

Sorption of Carbon Tetrachloride in Low-Density Polyethylene Pellets

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Synopsis

Unsteady-state conjugate sorption curves for carbon tetrachloride in low-density polyethylene (LDPE) pellets at temperatures between 40 and 70°C suggested there was a maximum in the diffusivity-concentration relationship at high values of concentration. The sorption curve at 70°C also displayed features characteristic of pseudofickian behavior, which was attributed to clustering of the penetrant at the high vapor activity corresponding to this temperature.

INTRODUCTION

Studies of diffusion in polymer solids are of interest because of the importance of transport properties in several applications. Also, the nature of the movement of penetrant in a polymer can provide information about certain characteristics of the solid, such as the flexibility of the molecular chains, the nature of the interaction between adjoining molecular segments, and the overall morphology.¹

In this paper we report sorption measurements of carbon tetrachloride vapors in low-density polyethylene (LDPE) pellets. These results are part of a larger investigation into the effects of morphology of extruded LDPE rods on the diffusivity of various vapors. Carbon tetrachloride was used as a probe molecule because of its suitability for detection by energy dispersive x-ray spectrometry, which was used to determine its concentration profile after various periods of absorption.²

MATERIALS AND METHODS

Materials

Low-density polyethylene (CIL 300 GXN7218) was supplied by Canadian Industries Ltd. (Edmonton, Alberta) in the form of nearly cylindrical pellets (4.0 mm in diameter \times 3.5 mm long, surface-to-volume ratio $\sim 1.57 \text{ mm}^{-1}$). The melt index was 2.07 (ASTM D1238-73), density was 928.7 kg/m^3 (ASTM D1506-68), and percentage crystallinity (DSC) was 32 ± 2 . Carbon tetrachloride (Caledon Laboratories Ltd., Caledon, Ontario) was used with density $1583.0\text{--}1585.0 \text{ kg/m}^3$ at 25°C and boiling range $76.7 \pm 0.1^\circ\text{C}$.

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Sorption Measurements

The unsteady sorption of carbon tetrachloride in low-density polyethylene pellets at various temperatures and atmospheric pressure was measured as before³ with a Cahn electrobalance (Model 2000, Cahn Instruments, Cerritos, California). Temperature was maintained at 40–70°C ($\pm 0.1^\circ\text{C}$) by circulation of hot water (water bath circulator RC3, Lauda, FRG) through a jacketed tube surrounding the sample and carbon tetrachloride. The carbon tetrachloride reservoir was maintained at the temperature of interest for 1 h prior to insertion of the sample. The rate of mass uptake was determined by suspending a LDPE pellet from the balance 1 cm above the level of carbon tetrachloride in the sample tube during absorption; after equilibrium was achieved, the system was evacuated to begin the desorption experiment. In one series of experiments at 70°C, the level of pellet above the CCl_4 reservoir was varied from 1 to 8 cm. No effect of pellet position on the rate of absorption or on the equilibrium uptake was noted, indicating that the pellet was exposed to saturated vapor. Time lag calculations suggest that the vapor at the pellet surface would be saturated within a minute even if the air space above the reservoir were completely vapor free to begin with; thus only the first data point in Fig. 1 would be expected to be in error. This technique was used since it was used previously³ for sorption measurements with low-vapor-pressure compounds, such as dicumyl peroxide, for which the more conventional method involving cracking the vapor from a large ballast volume was not effective.

The diffusivity was estimated from the slope of a plot of M_t/M_∞ versus \sqrt{t} using the surface-to-volume ratio of the LDPE pellet⁴:

$$\frac{M_t}{M_\infty} = 2a \left(\frac{Dt}{\pi} \right)^{1/2} \quad (1)$$

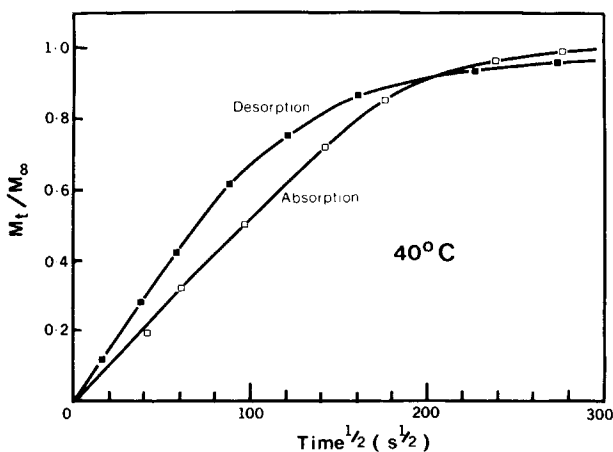


Fig. 1. Absorption and desorption curves obtained from conjugate sorption experiments for carbon tetrachloride in as-supplied low-density polyethylene pellets (4-mm diameter): \square , absorption; \blacksquare , desorption; (a) 40°C (b) 50°C (c) 60°C (d) 70°C.

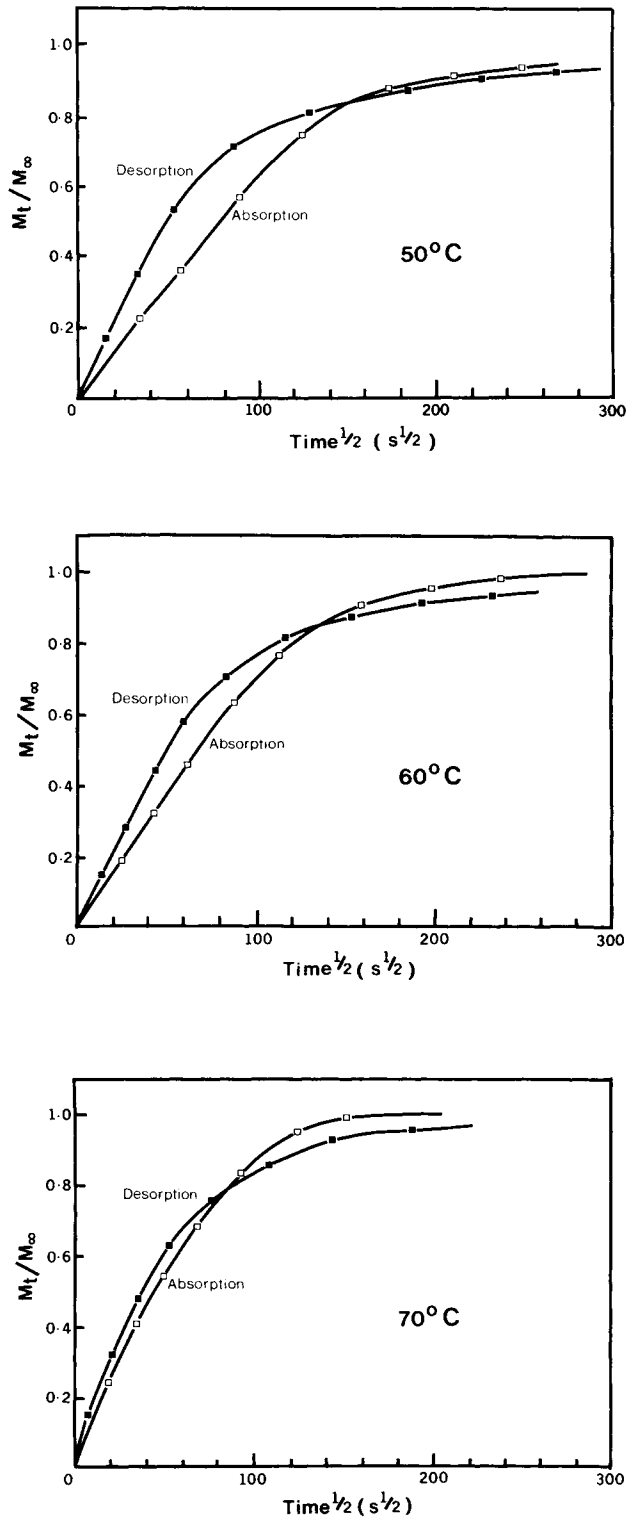


Fig. 1. (continued from previous page.)

where M_t = mass gained at time t , M_∞ = mass gained at equilibrium, a = surface-to-volume ratio, D = diffusivity, and t = time. The error associated with the application of this equation based on one-dimensional diffusion to cylindrical pellets with a small aspect ratio was checked and found to be negligible.³

RESULTS AND DISCUSSION

Figure 1 shows the sorption curves (plot of M_t/M_∞ against \sqrt{t}) for carbon tetrachloride in LDPE pellets at temperatures between 40 and 70°C obtained by conjugate sorption experiments. Average values of diffusivity estimated from these curves using eq. (1) are represented in an Arrhenius plot (Fig. 2); with the exception of sorption at 70°C, a linear relationship was found. From the plot of average diffusivities the pre-exponential factor D_∞ and energy of activation E_d in the Arrhenius expression over the linear range 40–60°C were determined to be $E_d = 48.24$ kJ/mol and $D_\infty = 8.48$ cm²/s. The equilibrium uptake values were also represented by a linear Arrhenius-type relationship, as shown in Fig. 3.

Figure 1 shows that desorption proceeded more rapidly than absorption in the early stage, but the final stages of desorption were slower than those of absorption. In Fig. 4, the sorption data at 60°C for large times were replotted as $\ln(1 - M_t/M_\infty)$ against time to show an abrupt change in slope at a certain stage of sorption. Similar breaks in slope were found at all sorption temperatures. Several systems in the literature have been found

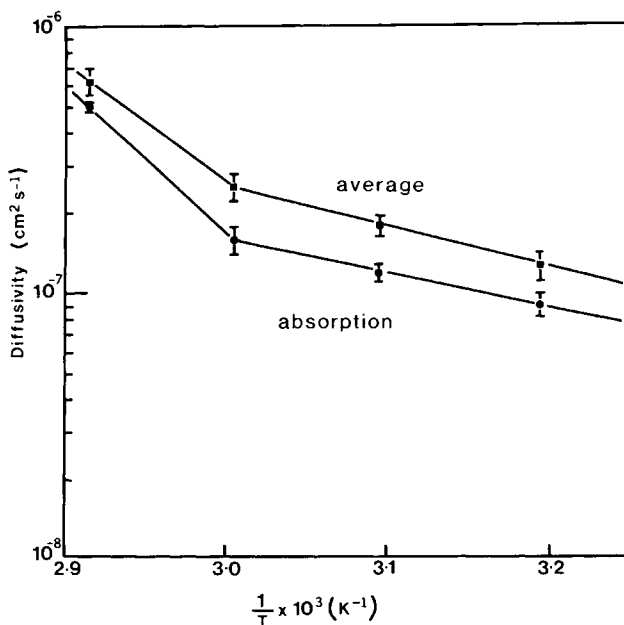


Fig. 2. Temperature dependence of diffusivity of carbon tetrachloride in as-supplied low-density polyethylene pellets. Mean of three to four samples \pm standard deviation: ●, absorption; ■, average diffusivity obtained from both absorption and desorption coefficients.

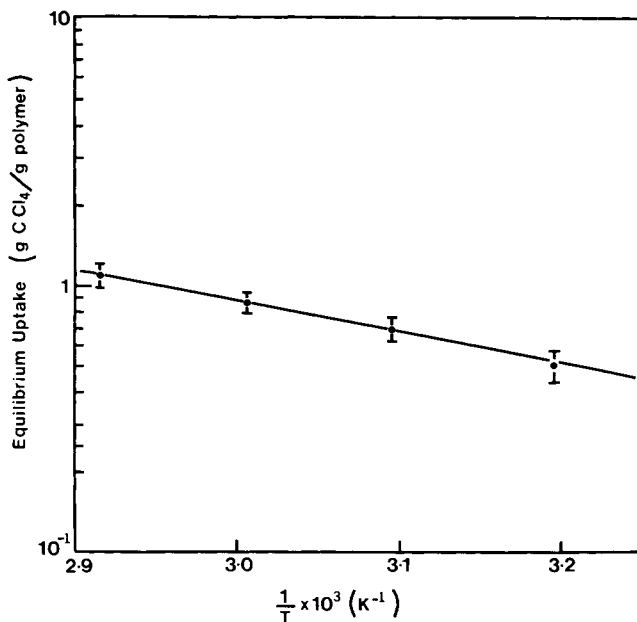


Fig. 3. Temperature dependence of equilibrium uptake of carbon tetrachloride in as-supplied pellets of low-density polyethylene. Mean of three to four samples \pm standard deviation.

to exhibit similar behavior. The standard examples are the sorption of benzene in polybutadiene-co-methacrylate^{5,6} or polyisobutylene⁷ and acetone in polyvinyl acetate.⁸ Crank⁹ has shown that the relative rates of desorption and absorption would reverse themselves at a particular stage if there were a maximum in the diffusion coefficient-concentration relationship, provided the value of D at the equilibrium concentration was greater than at zero concentration. The points of intersection of the two sorption curves varied from a M_t/M_∞ value of 0.75 to 0.95 as the sorption temperature decreased from 70 to 40°C. These points of intersection correspond to the values of C/C_0 at the maximum in the curves relating diffusivity to concentration.

Also, the early time region of the absorption curve at 70°C in Fig. 1d had a pronounced curvature toward the \sqrt{t} axis as it steadily approached the final equilibrium value. Rogers¹⁰ termed such behavior during absorption and desorption pseudofickian. Davis and Rooney¹¹ reported a similar observation for SO_2 sorption in polycarbonate. Sorption curves at 40, 50, and 60°C were linear in the initial stages and had the shape expected for fickian sorption.

This pseudofickian behavior could be due to a diffusion coefficient decreasing with time, which is possible if clustering of the penetrant occurred. Rogers et al.¹² used correlations developed by Zimm and Lundberg to show that a considerable amount of clustering occurs during sorption of certain organic vapors (e.g., methyl bromide, *n*-hexane, and *p*-xylene) by polyethylene. Clustering may cause the diffusion coefficient to decrease with time, since relaxation of the polymer chains in the same time scale as that of

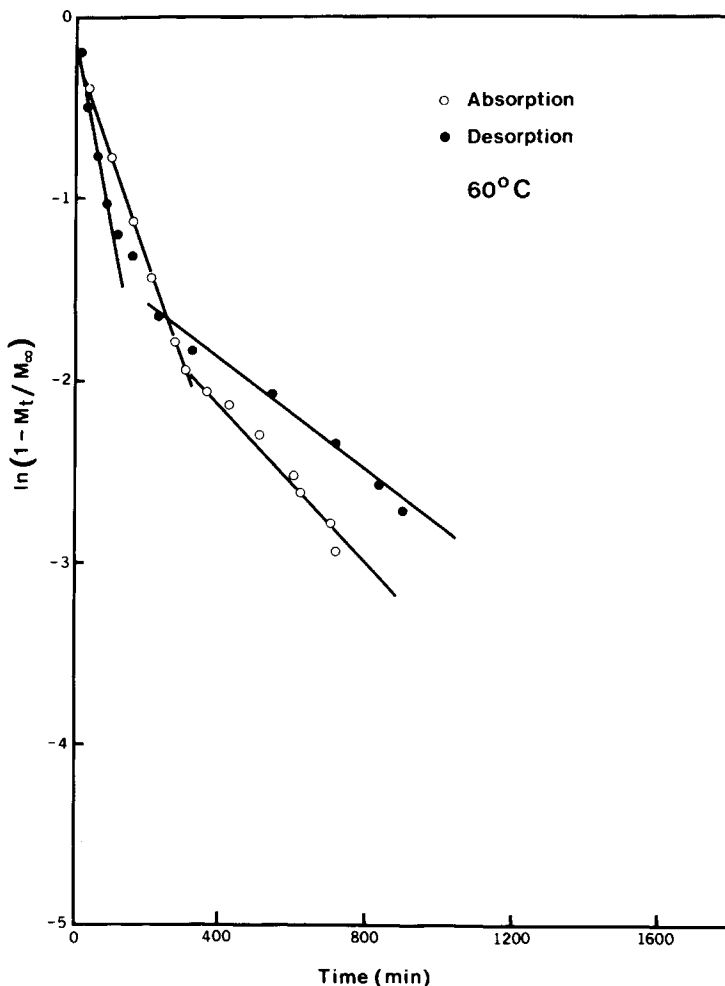


Fig. 4. A typical large-time sorption plot of carbon tetrachloride in as-supplied low-density polyethylene pellets (4-mm diameter) at 60°C.

diffusion may result in a net transfer of penetrant molecules from a free to aggregated state.¹³ Berens and Hopfenberg¹⁴ obtained sorption curves of a pseudofickian type based on a model that assumed both relaxation and fickian diffusion.

It is not clear, however, why clustering in this system should occur and why only at 70°C. It is conceivable that the diffusion coefficient may be time dependent in the early time region as the polymer chains may be unable to change their configuration quickly enough to adjust to the change in concentration at the high vapor activity corresponding to 70°C (equilibrium uptake ~ 0.508 g/g dry polymer). The desorption curve at 70°C also shows a decrease in the slope at early times, presumably due to consolidation of polymer chains, which may result in a diffusion coefficient decreasing with time. At the lower vapor activities corresponding to lower temperatures, it is assumed that clustering is less apparent and hence this nonfickian anom-

ally disappears. It would be of interest to examine the mean cluster size at higher sorption temperatures using the Zimm-Lundberg theory¹⁵ to further clarify this question.

The financial support of Canadian Industries Limited and the Natural Sciences and Engineering Research Council is gratefully acknowledged.

References

1. M. V. Sefton and K. T. Chiang, *Advan. Chem.*, **174**, 243-257 (1979).
2. J. P. Gupta and M. V. Sefton, *J. Appl. Polym. Sci.* (in press).
3. J. P. Gupta and M. V. Sefton, *J. Appl. Polym. Sci.*, **29**(7), 2383 (1984).
4. R. McGregor, *Diffusion and Sorption in Fibres and Films*, Vol. I, Academic Press, London, (1979), p. 212.
5. D. Machin and C. E. Rogers, *Makromol. Chem.*, **155**, 269-281 (1972).
6. D. Machin and C. E. Rogers, *CRC Critical Rev. Macromol. Sci.*, **1**, (1972).
7. M. J. Hayes and G. S. Park, in *Diffusion in Polymers*, J. Crank, G. S. Park, Eds., Academic Press, London, (1968), p. 142.
8. R. K. Kokes, F. A. Long, and J. C. Hoard, *J. Chem. Phys.*, **20**, 1704 (1952).
9. J. Crank, *The Mathematics of Diffusion*, second edition, Oxford University Press, London, (1976), pp. 179-189.
10. C. E. Rogers, in *Physics and Chemistry of the Organic Solid State*, Vol. 2, D. Fox, M. M. Labes, and A. Weissberger, Wiley, New York, Chapter 6, (1965), p. 606.
11. G. Davis and M. L. Rooney, *Kolloid Z.*, **249**, 1044 (1971).
12. C. E. Rogers, V. Stannett, and M. Szwarc, *J. Polym. Sci.*, **45**, 61 (1960).
13. J. H. Petropoulos and P. P. Roussis, *J. Chem. Phys.*, **47**, 1491 (1967).
14. A. R. Berens and H. B. Hopfenberg, *Polymer*, **19**, 489 (1978).
15. B. H. Zimm and J. L. Lundberg, *J. Phys. Chem.*, **60**, 425-428 (1956).

Received June 3, 1985

Accepted November 15, 1985