

# Difficulties Associated with the Measurement of the Diffusion Coefficient of Solvating Liquid or Vapor in Semicrystalline Polymer. II. Sorption-Desorption Kinetics

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## Synopsis

The diffusion coefficient of a solvating liquid or vapor in a semicrystalline membrane can be measured in a number of ways. In a previous paper, we discussed methods based on permeation rates. Here, we consider sorption-desorption kinetics at near-ambient temperatures. Anomalies are identified and possible causes discussed in the light of new experiments, mostly involving *p*-xylene and polyethylene.

## INTRODUCTION

The determination of the diffusion coefficients of solvating liquids and vapors in polyethylene by nonsteady- and steady-state permeation methods was considered in a previous paper.<sup>1</sup> It was shown that such methods are susceptible to errors arising from internal stress effects. Sorption-desorption kinetics provide another potentially convenient means of measuring these diffusion coefficients, though the literature strongly suggests that anomalous results are again common. For example, in their experiments on high- and low-density polyethylene, Rogers et al.<sup>2</sup> obtained plots of vapor sorption against time which were sigmoidal, yet the corresponding plots for desorption were Fickian in appearance. The non-Fickian characteristics were attributed to slow changes in the crystalline regions. A number of authors have noted that diffusion coefficients calculated from sorption kinetics agree with those obtained by steady-state measurements only under limiting conditions. Kishimoto and Matsumoto<sup>3</sup> brought the two methods into agreement by extrapolating to zero concentration. They also observed that the diffusion coefficient calculated from sorption kinetics increased with membrane thickness, but, on extrapolating to infinite thickness, agreement with steady-state methods was secured, the latter measurements being due to Meares.<sup>4</sup>

All of these observations prompt some reconsideration of the physical situation when a solvating molecule diffuses into a semicrystalline polymer.

## THEORY

Consider a plane, outgassed, isotropic membrane of thickness  $l$ , contacted at time zero with a vapor at fixed pressure and temperature. If the concentration just within the membrane instantly attains the value corresponding to the equilibrium solubility of the vapor in the polymer, the amount  $M_t$  of vapor absorbed at time  $t$  may be written as follows<sup>5</sup>:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_0^\infty \frac{1}{(2m+1)^2} \exp \left\{ \frac{-D(2m+1)^2 \pi^2 t}{l^2} \right\} \quad (1)$$

where  $M_\infty$  is the amount of vapor taken up by the sheet at sorption equilibrium, and  $D$  is the diffusion coefficient of the permeant. In this analysis,  $D$  is assumed constant and independent of concentration.

If  $t_{1/2}$  is the time for which the fractional uptake  $M_t/M_\infty = 0.5$ , it is possible to write, with negligible error,

$$\frac{t_{1/2}}{l^2} = \frac{1}{\pi^2 D} \ln \left\{ \frac{\pi^2}{16} - \frac{1}{9} \left( \frac{\pi^2}{16} \right)^9 \right\} = \frac{0.0492}{D} \quad (2)$$

The diffusion coefficient may be determined by means of eq. (2) if the half-time for a sorption experiment is known. The same equation, with suitable redefinition of  $M_t$  and  $M_\infty$ , also applies to a desorption experiment in which the membrane, initially equilibrated to some uniform concentration of vapor, is suddenly exposed to vapor at a lower or zero pressure.

For systems in which  $D$  is a function of concentration, application of eq. (2) to sorption-desorption data yields a value for the diffusion coefficient which is some sort of average over the concentration range existing in the membrane during the experiment. In this paper, an experiment in which one end of the concentration range was zero is described as an integral sorption (or desorption) experiment. Integral sorption and desorption experiments covering the same concentration range give two apparent diffusion coefficients,  $D_a$  and  $D_d$ . These are functions of  $C_0$ , defined as the concentration of vapor in the sheet at the end (sorption) or beginning (desorption) of the experiment. They may be related to the true diffusion coefficient,  $D$ , by means of correction methods due largely to Crank and Park.<sup>6</sup> Values of  $D$  obtained in this way are diffusion coefficients relative to the stationary membrane.

## EXPERIMENTAL

## Materials

**Polyethylenes.** Rigidex 50 high-density polyethylene of thickness 0.075 mm and density 955 kg/m<sup>3</sup> was supplied by BP Chemicals. Chips of Rigidex 50 were also used. A similar Rigidex was quoted as having an  $\bar{M}_w$  value of about 80,000 and with  $\bar{M}_w/\bar{M}_n$  equal to about 5. Alkathene low-density polyethylene was obtained from Imperial Chemical Industries Ltd. in the form of sheets 4.7 mm thick and with a density of 927 kg/m<sup>3</sup>;

$\bar{M}_w$  was about  $1.5 \times 10^6$ . When films of a particular thickness were required, they were cast from either of the above polyethylenes in a suitable Melinex-lined press as previously described.<sup>1</sup> Melting at 145°C was followed by cooling at 10°C/hr.

**Solvents.** *p*-Xylene, 99%, was supplied by Imperial Chemical Industries Ltd. and used as received. The major contaminants were the other isomers of xylene. Other liquids were of A.R. or spectroscopic grade and were used as received.

### Apparatus and Procedures

**Vapor Sorption-Desorption Kinetics.** The apparatus used was described briefly in a previous paper<sup>7</sup> and was of the familiar type in which the amount of vapor sorbed is determined from the extension of a calibrated quartz spiral bearing the polymer specimen. The important unit for vapor generation was shown as Figure 3 in another paper.<sup>8</sup> The mass of a specimen was normally between 40 and 60 mg, and the half-times for sorption and desorption varied between 30 sec and several hours.

**Liquid Sorption-Desorption Kinetics.** Blocks of polymer, about 30 mm square, were cut from the Alkathene sheets of thickness 4.4 mm. They were placed in tubes filled with liquid permeant, and the tubes were immersed in a thermostat at  $25^\circ \pm 0.05^\circ\text{C}$ . At selected times the blocks were withdrawn from the liquid, wiped quickly with a tissue, transferred to a stoppered tube, and weighed to  $\pm 0.2$  mg. They could be replaced in the liquid after a total time lapse of between 1 and 2 min. Permeant losses in this time amounted to less than 0.5 mg, which was negligible compared with the equilibrium uptake of about 300 mg. Sorption equilibrium was considered to have been attained when successive weighings 48 hr apart showed no further increase in the mass of the swollen polymer. The time required for the attainment of equilibrium was not less than one week. Liquid uptakes were calculated on the basis of the original mass of dry polymer. At the end of a sorption experiment the surfaces of the blocks were wiped dry and they were placed on a wire mesh tray directly below a slow moving fan in a room maintained at  $25^\circ \pm 1^\circ\text{C}$ . The rate of desorption was determined by weighing the blocks periodically. When desorption had proceeded far enough for a particular experiment, final drying out was hastened by placing the block in an oven at 80°C until the mass became constant. The mass of the dried block was used in all calculations concerning the rate of desorption. Typically, it was about 0.7 wt-% less than the original mass of the dry block before sorption.

**Density.** Polymer densities were measured at 25°C by means of a gradient column containing carbon tetrachloride and *p*-xylene.

## RESULTS

Reduced integral sorption-desorption curves for *p*-xylene vapor and polyethylene at 30°C are shown in Figure 1. The three films of different

thicknesses were cast<sup>1</sup> from pellets of Rigidex 50, and three different vapor activities were used, hence the set of nine separate experiments.

It was important to compare the films of different thicknesses with respect to sorption-desorption characteristics. Table I shows, for each film, the density, the measured *p*-xylene vapor uptake at the lowest and the highest vapor activities, and the apparent diffusion coefficients  $D_a$  and  $D_d$

TABLE I  
Sorption-Diffusion Data for *p*-Xylene and Membranes of High-Density Polyethylene<sup>a</sup>

Thickness, mm	Density, kg/m <sup>3</sup>	$C_0$ , kg/kg		Apparent diffusion coefficient $\times 10^{12}$ , m <sup>2</sup> /s			
		$a = 0.39$	$a = 0.92$	$a = 0.39$		$a = 0.92$	
				$D_a$	$D_d$	$D_a$	$D_d$
0.0449	975 <sub>3</sub>	0.0144	0.0492	0.48	0.45	1.34	3.41
0.0766	975 <sub>5</sub>	0.0138	0.0503	0.53	0.46	1.94	2.91
0.1774	975 <sub>4</sub>	0.0144	0.0504	0.53	0.46	2.34	2.42

<sup>a</sup> Activity of *p*-xylene vapor =  $p/p_0 = a$ .

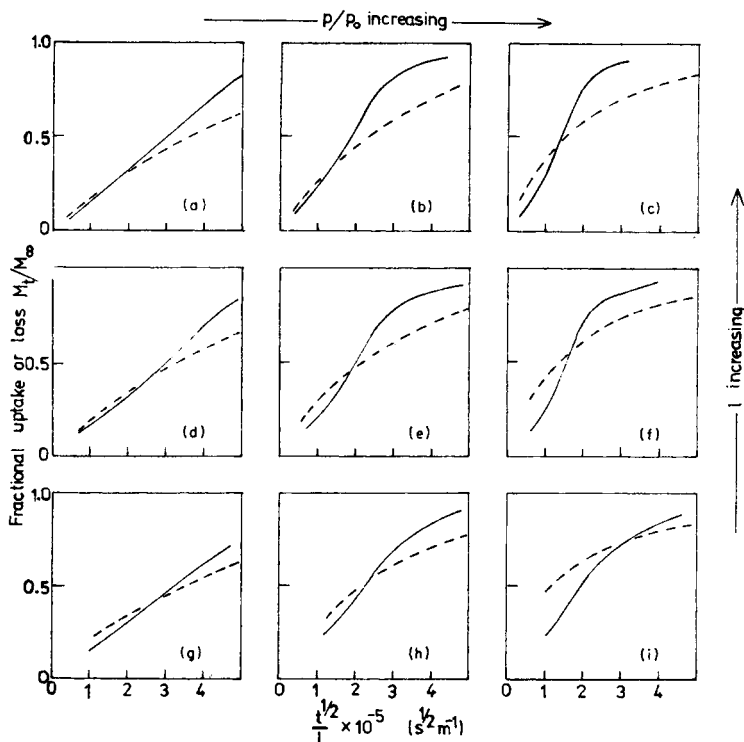


Fig. 1. Reduced integral sorption-desorption curves for *p*-xylene vapor and high-density polyethylene at 30°C: (a), (b), (c)  $l = 0.1774$  mm; (d), (e), (f)  $l = 0.0766$  mm; (g), (h), (i)  $l = 0.0449$  mm; (a), (d), (g)  $p/p_0 = 0.39$ ; (b), (e), (h)  $p/p_0 = 0.70$ ; (c), (f), (i)  $p/p_0 = 0.92$ ; (—) sorption; (---) desorption.

for these activities. The diffusion coefficients were calculated from the measured half-times for the integral sorption and desorption experiments shown in Figure 1. The data show good agreement between samples for the lower vapor activity but, for the higher activity, the diffusion coefficients are in poor agreement for the films of lowest and intermediate thickness.

For the highest vapor activity, the detailed results for sorption into the three Rigidex films appear in Figure 2, and similar results for three Alkathene films are in Figure 3. The reduced integral sorption curves for these experiments are all plotted in Figure 4, while Figure 5 presents the corresponding desorption data in reduced form. Some experiments on the sorption and desorption of liquid toluene or cyclohexane constitute Figure 6.

### DISCUSSION

It may appear strange that the desorption curves in Figure 1 fail to pass through the origin, but there is a trivial explanation for this. At the start of a desorption run, the apparatus was opened to the vacuum system by slowly turning a large glass tap with both hands. This required some 2 or

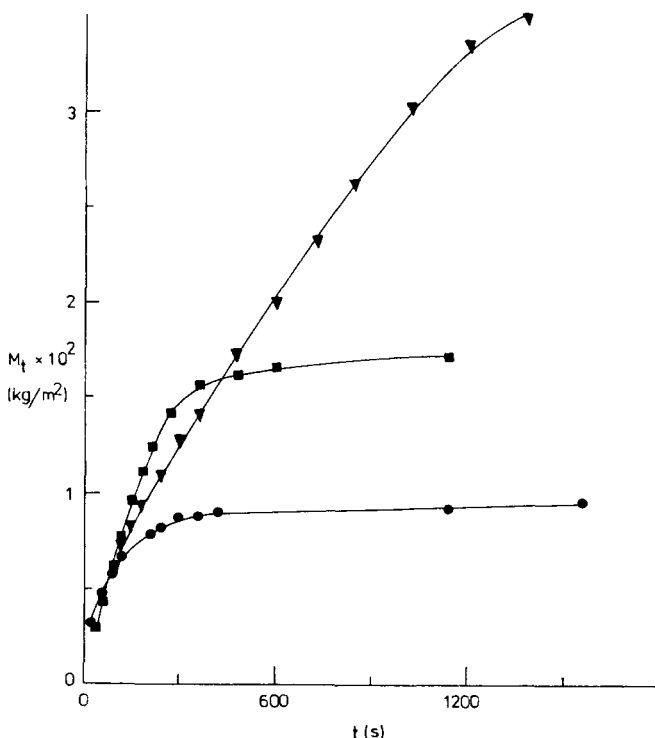


Fig. 2. Sorption of *p*-xylene vapor ( $p/p_0 = 0.92$ ) into high-density polyethylene at 30°C: ( $\blacktriangledown$ )  $l = 0.1774$  mm,  $M_\infty \times 10^2 = 4.37$  kg/m<sup>2</sup>; ( $\blacksquare$ )  $l = 0.0766$  mm,  $M_\infty \times 10^2 = 1.89$  kg/m<sup>2</sup>; ( $\bullet$ )  $l = 0.0449$  mm,  $M_\infty \times 10^2 = 1.08$  kg/m<sup>2</sup>.

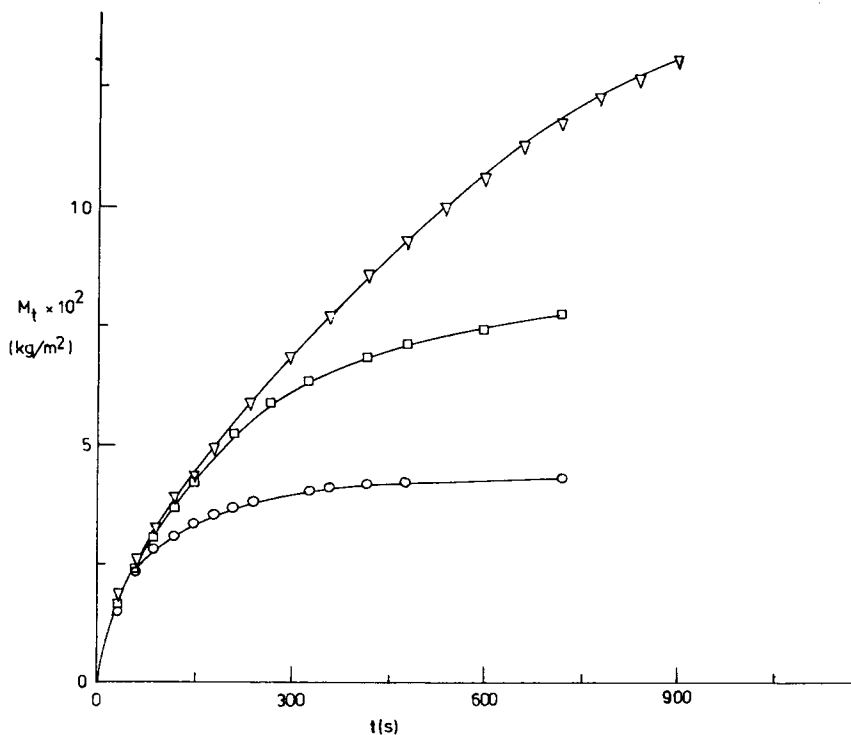


Fig. 3. Sorption of *p*-xylene vapor ( $p/p_0 = 0.92$ ) into low-density polyethylene at 30°C: ( $\nabla$ )  $l = 0.227$  mm,  $M_\infty \times 10^2 = 16.6$  kg/m<sup>2</sup>; ( $\square$ )  $l = 0.122$  mm,  $M_\infty \times 10^2 = 8.7$  kg/m<sup>2</sup>; ( $\circ$ )  $l = 0.060$  mm,  $M_\infty \times 10^2 = 4.4$  kg/m<sup>2</sup>.

3 sec. and the stopwatch was started immediately afterward. Extrapolation of the desorption curves to  $M_t/M_\infty = 0.0$  gives a time intercept of the appropriate magnitude. These errors of a few seconds had a negligible effect on  $D_a$  values calculated from half-times, and it was not necessary to apply a correction.

Inspection of Figure 1 shows that for the thickest film at the lowest vapor activity, the curves are apparently consistent with the requirements for Fickian diffusion with a concentration-dependent diffusion coefficient. For higher vapor activities or thinner films, two anomalies appear, similar to those reported by Rogers et al.<sup>2</sup>: (i) the sorption curves assume a sigmoid shape and (ii) desorption becomes faster than sorption.

Previous work<sup>1</sup> established the effect of stress when a membrane used for permeation experiments approached equilibrium from an initially solvent-free state. It is therefore appropriate to consider the possibility that similar stresses influence the sorption-desorption kinetics. Sorption of organic vapor into an initially dry membrane will result in an attempt by the outer regions to swell isotropically, but the inner solvent-free core will restrain the increase in area. This may lead to two separate effects. Firstly, the outer regions of the specimen will be compressed by the core

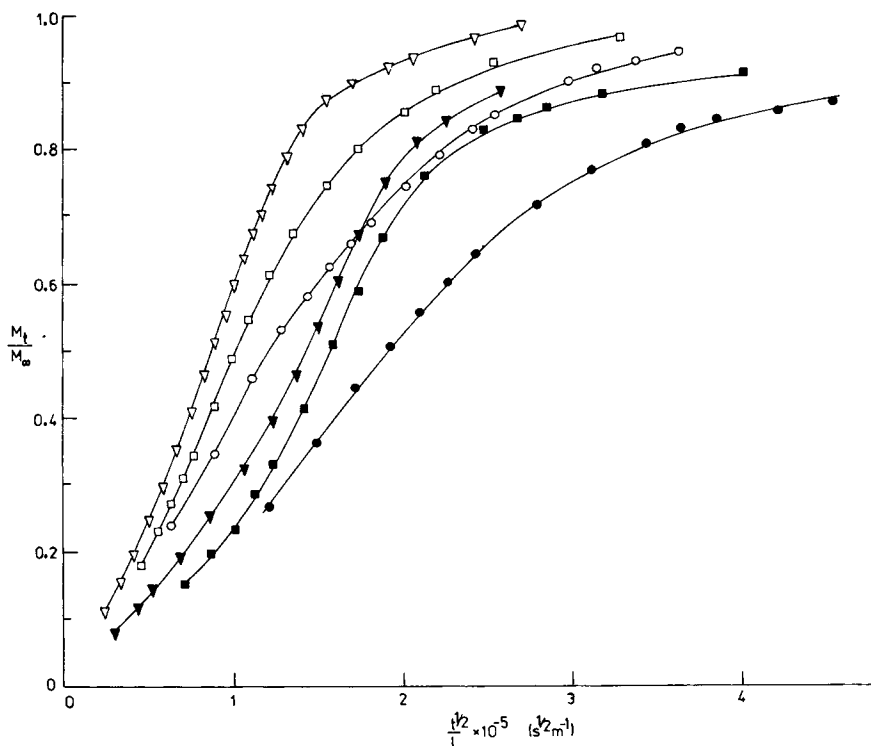


Fig. 4. Reduced integral sorption curves for *p*-xylene vapor and high- or low-density polyethylene at 30°C. (Data from Figs. 2 and 3: see legends of these figures.)

which will, in turn, be stretched. Secondly, the surface concentration will not immediately reach the true equilibrium value appropriate to unconstrained polymer.

Crank<sup>9</sup> has described a simplified mathematical analysis of the former effect. He assumed that internal stress affected the diffusion coefficient but not the surface concentration. By means of a stepwise approximation to the concentration dependence of the diffusion coefficient, he was able to show that these compression-extension effects could lead to sigmoidal sorption curves. A consequence of the model for a given system is that there should be a certain period during the sorption process when a thin sheet of film will have absorbed more penetrant per unit area than a thicker film. This prediction is borne out by the plots on Figure 2 for the high-density polyethylene, but not by Figure 3, which concerns the low-density material. The reason for this difference is uncertain, but the noncrystalline regions in low-density polyethylene may perhaps accommodate a change in the shape of the specimen more easily.

A further implication of Crank's analysis is that when sorption data are plotted in reduced form ( $M_t/M_\infty$  against  $t^{1/2}/l$ ), the curves for films of

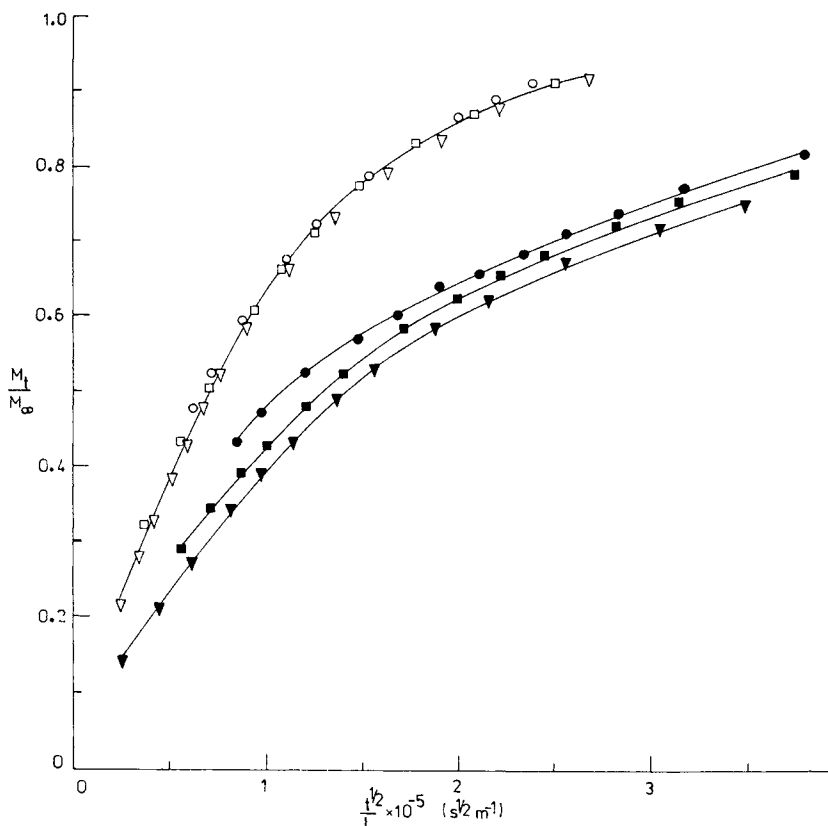


Fig. 5. Reduced integral desorption curves for *p*-xylene vapor and high- or low-density polyethylene at 30°C. (See legends for Figs. 2 and 3.)

different thicknesses should superpose. Figure 4 shows that the curves are not superposable, and the effect of internal stress on the diffusion coefficient is an insufficient explanation of the anomalous sorption effects. For both high and low-density polyethylene, the trend is toward higher rates of absorption with increasing film thickness.

It is impossible to deduce from Figure 4 that the effect of stress on the surface concentration is actually the sole, or even a contributing, cause of the observed dependence of the rate of vapor uptake on film thickness. Slow relaxation processes in the noncrystalline regions (shown to be important in the nonsteady-state permeation of *p*-xylene through polyethylene<sup>1</sup>) could lead to sigmoidal sorption curves and to the observed rate dependence. These slow processes could also lead to time dependence in the surface concentration, as observed by Long and Richman<sup>10</sup> during the sorption of methyl iodide by glassy cellulose acetate, and to time dependence in the diffusion coefficient at a particular concentration, as shown by Crank.<sup>9</sup> Either of these two effects of slow relaxation could account<sup>9,10</sup> for the observations plotted in Figure 4.



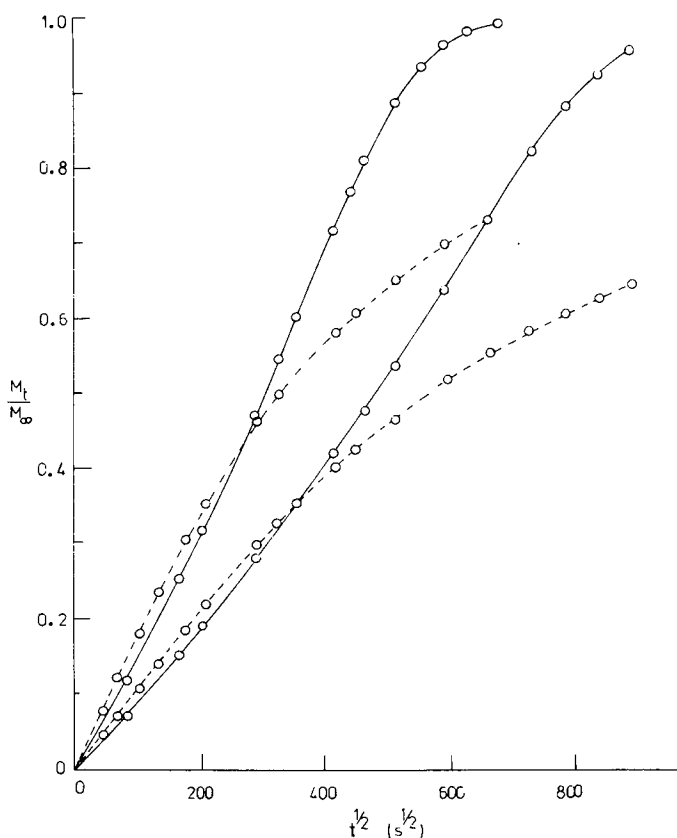


Fig. 6. Reduced integral sorption and desorption curves for liquid toluene (upper pair of curves) and liquid cyclohexane (lower pair of curves) and low-density polyethylene at 25°C: (—) sorption; (---) desorption. (Abscissa is  $t^{1/2}$  rather than  $t^{1/2}/l$  because films were of such uniform thickness.)

Fortunately, the influence of time dependence on the diffusion coefficient can be studied qualitatively from the reduced integral desorption curves shown in Figure 5. In an integral desorption experiment, the concentration is more uniform through the film than during sorption, so the effects of internal stress will be small.<sup>9</sup> Furthermore, the surface concentration is unambiguously zero at all times. The effect of any slow relaxation processes must therefore be confined to the introduction of a time dependence in the diffusion coefficient. The direction of this effect will be opposite to that acting during sorption, because in desorption the diffusion coefficient will approach its equilibrium value from above. On this basis, the rate of desorption should be seen to increase with decreasing film thickness when the data are plotted in reduced form. This is borne out by Figure 5, and comparison with Figure 4 shows that the effect of film thickness is much less for desorption. Indeed, for low-density polyethylene, the curves actually superpose and are outwardly Fickian.

These results suggest that sorption, unlike desorption, is affected by time dependence in the surface concentration, and this may be due to internal stresses or slow relaxations (or both). The integral sorption curves presented on Figure 6 strongly point to internal stress as the major cause. The experiments concerned the sorption of liquid toluene and liquid cyclohexane into relatively thick (4.4-mm) sheets of low-density polyethylene. Under these conditions the time scale was such as to minimize the influence of any slow relaxation processes. The fact that the integral sorption curves are nevertheless sigmoidal indicates an internal stress effect, especially as desorption is initially faster than sorption.

### CONCLUSIONS

Important and unavoidable internal stress effects are in operation during the sorption of organic permeants into polyethylene. These effects preclude the use of integral sorption experiments as a means of determining the diffusion coefficients of solvating molecules in a semicrystalline polymer. Integral desorption experiments, in which the effects of internal stress are small, offer some hope for the measurement of these diffusion coefficients, but further work is required.

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