Results

This work includes studies of the effects on diffusion of flake loading, aspect ratio, orientation, and polydispersity. Measurements and simulations on the effects of loading ϕ, as shown in Figure 6, use flakes which are parallel to the membrane surfaces, and hence perpendicular to the membrane diffusion. This orientation is expected to give the largest effect on diffusion.

The experimental values of carbon dioxide diffusion in Figure 6a show that the altered diffusion varies with $\phi^2/(1-\phi)$, as predicted by analytical approximations of these effects. The data in the inset of Figure 6a show that the altered diffusion varies nonlinearly with the loading, which is inconsistent with the theory of Barrer (1968). The aspect ratio inferred from the slope of these data is 30. While the aspect ratio measured for these flakes ranges widely from 10–150, the weighted average is 50 in the same range as the experimental inference.

These measurements of carbon dioxide diffusion show the same variations with loading as those predicted with the simulations, shown in Figure 6b. In this simulation, the aspect ratio is 20, the ratio of flake spacing to slit size is 1.0, and the fillers are all oriented at 0°. The simulation does not depend on any assumptions about carbon dioxide or membrane polymer chemistry, but only on geometry. Thus, both experiments and simulations are consistent with each other, with the analytical models, and with the earlier experiments.

Experiments with mica samples of varying aspect ratio, shown in Figure 7a, support the prediction that the ratio D_o/D increases with the square of the aspect ratio. Like the mica experiments, the simulation results in Figure 7b also show D_o/D varying with the square of the aspect ratio. These simulations assume a loading of 0.1, a flake orientation of 0°, and a ratio of flake spacing to slit size of 1.0.

Interestingly, results with vermiculite flakes, prepared in the same way, are different. When the same size vermiculite flakes are cast into membranes at different loadings, D_o/D is proportional to $\phi^2/(1-\phi)$, just as predicted. However, membranes with different sizes of vermiculite flakes give approximately the same fluxes when the volume fraction of flakes is the same. In other words, the largest particles reduce the flux by the same amount as the smallest particles. This result was puzzling until scanning electron microscopy revealed that the largest flakes are thicker than the smallest flakes, so all vermiculite particles have approximately the same aspect ratio (Eitzman, 1992). This inadvertently verified the theory's prediction that diffusion depends on flake aspect, but not on flake size.

Finally, the effects of flake orientation for carbon dioxide transport are shown for small angles in Figure 8a. Tipping the flakes is a major effect: even changing the orientation from 0° to 10° reduces the effect of the flakes by about 40%. These experimental results agree closely with the simulation, shown as the solid line in Figure 8a. This simulation assumes a flake-filled film with a loading of 0.10 and an aspect ratio of 30. The loading is that used in the experiments; the aspect

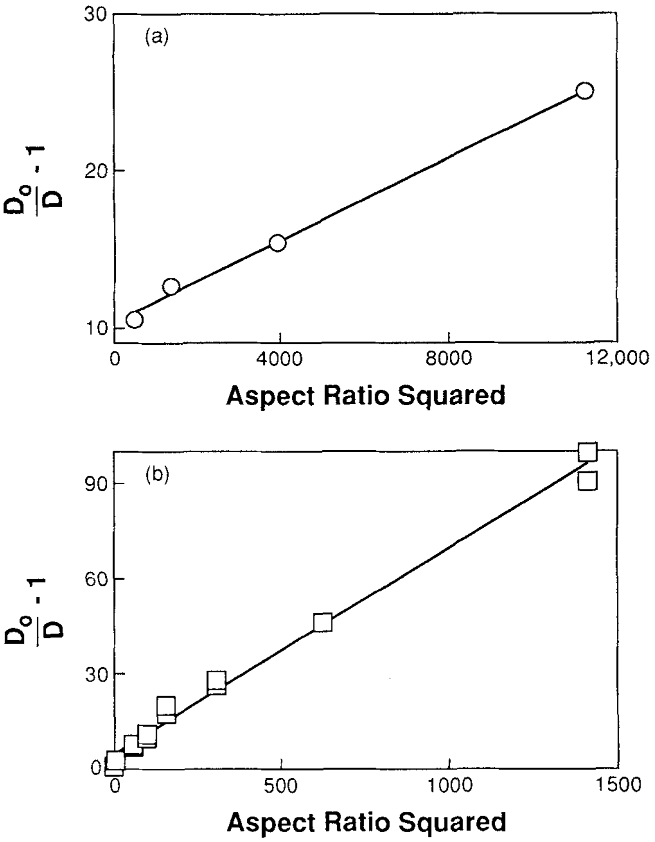

Figure 7. Diffusion vs. aspect ratio.

Diffusion varies with the square of aspect ratio, both for carbon dioxide diffusing across mica filled membranes (a) and for Monte Carlo simulation (b).

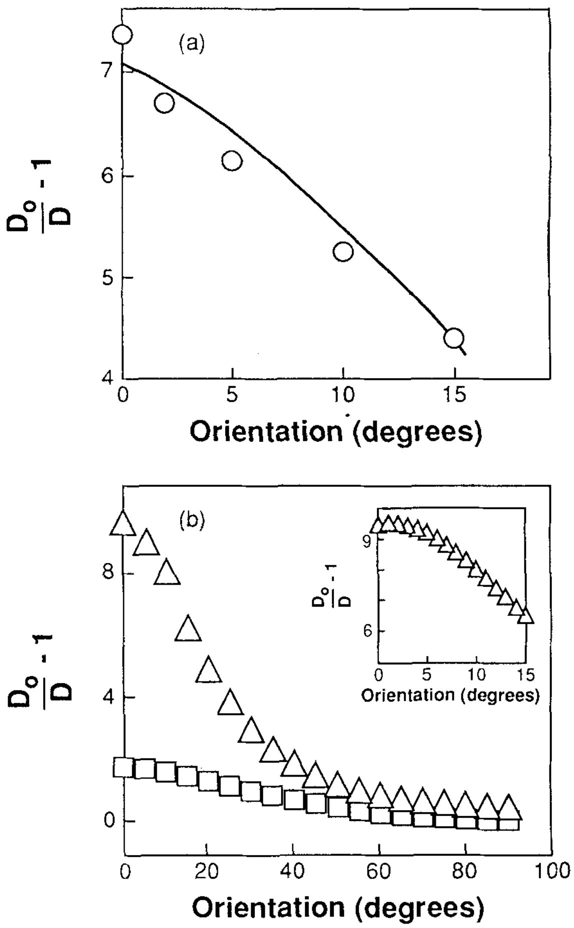

Figure 8. Diffusion vs. flake orientation.

Experiments at small angles (O) agree with simulations (——) (a). Simulations in (b) show the effect of small and large angles. The triangles and squares are for aspect ratios of 30 and 10, respectively.

ratio, inferred from the slope of the data in Figure 6a, is consistent with the size range of the mica used.

Unfortunately, the close agreement between experiment and simulation observed at small angles could not be verified at larger angles, because the experimental data scatter. The simulations shown in Figure 8b give a more reliable picture. Again, the loading is assumed 0.1 and the ratios of flake to slit size is taken as 1.0. As expected, the effect on diffusion is greatest at small angles. It is strongly dependent on angle, with an inflection at around 15°. However, at the small angles shown in the inset of Figure 8b, the diffusion becomes less dependent on angle, perhaps implying a cosine dependence. This point is discussed below.

The effect of flake polydispersity was studied for the specific case of a varying aspect ratio. In this study the flakes were still regularly ordered, as in Figure 1b; however, their aspect ratios were assumed to fit a Gaussian distribution whose standard deviation was either 10% or 30% of the mean aspect ratio. The random structures generated with these characteristics are exemplified by one structure with a 10% variation as shown in the inset of Figure 9. The simulated diffusion ratios, shown in the body of Figure 9, demonstrate that polydispersity does have the large effect expected. As the flakes become more polydisperse, they become a less effective barrier, especially when the orientation varies significantly from zero degrees. Even at zero degrees, the effect is more than expected from a harmonic average of flake sizes.

Discussion

The experiments and simulations reported in this article investigate the change in diffusion across a membrane containing impermeable flakes. The flakes divert the diffusing species, effectively resulting in a thicker membrane. The flakes also reduce the cross-sectional area normal to the diffusion. The combination of these two effects means that the alteration of diffusion is proportional to the square of loading, that is, to the square of the volume fraction of flakes. It is also proportional to the square of the aspect ratio, that is, to the square of the flake shape.

Both experiments and simulations are consistent with most earlier studies of flake-filled membranes. The dependence on the square of both loading and aspect ratio is consistent with earlier theories assuming evenly spaced flakes (Cussler et al., 1988; Perry et al., 1988). It agrees with other experiments and with product bulletins for commercially available bottles made by extruding polymeric melts with suspensions of nylon flakes (Kamal and Jinnah, 1984; DuPont, 1992).

These results for flakes differ from studies of other types of composites (Wong et al., 1984; Tassopoulos and Rosner, 1992). These other studies tend to use impermeable spheres or cylinders, or clusters of these shapes. The theories give

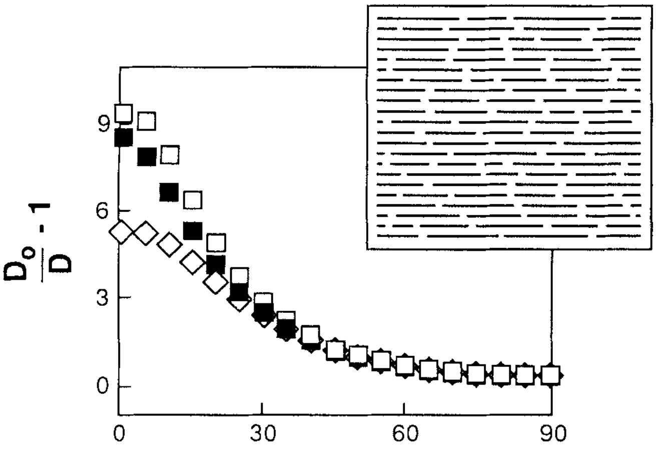

Figure 9. Diffusion vs. flake polydispersity.

Polydispersity of 10% (■) or 30% (◇) reduces the effect from monodisperse flakes (□). A typical membrane with 30% polydispersity is shown in the inset.

different results in the Knudsen and the continuum regimes; it is the continuum regime which is closer to the work in this article. These continuum theories give an effective diffusion coefficient D which is a function of the diffusion coefficient in the continuum D_o and of the void fraction $(1-\phi)$. They do not predict the variation of D with the aspect ratio α, because nothing in spheres or cylinders corresponds to such a ratio. Flakes have two large dimensions and one small dimension. Spheres have only one dimension; and cylinders have one large and one small dimension. Thus the results in this article differ because the basic geometry is different.

The key results of this work, given in Figures 6–9, show experiments and simulations with the same variations with loading and aspect ratio. However, they are not giving the same changes in D_o/D. For example, the experiments suggest that D_o/D is around 12 when the aspect ratio is 30 (Figure 7). However, the simulations predict that D_o/D should be 60 at this aspect ratio. Corresponding differences for the variations with loading are smaller but still significant, as shown in Figure 6.

While the cause of these discrepancies is uncertain, one possible culprit is the alignment of the flakes. The experiments use flakes which are randomly positioned within each course, but the simulations assume identical flakes whose centers are aligned like bricks, as shown in Figure 1b. The random alignment in the experiments will produce many parallel paths for diffusion, some of which will be unusually fast. The average over these parallel paths will give a faster flux, and hence a smaller ratio of D_o/D, than the corresponding average over the identical and parallel paths in the simulation.

The results in Figures 8–9 also show the large effects of flake orientation. Tipping the flakes by less than two degrees has little effect on diffusion; however, tipping the flakes by about 20° cuts the effect of the flakes in half. The experiments and simulations are in excellent agreement at small angles, but the experiments scatter at large angles. There are three possible causes for this scatter. First, when the membranes containing fillers at high angles are coated with pure polymer, the coating procedure can disorient the flakes (Eitzman, 1992). This disorientation, which sometimes is visible in the scanning electron microscope, can cause a film microtomed at 60° to be less permeable than one microtomed at smaller angles. Second, films containing flakes oriented at large angles have a smaller number of flake-filled layers, and so are prey to edge effects. Third, the aspect ratio of some mica flakes is so large that these flakes span the entire thickness of the microtomed sample. When the flakes span the entire thickness, they may move during the microtoming, producing leaks.

The effect of flake orientation can be rationalized as follows. For diffusion across any membrane

$$\begin{bmatrix}\text{Total}\\ \text{Flux}\end{bmatrix} = \frac{\begin{bmatrix}\text{Diffusion}\\ \text{Coefficient } D_o\end{bmatrix}\begin{bmatrix}\text{Concentration}\\ \text{Diffusion } \Delta c\end{bmatrix}\begin{bmatrix}\text{Cross-Sectional}\\ \text{Area}\end{bmatrix}}{[\text{Diffusion Distance}]} \tag{7}$$

For example, for a membrane with flakes oriented at 0°, as shown in Figure 1b, the total flux is

$$J = \left[\frac{D_o \Delta c}{nd}\right](bW) \tag{8}$$

where b and d are the distances between flakes and half the flake width, respectively; W is the largest flake dimension; and n is the number of layers of flakes. If the flakes have the same permeability as the surrounding continuum, then the flux becomes

$$J_o = \frac{D_o \Delta c}{n(a+b)}(dW) \tag{9}$$

where a is the flake thickness. The change in flux caused by the flakes is thus

$$\frac{D_o}{D} = \frac{J_o}{J} = \frac{d^2}{(a+b)b} = \left(\frac{d}{a}\right)^2\left(\frac{a}{a+b}\right)^2\left(\frac{a+b}{b}\right) = \frac{\alpha^2\phi^2}{1-\phi} \tag{10}$$

where (d/a) is the flake's aspect ratio α and $[a/(a+b)]$ is the flake loading ϕ. This result is an approximate derivation of Eq. 4, developed elsewhere in detail (Cussler et al., 1988).

If the flakes are tipped, the quantities in Eq. 8 do not change much, but those in Eq. 9 do. In particular, the area for diffusion (dW) is reduced to $(dW\cos\theta)$, and the thickness of each layer is increased from $(a+b)$ to $[(a+b)/\cos\theta]$. When we insert these changes into Eq. 9 and combine with Eq. 8, we find for tipped flakes

$$\frac{J_o}{J} = \frac{d^2\cos^2\theta}{(a+b)b} = \frac{\alpha^2\phi^2\cos^2\theta}{1-\phi} \tag{11}$$

This derivation fits the data of small angles, but not at larger ones, probably because the geometry is oversimplified.

Because the experiments and simulations appear consistent, the simulations can be used to investigate situations where experiments are difficult. In this work, the study of polydisperse flakes is one example of this approach showing that harmonic averages of flake size are more appropriate. Important problems which have not been studied include the cases of dilute flakes and of tightly packed flakes. Each case merits more discussion.

The case of dilute flakes does have two well understood limits which are implied by Eq. 4. One limit occurs when there are no flakes ($\phi = 0$), so D_o/D equals unity. The second limit is the antithesis, when the product of loading and aspect $\phi\alpha$ is much greater than one. However, the theoretical background between these limits is nonexistent: the existing derivation blatantly assumes that the two results can be added together. This assumption has no basis, and merits study.

The case of tightly packed flakes also deserves more attention. Past analytical theories suggest that diffusion in flake-filled membranes will be strongly affected both by wiggling around the flakes and by necking down to get through the slits between flakes. In these analytical theories, the wiggling and necking down seem to be roughly equal effects. However, the predictions of wiggling are consistent with experiment and the predictions of necking down are not. It is by no means clear why this should be. Moreover, while wiggling certainly dominates the flake-filled membranes studied to date, it is by no means clear that wiggling will be the most important factor in other flake-filled structures, including human skin. Future simulations will investigate both these and other cases.

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