Diffusion in Glassy Polymers. V. Combination of Fickian and Case II Mechanisms

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ABSTRACT: The diffusion of acetone in poly(vinyl chloride) was studied by the measurement of the gain in weight and the distance of penetration as a function of time. The experimental results were analyzed by the use of the generalized diffusion equation which took into account both Fickian and case II mechanisms. Excellent agreement was obtained. Similarity between the results of the present study and the phenomenon of "anomalous" sorption in glassy polymer was suggested.

In several previous publications,[1–3] the diffusion of organic liquids in glassy polymers was discussed in terms of Fickian and case II[4] mechanisms. Experimental results also indicated that in certain cases the two mechanisms were operative simultaneously. A generalized diffusion equation which embodied both Fickian and case II contributions was derived. Analytical expressions were obtained for the penetration of the advancing solvent front and the weight gain as a function of time.[3] Some aspects of the experimental data on the distance of penetration agree with the prediction of the equation. A more critical test of the generalized diffusion equation, however, lies in the comparison of both weight gain and penetration data with theoretical expressions. In this report, we would like to present the results of our study of acetone diffusion in poly(vinyl chloride) and the analysis of the experimental data according to the generalized diffusion equation.

Experimental Section

Poly(vinyl chloride), Opalon 630 from Monsanto Co., was molded at 170° into sheets about 0.33 cm in thickness. The methods of measuring the distance of solvent penetration, l, and the weight gain, M_t, were described previously.[1] The distance of penetration was measured from the outer swollen surface of the polymer to the advancing solvent front, in keeping with the proper choice of the moving frame of reference.[2,3] All experiments were carried out at room temperature.

Results

The equilibrium concentration of acetone in a swollen PVC is 0.50 g cm^{-3}. The results of weight gain and solvent penetration measurements are plotted against time in Figure 1. The initial, rapid rise in the magnitude of M_t is followed by a slower and *approximately* linear increase with time. The quantity l increases in a similar manner, but it appears that a slight curvature may persist in the distance–time plot at long times.

Discussion

In the ensuing paragraphs, both the weight gain and the penetration results will be discussed in the framework of the generalized diffusion equation[2,3] previously derived to describe the combination of Fickian and case II mechanisms. The expression for diffusion in one dimension is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial c}{\partial x} - vc\right] \qquad (1)$$

The second term in the square brackets describes the contribution of internal stress arising from swelling of the polymers, and the quantity v represents the velocity of solvent penetration as a direct consequence of the internal stress effect. Both D and v are assumed to be constant in eq 1.

For diffusion in a semiinfinite polymer with a constant penetrant concentration C_0 at the surface, the concentration profile of the penetrant in the swollen polymer is given by

$$C(x,\, t) = \frac{C_0}{2}\left[e^{xv/D}\,\mathrm{erfc}\left(\frac{x + vt}{2\sqrt{Dt}}\right) + \mathrm{erfc}\left(\frac{x - vt}{2\sqrt{Dt}}\right)\right] \qquad (2)$$

The total amount of the penetrant per unit area entering the polymer, M_t, is

$$M_t = C_0\left\{\frac{D}{v}\,\mathrm{erf}\left[\frac{v}{2}\left(\frac{t}{D}\right)^{1/2}\right] + \frac{vt}{2}\,\mathrm{erfc}\left[-\frac{v}{2}\left(\frac{t}{D}\right)^{1/2}\right] + \left(\frac{Dt}{\pi}\right)^{1/2}\exp(-v^2t/4D)\right\} \qquad (3)$$

which reduces at large times to

$$M_t = C_0\left[\frac{D}{v} + vt\right] \qquad (4)$$

Equations 2–4 will be used in the analysis of our experimental data to obtain v and D. We have also adopted Crank's[5] idea that the sharp advancing front of the penetrant is a consequence of the discontinuity in the diffusion coefficient as concentration changes. In particular, we assume $D = D_1$ at $C > C_X$ and $D = D_2 \cong 0$ at $C < C_X$. The advancing solvent front is located at C_X. It will be shown that the value of C_X can be calculated from the l *vs.* t curve by the use of eq 2. The three parameters, v, D, and C_X define the concentration profile of diffusion.

First, we note that the observed linear relationship between M_t and t at large times is in accord with the prediction of eq 4. From the slope and intercept of this linear region, v and D can be readily calculated. (In this calculation, the equilibrium concentration of acetone in the swollen PVC is taken as the surface concentration C_0.) The values of v and D from least-squares calculations are

$$v = 1.82 \times 10^{-5}\ \mathrm{cm\ sec^{-1}}$$

$$D = 7.05 \times 10^{-8}\ \mathrm{cm^2\ sec^{-1}}$$

When these values are inserted in eq 3, the computed M_t curve is shown by the solid line in Figure 1.

We now calculate l as a function of time by the use of eq 2. A series of curves is calculated for different values of C_X,

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(1) T. K. Kwei and H. M. Zupko, *J. Polym. Sci., Part A-2*, 7, 867 (1969).

(2) H. L. Frisch, T. T. Wang, and T. K. Kwei, *ibid.*, 7, 879 (1969).

(3) T. T. Wang, T. K. Kwei, and H. L. Frisch, *ibid.*, 7, 2019 (1969).

(4) T. Alfrey, Jr., E. F. Gurnee, and W. G. Lloyd, *J. Polym. Sci., Part C*, No. 12, 249 (1966).

(5) J. Crank, "The Mathematics of Diffusion," Oxford University Press, London, 1956, Chapter 7.

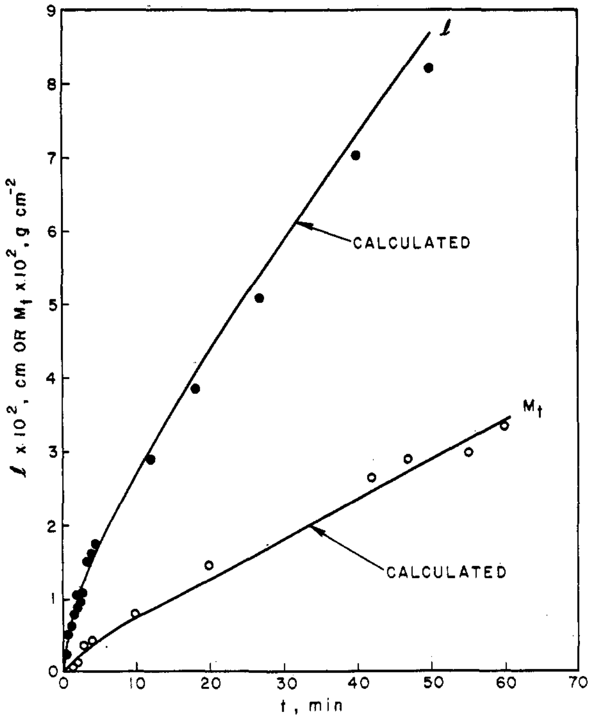

Figure 1. Diffusion of acetone in poly(vinyl chloride).

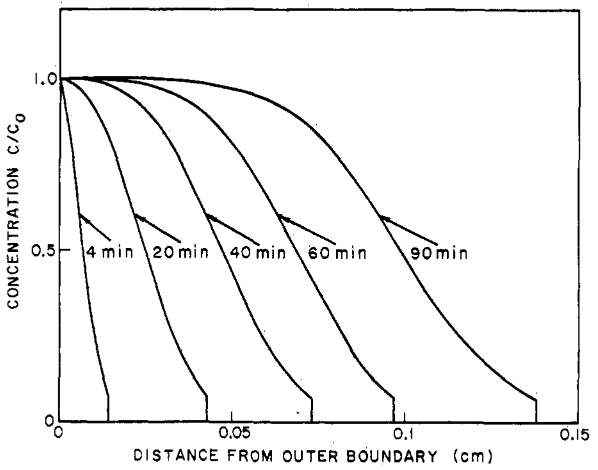

Figure 2. Concentration profiles of diffusion.

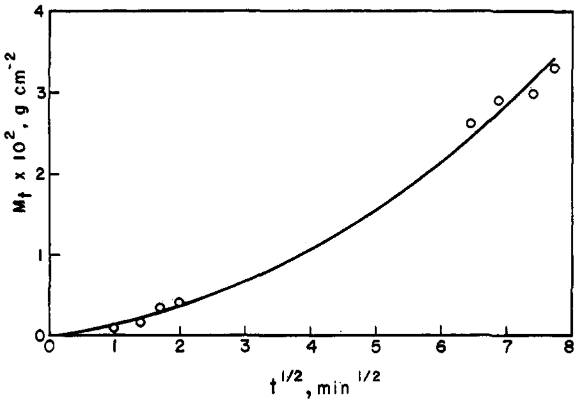

Figure 3. Experimental results reported as M_t *vs.* $t^{1/2}$.

using the above values of v and D, and compared with the experimental l curve. The calculated curve for $C_X = 0.034$ g cm^{-3} shows satisfactory agreement with experimental data, although even better fit of the l curve can be achieved by assuming a slightly smaller value of v, *e.g.*, 1.7×10^{-5} cm sec^{-1}. However, since the exact values of v, D, and C_X are not particularly pertinent to our discussion, no further attempt was made to obtain the best set of values to fit the two curves.

The significance of C_X and the assumption of discontinuity of diffusion coefficient as concentration changes need reiteration although the arguments have already been expounded in ref 2. The physical reason for the "apparent" discontinuity of D *vs.* c in the diffusion of liquid in glassy polymers is as follows. Although the dry polymer is in the glassy state at the temperature of the experiment, the polymer-solvent mixture, depending on the composition, may exist in the rubbery state in certain parts of the swollen region. Now, the diffusion constant is about 10^{-7} cm^2 sec^{-1} or higher in the rubbery state but 10^{-9}–10^{-12} cm^2 sec^{-1} in the glassy state (from gas or vapor diffusion data). Thus, the polymer-solvent mixture at the outer swollen surface may exist in the rubbery or leathery state because the solvent concentration is high, namely, 0.5 g cm^{-3} of mixture; consequently, a high diffusion constant is expected. As solvent concentration decreases toward the interior of the glassy polymer, a point may be reached where the polymer–solvent mixture is no longer rubbery and there is a rapid decrease in the diffusion constant when the solvent concentration is lower than a certain critical value. This gives rise to the "apparent" discontinuity in D and the sharp advancing front. The critical concentration is identified as C_X in our treatment. This phenomenon does not occur in ordinary diffusion in binary systems.

The three parameters v, D, and C_X define the concentration profiles of diffusion which are shown in Figure 2. At the beginning of the diffusion process, *e.g.*, 4 min, the shape of the concentration–distance curve is essentially that described by Crank[5] for Fickian diffusion with a discontinuity in the concentration dependence of D. At longer times, the concentration profile assumes a different shape and a substantial portion of the swollen polymer contains acetone at a concentration not far from the surface concentration. At 20 min, for example, approximately 30% of the swollen polymer has a solvent concentration exceeding 95% of C_0. This is a rather dramatic demonstration of the influence of the case II mechanism.

We are aware of the fact that the assumption of a concentration-independent diffusion coefficient for $C > C_X$ is a gross simplification made solely for the purpose of convenience in calculation. Nevertheless, the excellent agreement between theory and experiment seems to substantiate the essential validity of the generalized diffusion equation. In order to take into account the concentration dependence of D, it is necessary to introduce an additional parameter, for example, $D = D_0 \exp \beta c$. The solution of the differential equation becomes more complicated. Although a better fit of the experimental results is expected with the additional parameter β, it is felt that such a procedure does not strengthen our argument materially and is therefore not attempted. It is important to bear in mind, though, that our computation yields an average diffusion coefficient.

We have also noted that the same data, when plotted in a conventional way as M_t *vs.* $t^{1/2}$, resemble one of the "anomalous" sorption[6] curves (Figure 3). It is our hope that the implication of this finding may provide some insight to the understanding of the "anomalous" sorption behavior.

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(6) J. Crank and G. S. Park, "Diffusion in Polymers," Academic Press, New York, N. Y., 1968, Chapter 5.