

Non-Fickian Diffusion Through Polymer Films

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The dual-mode sorption model, developed originally by Vieth and Sladek (1965) and Vieth et al. (1976) and expanded and applied by Paul and Koros (1976), Felders et al. (1981) and Chern et al. (1983), has been used successfully to explain non-Fickian diffusion and vapor sorption in polymers. It is shown here that a modified form of this theory correlates the uptake of cyclohexane in a glassy-rubbery, block copolymer of styrene and butadiene.

The original theory proposes dissolution according to Henry's law and Langmuir-type sorption. It is assumed that the Henry's law part of the uptake of sorbent follows Fick's law, while the Langmuir part is immobilized and in local equilibrium with the mobile diffusant within the polymer film. The assumption of local equilibrium was replaced by Vieth et al. (1969) and Tschudy and von Frankenberg (1973) in favor of finite rates of immobilization. In the latter study it was assumed that the immobilizing sites are uniformly distributed throughout the polymer, that each site can immobilize one molecule of diffusing gas, and that immobilization can be represented as a reversible, bimolecular reaction between the gas molecules and the vacant sites. When the forward reaction is dominant, immobilization can be described as a second-order irreversible process. This restriction is employed in the treatment of our data.

EXPERIMENT

A Cahn balance was used to measure the increase in weight of a film of Phillips Petroleum Company K-resin suspended in a large chamber of cyclohexane vapor maintained at 323 K. The resin, a copolymer of styrene and butadiene (polybutadiene 25%), consisted of a mixture of rubbery and glassy components. Properties of the resin are given in Table 1; the morphology for this polymer is described by Fodor et al. (1974).

The polymer film (8×10^{-5} m in thickness) was 8.5×10^{-2} m wide and 0.265 m long, and the gas chamber had a volume of 3.82×10^{-3} m³. During a run the uptake of cyclohexane by polymer was less than 2% of the vapor in the chamber. Therefore, the pressure change was neglected. Since the run time was several hours, equilibrium was assumed at the exposed polymer surfaces. With constant pressure this meant that the surface concentration, C_s , of cyclohexane in the film was constant during a run.

The first run was made by first evacuating the chamber and then introducing cyclohexane. Then the weight increase was recorded at time intervals of about 94 s. The run was stopped, and equilibrium assumed between cyclohexane and polymer, when the weight became constant. Subsequent runs were made by introducing more cyclohexane to increase its pressure, closing the chamber, and again measuring the weight increase vs. time.

Figure 1 shows experimental sorption curves (weight uptake vs. time) for three successive runs. The rapid uptake at short times follows Fickian

diffusion, as verified by the initial linear section of the curves of fractional uptake vs. $t^{1/2}$, shown in Figure 2. After this initial period there is a slower but sustained sorption that is non-Fickian. The first stage takes little time. This suggests that Fickian diffusion rapidly establishes a uniform cyclohexane concentration throughout the film. The second stage of slower, sustained sorption may be explained by the adsorption of cyclohexane on the immobile sites of the polymer. Since diffusion is relatively fast, the rate of sorption during this second stage is determined primarily by the kinetics of the immobilization process.

Berens and Hopfenberg (1978) and Bagley and Long (1955) observed similar behavior in their studies of vinyl chloride gas sorption in vinyl chloride polymer and acetone sorption in cellulose acetate, respectively. In their data non-Fickian uptake was only observed at higher pressures of penetrant, while Figure 1 shows this behavior for our system at 1900 Pa.

THEORY

If irreversible second-order immobilization is assumed, the mass balance of cyclohexane within the film (of thickness $2L$) may be written

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - k'nC \quad (1)$$

where n represents the concentration of vacant sites per unit volume of polymer. Since diffusion is seen from the data (Figure 1) to be fast with respect to the rate of immobilization, the second term on the right side may be neglected. Then Eq. 1 becomes

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

This simplification means that the concentration profile within the film is not significantly affected by immobilization.

For a unit area (perpendicular to the direction of diffusion) of the whole film, the change in concentration of vacant sites N according to second-order kinetics may be written

$$\frac{dN}{dt} = -kNM_D \quad (3)$$

where M_D is the uptake of the whole thickness of the film due to diffusion; that is, M_D is the concentration of the mobile cyclohexane over the whole film. It can be obtained from the concentration profile with the equation

$$\frac{M_D}{M_{D\infty}} = \frac{2 \int_0^L (C - C_o) dx}{2L(C_s - C_o)} \quad (4)$$

TABLE 1. PROPERTIES OF POLYMER FILM, K-RESIN KR03

Molecular weight	
Weight average ^a	2.17×10^5
Number average ^a	1.06×10^5
Melt flow index	8.6
Weight fraction styrene	0.748
Density	$1.10 \times 10^3 \text{ kg/m}^3$

^a Fodor et al. (1974).

The boundary and initial conditions for our experiments, where the film is placed in the chamber at $t = 0$, are

$$C = C_s \quad \text{at } x = L \quad (5)$$

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } x = 0 \quad (6)$$

$$C = C_o, N = N_o \quad \text{at } t = 0 \quad (7)$$

Equation 2 with Eqs. 5 to 7 can be solved for $C(x, t)$ and substituted in Eq. 4 to obtain $M_D(t)$. The result is

$$\frac{M_D}{M_{D\infty}} = 1 - \sum_{r=0}^{\infty} \frac{8}{(2r+1)^2 \pi^2} \exp \left[-(2r+1)^2 \pi^2 \tau / 4 \right] \quad (8)$$

where τ is the dimensionless time, Dt/L^2 .

The total uptake by diffusion M_D and by immobilization M_I is

$$M_t = M_D + M_I \quad (9)$$

and at equilibrium

$$M_{t\infty} = M_{D\infty} + M_{I\infty} \quad (10)$$

Suppose the fraction of the equilibrium uptake due to diffusion is α :

$$\alpha = \frac{M_{D\infty}}{M_{t\infty}} \quad (11)$$

Then the total fractional uptake from Eqs. 9 to 11 can be expressed in terms of the fractional uptake for each mode, or

$$\frac{M_t}{M_{t\infty}} = \alpha \frac{M_D}{M_{D\infty}} + (1 - \alpha) \frac{M_I}{M_{I\infty}} \quad (12)$$

The fractional uptake due to immobilization $M_I/M_{I\infty}$ can be expressed in terms of N by the equation

$$\frac{M_I}{M_{I\infty}} = \frac{N_o - N}{N_o} \quad (13)$$

The quantity N as a function of t can be found by integrating Eq. 3 with $M_D(t)$ given by Eq. 8. Using the result in Eq. 13 yields

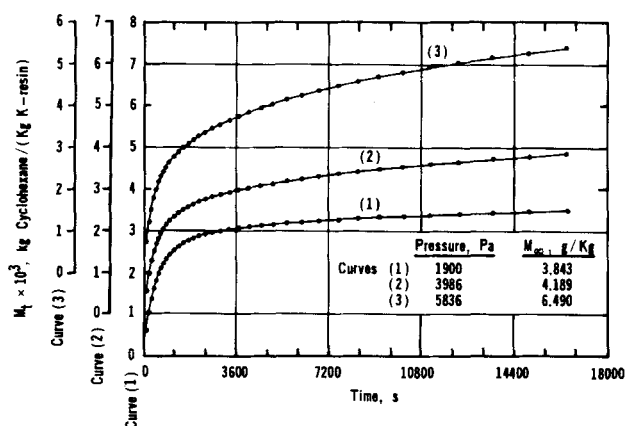


Figure 1. Cyclohexane sorption in K-resin at 323 K.

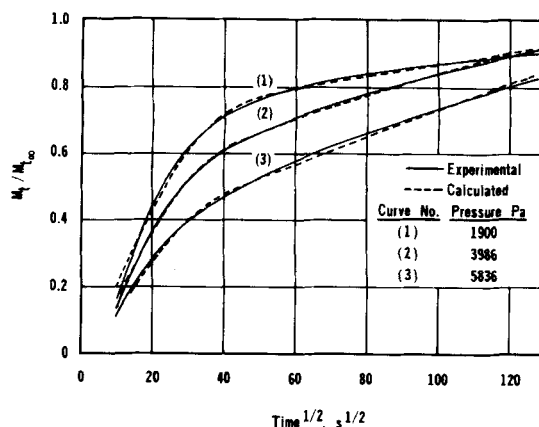


Figure 2. Comparison of experimental and calculated sorption curves.

$$\frac{M_I}{M_{I\infty}} = 1 - \exp \left\{ -\alpha \phi \left[\tau - \sum_{r=0}^{\infty} \frac{32 \exp [-(2r+1)^2 \pi^2 \tau / 4]}{(2r+1)^4 \pi^4} \right] \right\} \quad (14)$$

where

$$\phi = L^2 k M_{t\infty} / D \quad (15)$$

Equations 8 and 14 substituted into Eq. 12 give a predicted value for the total uptake, which then may be compared with the experimental data. The series in Eq. 14 converges rapidly; five terms are sufficient to obtain $M_I/M_{I\infty}$ accurate to three significant figures. The predicted total uptake depends on three parameters, L^2/D , α , and ϕ .

RESULTS AND DISCUSSION

The optimum values of the three parameters were obtained by fitting the predictions from Eq. 12 to the experimental sorption curves. The Rosenbrock method (Kuester and Mize, 1973) was used for the optimization calculations. The best fit was sought by minimizing the sum F of the squares of the deviations, as evaluated from the equation

$$F = \sum \left[\left(\frac{M_t}{M_{t\infty}} \right)_{\text{pred}} - \left(\frac{M_t}{M_{t\infty}} \right)_{\text{exp}} \right]^2 \quad (16)$$

Figure 2 shows the experimental and predicted curves plotted as fractional total uptake vs. the square root of time. The values of the parameters are given in Table 2.

The dual-mode model satisfactorily explains the measured uptake, as indicated by the agreement between predicted and experimental curves in Figure 2. The diffusivity for the Fickian contribution is nearly the same (equal to about $1.2 \times 10^{-12} \text{ m}^2/\text{s}$) for all three pressure levels. This suggests that immobilization, which is greatest for the third, highest pressure run, does not significantly affect diffusion in the polymer. The linear portion of the curves in Figure 2, which correspond to the Fickian diffusion uptake, ends at about 600 s. Thus, quasiequilibrium for diffusion is reached at about this time and is followed by the much slower irreversible adsorption.

The linear section of the curves in Figure 2 extends to higher fractional uptakes the lower the pressure of cyclohexane. So the fraction α decreases as the pressure increases, reflecting the increase in immobilization. This increase suggests that the styrene-butadiene interface provides more sites for immobilization as the cyclohexane pressure increases.

Figure 3 shows the total uptake, $M_{t\infty}$, and $M_{D\infty}$ for the three runs plotted vs. the pressure of cyclohexane in the chamber. While there are only three points, the total sorption does deviate positively from Henry's law. Similar positive deviations have been reported (Holley et al., 1970) for diffusion of *n*-pentane in polystyrene. The relax-

TABLE 2. EQUILIBRIUM SORPTION AND MODEL PARAMETERS

Run	1	2	3
Cyclohexane Pressure, Pa	1,900	3,986	5,836
$M_{t\infty}$, kg/kg	3.843×10^{-3}	4.189×10^{-3}	6.490×10^{-3}
α	0.741	0.578	0.431
ϕ	0.145	0.236	0.237
$D \times 10^{12}$, m ² /s	1.03	1.18	1.21
$(F \times 10^3)^a$	3.55	1.49	2.09

^a Evaluated from Eq. 16 by summing 36 points.

ation of the polymer structure could be responsible for the increased sorption. The contribution to the uptake due to Fickian diffusion does show a linear dependence with cyclohexane pressure. The slope of the $M_{D\infty}$ curve gives a Henry's constant of 7.3×10^5 Pa/(kg/kg).

The values of ϕ in Table 2 can be converted to a second-order Thiele-type modulus, $L^2(kN_o)/D$ for the second-order immobilization reaction. The resultant values are 0.04, 0.10, and 0.14 for the three runs. This suggests that the concentration profile in the film is not much affected by immobilization, thus lending validity to neglecting the second term on the right side of Eq. 1.

Sefcik and Raucher (1983) have shown that a matrix theory, allowing for a continuous change in gas-polymer properties, also can fit non-Fickian diffusion data.

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NOTATION

- C = concentration of cyclohexane, which conforms to Fickian diffusion, inside the polymer film, kg cyclohexane/kg polymer; C_d = initial concentration in the film; C_s = concentration at the surface
- D = diffusivity of cyclohexane in Fickian mode in the polymer film, m²/s
- F = objective function for curve fitting, defined in Eq. 16
- H = Henry's constant for cyclohexane, defined by the equation $p = HM_{D\infty}$, Pa/(kg/kg)
- k = Adsorption rate constant based on concentration N in the whole film, s⁻¹; k' = adsorption rate constant based on local concentration n within the film, s⁻¹
- L = half-thickness of the polymer film, m
- M_D = weight uptake due to diffusion alone, per unit mass of polymer, kg/kg; $M_{D\infty}$ = equilibrium uptake by diffusion

- $M_{t\infty}$ = total uptake, kg/kg
- n = local concentration of vacant sites within the polymer film, kg of vacant sites/(kg polymer); n_o = initial concentration of the sites
- N = concentration of vacant sites in the whole polymer film, kg of vacant sites/(kg polymer); N_o = initial concentration of the sites
- t = time, s
- x = position variable inside the film, m

Greek Letters

- α = fraction of weight uptake at equilibrium by diffusion, $M_{D\infty}/M_{t\infty}$
- ϕ = parameter, $M_{t\infty}L^2k/D$
- τ = dimensionless time variable, Dt/L^2

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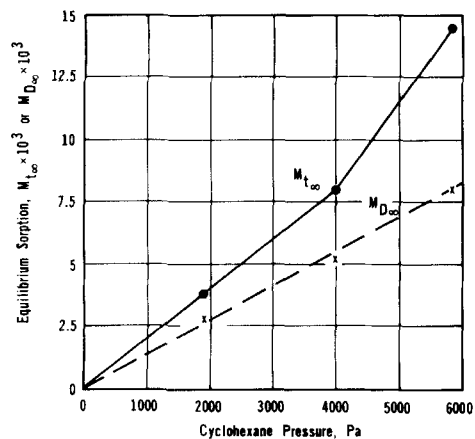


Figure 3. Equilibrium sorption.

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