DIFFUSION IN POLYMER FILMS WITH LANGMUIR ADSORPTION AND PARTIAL IMMOBILIZATION

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Sorption of several solute-polymer systems can be characterized by a combination of Henry's law sorption and Langmuir adsorption. The sorbate in the Langmuir adsorption is assumed to have different diffusivity compared to the sorbate in Henry's sorption. The concentration distribution and mass uptake of a polymer film subject to a step increase of sorbate at the surface were solved by the Crank-Nicholson method. With a smaller value of diffusivity for the Langmuir adsorbed molecules the normalized concentration distribution and mass uptake increased more slowly than the corresponding sorption without the Langmuir adsorption. The mass uptake after a step increase of the sorbate concentration is proportional to $\sqrt{t}$ at the beginning stage of sorption. From the parameters of sorption isotherms and the initial slopes of normalized mass uptake vs. $\sqrt{t}$ plots the diffusivities of both Henry's law sorption and Langmuir adsorption species can be determined.

INTRODUCTION

Gas sorption and diffusion are important characteristics of polymers for membrane applications. The rate of permeation of gases through a polymer film depends on both solubility and diffusivity of the gases in the polymer. The most simple case is that both solubility coefficient and diffusion coefficient are constants. In this case an analytical solution exists and these two parameters can be determined from a

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step increase of gas concentration surrounding an initially gas free film [1]. The solubility is determined from the mass increase of the film and the diffusivity is determined from the initial slope when the cumulative mass increase is plotted vs. $\sqrt{t}/\text{L}$ (L = half of the film thickness). Another approach is the time lag method, where the gas concentration on one side of a film is increased from zero to a finite concentration and the cumulative flux at the other side is determined as a function of time. From the slope and the intercept, solubility and diffusivity of the sorbate are calculated [1].

Several studies have shown that the sorption isotherms of small molecules in glassy polymers are generally concave to the pressure axis. A dual mode sorption model was proposed to describe such behavior [2–7]. The model described the sorption mechanism as a combination of Henry's law and a Langmuir isotherm. The former represents the sorbate dissolved in the polymer matrix while the latter is considered to occupy the unrelaxed free volume within the polymer. The total concentration of sorbate inside a polymer is:

$$\text{C}_{\text{total}} = \text{C} + \text{q} = \text{C} + \frac{K_2 C}{1 + K_1 C} \qquad (1)$$

where C represents the concentration of normally sorbed species, q represents the concentration of Langmuir adsorption species, and K_1 and K_2 are constants.

When the diffusivity is under consideration the molecules in normally absorbed state and in Langmuir adsorption are expected to be different. A simple assumption is that those in the Langmuir adsorption were nondiffusible. This was the total immobilization model [3]. Paul developed the time lag function for the total immobilization model [4]. A more general assumption is that the molecules in Langmuir adsorption can diffuse at a slower rate. This led to a partial immobilization model. Paul and Koros [5] developed the formula for time lag in the partial immobilization model. The model was experimentally demonstrated for carbon dioxide in polycarbonate films.

Both total and partial immobilization models yield the same isotherm. Their difference is their response with respect to time. Several initial gas concentrations would be needed to extract isotherm and diffusivity data of the system. Since the time lag method is experimentally more difficult than the weight increase measurement method, the latter method is discussed here. In this approach a step increase of sorbate concentrations is performed and the weight increases of polymer films are measured as function of time. When the sorption is described as Eq. (1), it is possible to obtain the diffusivity

information using a series of several step changes from zero to higher concentrations. The purpose of this study is to use a numerical method to explain this process.

CRANK-NICHOLSON METHOD

The diffusion of small molecules into a polymeric matrix can be described by a differential equation. In the case of constant diffusivity and solubility constant the diffusion equation is written as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{2}$$

where x is the distance, t is time and D is the diffusivity. In the study of diffusion of small molecules in polymer films, the polymer is initially free of the small molecules. The film is brought into contact with a controlled concentration of the sorbate. The increase of polymer weight is measured as a function of time. The analytical solution for the normalized mass uptake, M/M_o, versus time has been solved for the case of constant diffusivity with the linear sorption isotherm [1]. The expression suitable for the short time calculation is:

$$M/M_o = 2\frac{\sqrt{Dt}}{L}\left[1/\sqrt{\pi} + 2\sum_{n=0}^{\infty}(-1)^n \mathrm{ierfc}\left(\frac{nL}{\sqrt{Dt}}\right)\right] \tag{3}$$

where L is half of the thickness of the film. The equation predicts a linear relationship between the weight increase and $\sqrt{t}/L$ at the beginning of the measurement. This is a Fickian type behavior. From the slope of M/M_o vs. $\sqrt{t}$ the diffusivity can be calculated. Equation (3) is a solution of a linear differential equation and does not depend on the concentration of the solute.

In case of the partial immobilization model, Koros and Paul [6] used the following equation:

$$\frac{\partial}{\partial t}(C + q) = D\frac{\partial^2 C}{\partial x^2} + D_L\frac{\partial^2 q}{\partial x^2} = D\frac{\partial^2}{\partial x^2}(C + Fq) \tag{4}$$

where F is the ratio of diffusivity of sorbate in the Langmuir adsorbed state and diffusivity of sorbate in the normal state, D_L/D. The value of F is expected to lie between zero and unity because the diffusivity of a sorbate in the Langmuir absorbed state is considered to be less than that in the normal state. When $F = 0$ it is a total immobilization model. In case $F = 1$ Eq. (4) reduces to the problem of

constant diffusivity with $C + q$ as the variable and a solution similar to Eq. (3) can be obtained. When $F < 1$ the equation is nonlinear because of the Langmuir isotherm. The Crank-Nicolson method [8-10] can be used in this case. In the Crank-Nicholson method the film thickness was divided into equal intervals. The time of diffusion was also divided into intervals. The differential equation was then converted into a finite difference equation. After rearrangement of the equation the concentration of a point at a particular time was related to five other data points. These five data points included two nearby points at the same time, two nearby points of the previous time, and the same point of the previous time. Under this assumption, Eq. (4) was written as:

$$
\begin{aligned}
2[(C + q)_{i,j+1} &- (C + q)_{i,j}] \\
&= r[(C + Fq)_{i+1,j} - 2(C + Fq)_{i,j} + (C + Fq)_{i-1,j}] \\
&\quad + r[(C + Fq)_{i+1,j+1} - 2(C + Fq)_{i,j+1} + (C + Fq)_{i-1,j+1}]
\end{aligned} \qquad (5)
$$

where $r = D\Delta t / \Delta x L^2$

In the calculation the film thickness interval, $\Delta x / L$, was chosen to be 0.04 and the time interval, $D\Delta t / L^2$, is 0.0016. This gives $r = 1$. The equation was converted into:

$$
\begin{aligned}
C_{i,j+1} = [(2 - 2F)q_{i,j} &+ (C + Fq)_{i+1,j} + (C + Fq)_{i-1,j} + (C + Fq)_{i+1,j+1} \\
&+ (C + Fq)_{i-1,j+1}] / [4 + (2 + 2F)K_2 / (1 + K_1(C_{i,j+1}))]
\end{aligned} \qquad (6)
$$

The boundary conditions were $C = C_o$ and $q = q_o = K_2 C_o / (1 + K_1 C_o)$ at the surface for normally sorbed species and Langmuir adsorbed species, respectively. Equation (6) is not a linear simultaneous equation and cannot be solved by a matrix inverse method. The system of simultaneous equations can be solved by an iteration method [9,10]. In the iteration calculation the value of new array $C_{i,j+1}$ at the left hand side was calculated by using known value of $C_{i,j+1}$ at the previous time and an initial guess value of $C_{i,j+1}$. The calculated value of $C_{i,j+1}$ in turn was used in the next run of calculation until each element of $C_{i,j+1}$ no longer changed. The initial value of C was unity at both surfaces and zero for all interior points. The values of $C_{i,j}$ were used as the initial guess values of $C_{i,j+1}$. In the calculation it was found that fifteen iterations were sufficient for convergence. In the calculation q was not treated as a separate variable; it was calculated from C based on the Langmuir equation. After the calculation of C and q the total mass uptake, M, was calculated from integration of C and q throughout the film.

RESULTS AND DISCUSSION

Figure 1 shows the normalized total concentration vs. dimensionless coordinate at $Dt/L^2 = 0.4$ for several combinations of parameters. From the right hand side it can be seen that if there is a Langmuir adsorption the permeation of sorbate is slower as F decreased. This is because a slow diffusion rate of the Langmuir adsorbed molecules was accompanied by a slow rate of normally adsorbed molecules as both of them are in equilibrium locally. As mentioned previously, when $F = 1$ the distribution of C is the same as the case without absorption. In this case both the normal state molecules and Langmuir adsorbed molecules diffuse at an equal rate. The value of normalized concentration at midplane for $F = 1$ was 0.52552 in this calculation.
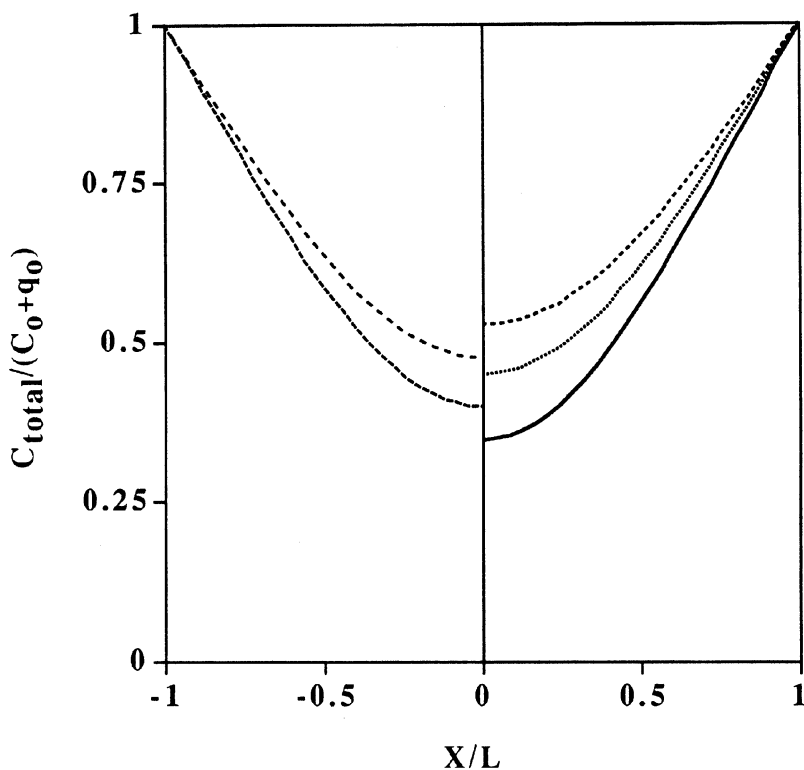
FIGURE 1 Normalized total sorbate concentration vs. x/L at $Dt/L^2 = 0.4$ for several combination of parameters after a step change of sorbate concentration. Right side from top to bottom: $K_1 = 1$, $K_2 = 1$, $F = 1$; $K_1 = 1$, $K_2 = 1$, $F = 0.5$; $K_1 = 1$, $K_2 = 1$, $F = 0$. Left side from top to bottom: $K_1 = 2$, $K_2 = 1$, $F = 0.5$; $K_1 = 1$, $K_2 = 2$, $F = 0.5$.

The corresponding value based on the analytical solution is 0.52551. This verifies the accuracy of the algorithm. When K_1 increased at constant K_2 and $F(F < 1)$ the concentration increased. This represented a decrease in occupancy of Langmuir sites. In case $F < 1$, this increased the rate of diffusion. When K_2 increased at constant K_1 and $F(F < 1)$ the concentration decreased because more Langmuir sites needed to be filled before the concentration profile moved forward.

Figure 2 shows the value of normalized mass uptake, M/M_o, at $Dt/L^2 = 0.4$ using $K_2 = 1$ and F as a parameter. The effect of K_1C_o can be seen. When K_1C_o was small the values of M/M_o approached constant values which depended on F. This was because when $K_1C_o \ll K_2$ Eq. (4) can be simplified as:

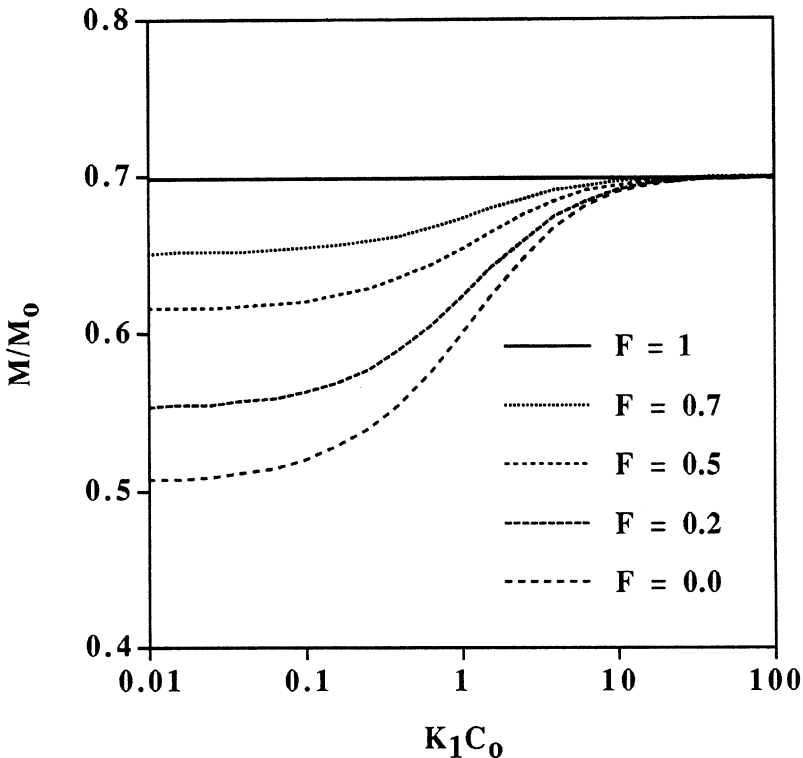$$\frac{\partial}{\partial t}C = D\frac{1 + FK_2}{1 + K_2}\frac{\partial^2}{\partial x^2}C \qquad (7)$$

FIGURE 2 Normalized mass uptake vs. K_1C_o at $Dt/L^2 = 0.4$ for $K_2 = 1$.

This equation is equivalent to a constant diffusivity situation with a smaller diffusivity. The physical picture is that Langmuir sites are far from fully occupied and a linear behavior existed. Therefore, on the left-hand side of Figure 2 the values approached separate constant values. When $K_1C_o \gg K_2$ the value of M/M_o approached a constant value 0.6979 for all F values. In this case Eq. (4) reduced to Eq. (2) and the results are independent of values of K_2 and F because the Langumir term diminished. The physical meaning is that the system has very few Langmuir sites and the Henry's sorption dominates the system. The case of $F = 1$ gave a constant value independent of the value of K_1C_o and K_2. This was mentioned previously. When $F = 1$, Eq. (4) can be treated as a linear differential equation of $C + q$, and the mass uptake is given in Eq. (2). The results shown in Figure 2 indicate that it is possible to determine the value of F by comparing the rate of sorption at different values of C_o, which is the substrate concentration at the surface.

Figure 3 shows the normalized cumulative mass uptake vs. time for several combinations of parameters. The figure is plotted on a double logarithm scale. It can be seen that at the very beginning of sorption the increase of mass was a Fickian behavior because the slope was one half. In a previous study similar calculation also gave Fickian behavior for substrate concentration when diffusivity is concentration dependent [10]. The intercept of the curve at short time region in Figure 3 gave the apparent diffusivity. It can be seen that the intercepts changed when parameters changed. Among parameters of the model K_1 and K_2 can be determined from the equilibrium sorption measurement. From experimental results of step concentration change with a series of substrate concentration K_1 and K_2 can be determined based on the equilibrium mass increase. The time dependent behavior then offers the possibility of obtaining the other parameters: diffusivity of normally sorbed species, D, and F. To obtain a relationship between mass increase with respect to time the dimensional analysis gave:

$$M/M_o = f(Dt/L^2, K_1C_o, K_2, F) \qquad (8)$$

The normalized mass uptake depends on four dimensionless groups. The derivative of M/M_o vs. $\sqrt{Dt}/L$ at $t = 0$ gives the initial slope. The use of the initial slope reduced the dependence to three dimensionless variables: K_1C_o, K_2, F. It is still not convenient to present the result in a two-dimensional graph. A further reduction on the number of variables is needed. A comparison of the ratio of the initial slope values at some fixed K_1C_o values can eliminate one more variable. Since Figure 2 showed that the change of the mass uptake is most sensitive
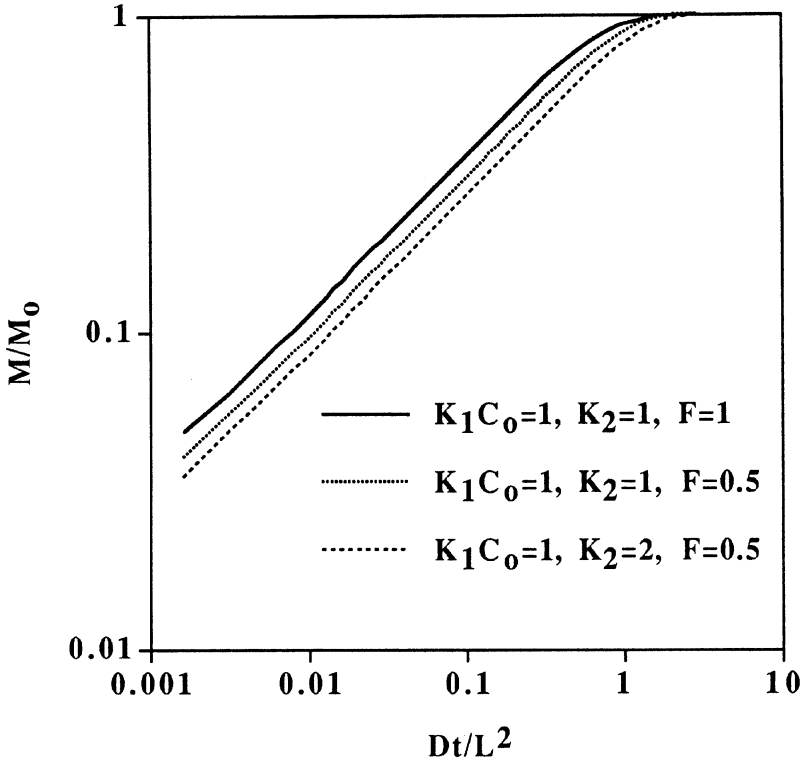
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FIGURE 3 Normalized mass uptake vs. Dt/L^2 for several combinations of parameters.

when K_1C_o was around 1.0, the ratio is calculated using $K_1C_o = 2.0$ and 0.5. This information could be generally available because in the determination of the sorption isotherm by the step change, the concentration of substrate in step change studied should be varied sufficiently to cover a range of K_1C_o. The ratio as a function of K_2 and F was calculated numerically. Figure 4 showed the result of the initial slope ratio at $K_1C_o = 2.0$ and 0.5 vs. K_2 using F as the parameter. Note that in Figure 4 the individual slope was calculated using M/M_o vs. $\sqrt{Dt}/L$ plot. But the ratio is the same as the ratio determined using M/M_o vs. $\sqrt{t}/L$ plot because diffusivities in both slopes were cancelled. This is important because the latter ratio can be determined experimentally without the knowledge of D.

In Figure 4 when $F = 1$ there was no change of the slope and the ratio was unity. When F decreased from unity the ratio also decreased from unity. When $F = 0$ the ratio had the lowest value. The effect of K_2
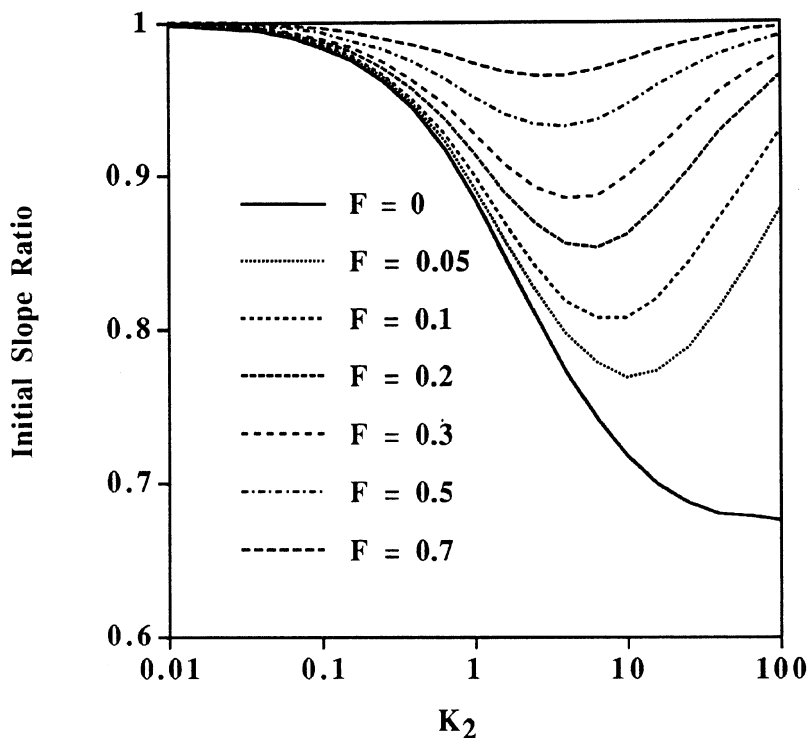
FIGURE 4 Ratio of the initial slope of M/M_o vs. $\sqrt{Dt}/L$ at $K_1C_o = 2$ to the similar slope at $K_1C_o = 0.5$ as function of K_2 and F.

can also be seen in Figure 4. When K_2 was small the value of the ratio approached unity for all F. This was because when K_2 was small Eq. (4) reduced to Eq. (2) and the ratio was independent of F. The physical meaning is that there is little Langmuir adsorption. When $K_2 \gg K_1C_o$ the value of the ratio also approached unity. In this case the Langmuir term dominates and Eq. (4) simplifies to Eq. (7). The diffusion equation is equivalent to a constant diffusivity situation with a smaller diffusivity. Again in this case there is no change of the initial slope by varying the substrate concentration. A different situation is seen in $F = 0$. This is probably the most common situation for dual adsorption mechanisms. For the case $F = 0$ the ratio does not approach unity when K_2 is large. At the beginning of sorption when $K_1C_o \ll 1$ the equation is:

$$\frac{\partial}{\partial t}C = \frac{D}{1 + K_2}\frac{\partial^2}{\partial x^2}C \qquad (9)$$

    When K_2 increased the apparent diffusivity decreased continuously.
This was also reflected by continuous decrease of the ratio in Figure 4.
In practice the value of K_2 can not increase indefinitely. It is a fixed
property of the system and is not affected by the sorbate concentration.
Figure 4 indicated that the method suggested here is more sensitive
when F is near zero and less sensitive when F is close to unity. Also
there is a zone for K_2 where the determination of F is more accurate.
This is region where the ratio of initial slopes shows a large reduction
from unity. When $K_1 C_o$ is 1.0 the range for K_2 is about 2 to 20.

    Once the value of F is determined from Figure 4 the value of D can
be obtained from the initial slope of M/M_o, vs. $\sqrt{t}/L$ at a particular
$K_1 C_o$ and the known value of F and K_2. The initial slopes of M/M_o vs.
$\sqrt{t}/L$ at $K_1 C_o = 1$ at different F were calculated and shown in Figure 5.
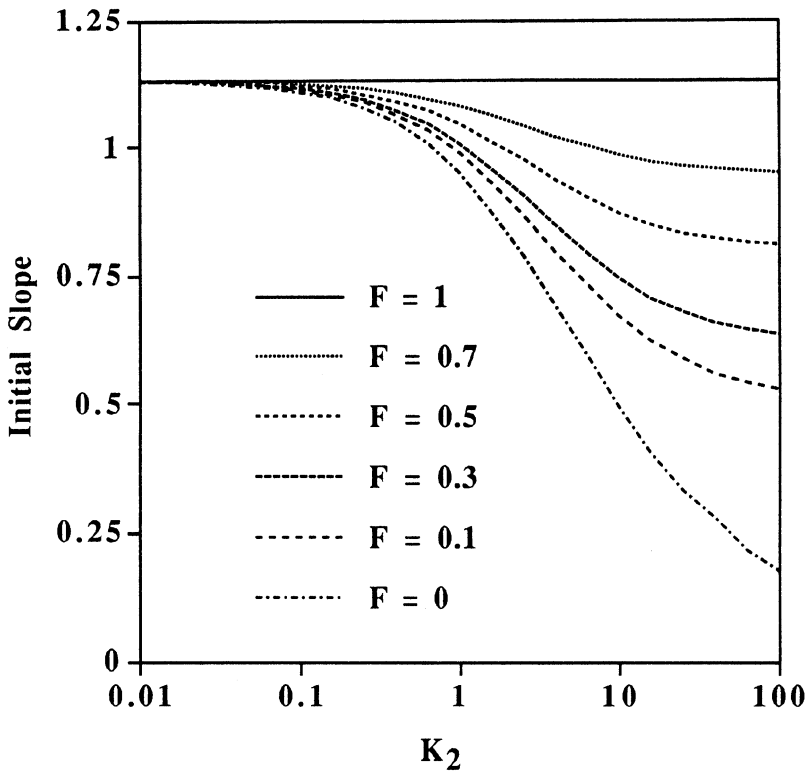It can be seen that when $F = 1$ the slope has a constant value of 1.128,

FIGURE 5 Initial slope of M/M_o vs. $\sqrt{Dt}/L$ at $K_1 C_o = 1.0$ as function of K_2
and F.

which was the theoretical value for a linear isotherm. For $F < 1$, the dimensionless initial slope of M/M_o vs. $\sqrt{Dt}/L$ can be read from Figure 5 for different F and K_2. From experimental results at $K_1C_o = 1$ the slope of M/M_o vs. $\sqrt{t}/L$ at the beginning of sorption can be obtained. A comparison of two will give the value of D. Finally, from D and F the diffusivity of the Langmuir adsorbed species, D_L, can also be calculated. Figure 5 can also be made for different value of K_1C_o but a value of unity is more convenient because the change of mass uptake is more sensitive to the change of C_o as shown in Figure 2.

CONCLUSIONS

Using the Crank-Nicolson method the mass uptake into a polymer film was calculated for a system with Henry's and Langmuir sorption isotherms and partial immobilization. The assumption of a small diffusivity for Langmuir sorbed molecules gave a slower overall permeation rate. The concentration vs. time showed a Fickian behavior at short time. A method was proposed to use the initial mass uptake rate at different sorbate concentration to determine diffusivity of each mode.

REFERENCES

[1] Crank, J. (1975). *The Mathematics of Diffusion*, 2nd. ed, Oxford University Press, London.
[2] Vieth, W. R. (1991). *Diffusion in and through Polymers: Principles and Applications*, Hanser-Gardner, Cincinnati.
[3] Frisch, H. L. (1957). *J. Phys. Chem.*, **61**, 93.
[4] Paul, D. R. (1969). *J. Polym. Sci.*, Pt. **A-2**, **7**, 1811.
[5] Paul, D. R. and Koros, W. J. (1976). *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 675.
[6] Koros, W. J., Paul, D. R. and Rocha, A. A. (1976). *J. Polym. Sci., Phys. Ed.*, **14**, 687.
[7] Hayashi, Y., Sugiyama, S., Kawanishi, T. and Shimizu, N. (1999). *J. Membrane Sci.*, **156**, 11.
[8] Hunt, D. (1980). *Polym.*, **21**, 495.
[9] Kreyszig, E. (1999). *Advanced Engineering Mathematics*, 8th ed., Wiley, New York.
[10] Huang, J. C., Liu, H. and Liu, Y. (2001). *Int. J. Polym. Mater.*, **49**, 15.