

# Diffusion of Organic Penetrants through Low Density Polyethylene (LDPE) Films: Effect of Size and Shape of the Penetrant Molecules

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## Synopsis

The diffusion coefficient at zero penetrant concentration  $D_0$  of dichloromethane, chloroform, carbon tetrachloride, cyclohexane, benzene, *o*-xylene, *m*-xylene, *p*-xylene, and *n*-hexane in LDPE were measured at 25°C, using the desorption method. The  $D_0$  values obtained in this way are correlated with the size, shape, and chemical nature of the penetrant molecules. The temperature dependence of the diffusion coefficients of toluene and *n*-hexane in LDPE are also reported in the limited temperature range of 25–45°C. It indicates that, in spite of a size larger than that of toluene, *n*-hexane has a lower activation energy of diffusion.

## INTRODUCTION

Through a score of studies, it has been well established that the diffusion of gases, vapors, and liquids in polymers mainly depends on the nature of the polymer, temperature, concentration of the penetrant, and shape and size of the diffusing molecule. The first three factors have been investigated more thoroughly whereas relatively fewer studies<sup>1–4</sup> pertain to the latter factors, namely, the size and shape of the penetrant molecule.

Investigations on polyisobutene, polybutadiene, polymethylacrylate, and plasticized poly(vinyl chloride) with various penetrants conclude a decrease in  $D_0$  with increasing the size of the penetrant. On the basis of the results obtained in this study, it was also noticed that smaller but more rigid diffusant molecules (e.g., cyclohexane) have a lower diffusion coefficient than a larger but linear molecule (e.g., *n*-hexane). This was attributed to molecular shape, which modifies the effect of molecular size. When the molecular diameter of the penetrant was correlated with  $\log D_0$ , it led to the suggestion that an elongated molecule such as *n*-hexadecane will have a larger diffusion coefficient than would be predicted purely from the cross-sectional area.<sup>4</sup>

According to Fujita's free volume theory,<sup>5</sup> the thermodynamic diffusion coefficient,  $D^*$  is related to the free volume by the following expression:

$$D^* = ART \exp(-B/f) \quad (1)$$

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where  $A$  and  $B$  are parameters that are assumed to be independent of diffusant concentration and temperature. However,  $A$  is a preexponential factor which depends on the properties of the diffusant and the polymer, whereas  $B$  is a constant characterizing the size of the "hole" needed for a diffusional jump.<sup>6</sup> The fractional free volume of the system is denoted by  $f$ .

On the basis of eq. (1), the following equation can be written for the diffusion coefficient at zero penetrant concentration,  $D_0$ :

$$D_0 = ART \exp(-B/f_0) \quad (2)$$

where  $f_0$  is the fractional free volume of the pure polymer. Increasing the diffusant size will, in general, cause an increase in  $B$  and possibly a decrease in  $A$ . With the exception of DDT (1,1-bis-4 chlorophenyl-2,2,2 trichloroethane), this was found to be true in the case of plasticized poly(vinyl chloride)/penetrant systems.<sup>4</sup> More recently, Fleischer<sup>6</sup> reported  $B$  values of 0.85 and 0.88 for cyclohexane and benzene, respectively, in LDPE. An increase in  $A$  has been shown by Fleischer<sup>6</sup> on going from benzene to cyclohexane. In these two cases the low values of  $B$  for DDT and cyclohexane can be attributed to the rigid nature of the two molecules, which in turn confirm that  $B$  depends on the size as well as the shape of the diffusing molecule.

Although the free volume theory predicts that the diffusion coefficient increases with an increase in the free volume of the system, it was found that the dependence of the diffusion coefficient on the size of the diffusing molecule becomes less pronounced.<sup>3,4</sup> Very little information is available on the free volume theory parameters of various polymer/penetrant systems. The available information have been used to interpret some of the results reported in the literature with varying degrees of success (e.g., Refs. 6-9). This is because the free volume theory parameters cannot be determined with sufficient accuracy. Some of the problems associated with determining these parameters have been discussed by Kreituss and Frisch.<sup>9</sup> Consequently, in the present study we did not resort to using the free volume theory in order to interpret our results; rather, we have employed a series of penetrants with varying sizes and chemical natures that helped us gather more information on the effect of diffusant nature on diffusion in LDPE. For this very reason the present study extends over a number of aliphatic, aromatic, and chlorinated penetrants, and it reveals the effect of size decoupled from the effect of shape of the penetrant.

## EXPERIMENTAL

### Materials

Low density polyethylene films of 0.15 mm thickness were employed in this study. The LDPE was produced by Canadian Industries Ltd. (CIL, grade 503). The density of the LDPE film is 0.918 kg/L. The manufacturer (CIL) indicated that the grade 503 LDPE contains 5000 ppm of a proprietary antiblocking agent. The fractional crystallinity of the grade 503 LDPE ranges from 0.45 to 0.55 and the glass transition temperature is around  $-75^\circ\text{C}$ .

Gold label grade dichloromethane, benzene, toluene, cyclohexane, *o*-xylene, *m*-xylene, *p*-xylene, *n*-hexane, chloroform, and carbon tetrachloride were purchased from Aldrich Chemical Co. and were used without further purification.

### Procedure

All the sorption experiments have been carried out in a water bath maintained at a temperature of  $25 \pm 0.02^\circ\text{C}$ . Rectangular specimens of LDPE ( $40 \times 18 \times 0.15$  mm) with a hole at the top were cut and weighed. Each of these specimens were immersed in a test tube containing the liquid under study, which was maintained at constant temperature using a water bath. The experiment was continued until a sorption equilibrium was achieved. This was checked by periodically weighing the sample.

Desorption experiments were performed on a Cahn 2000 electrorecording balance, which was enclosed in a temperature controlled chamber ( $\pm 0.05^\circ\text{C}$ ) by a heating and cooling arrangement and a Sargent-Welch temperature controller. In addition, the sample hangdown tube of the balance is fitted with a water jacket that kept the sample temperature fluctuations to within  $\pm 0.02^\circ\text{C}$ .

Once the sorption was complete, the sample was removed from the liquid and was hung on the balance. The desorption kinetics were followed by evacuating the balance enclosure to a pressure in the range of 0.01 mm Hg and monitoring the weight changes with time on a strip-chart recorder.

Before the sample was hung on the balance, excess liquid was carefully removed by placing the polymer film between two filter papers. This excess liquid was removed in order to ensure a reproducible initial surface concentration of the penetrant. Triplicate runs achieved consistent results ( $\pm 3\%$ ). Mean values of  $D_0$  are reported.

### RESULTS AND DISCUSSION

In the final stages of desorption experiments, the concentration of the penetrant tends to zero; therefore, a plot of  $\ln(M_t - M_\infty)$  vs. time approaches a straight line whose slope is given by the following expression<sup>10</sup>:

$$\frac{d}{dt} [\ln(M_t - M_\infty)] = -\frac{\pi^2 D_0}{(2l)^2} \quad (3)$$

where  $M_t$  is the amount of penetrant in the polymer film at time  $t$  and  $M_\infty$  is the equilibrium amount attained theoretically after infinite time per unit area;  $2l$  is the thickness of the polymer film. This method has been used on previous occasions.<sup>11</sup> In this work  $D_0$  has been evaluated from the final part of the  $\ln(M_t - M_\infty)$  against time plots. A typical plot for chloroform at  $25^\circ\text{C}$  is shown in Figure 1. In each case, the linear portion of these plots was fitted to the best straight line by using the Library Subroutine LEAST and the slope of the line was determined. The determined value of the slope is used to calculate  $D_0$ .

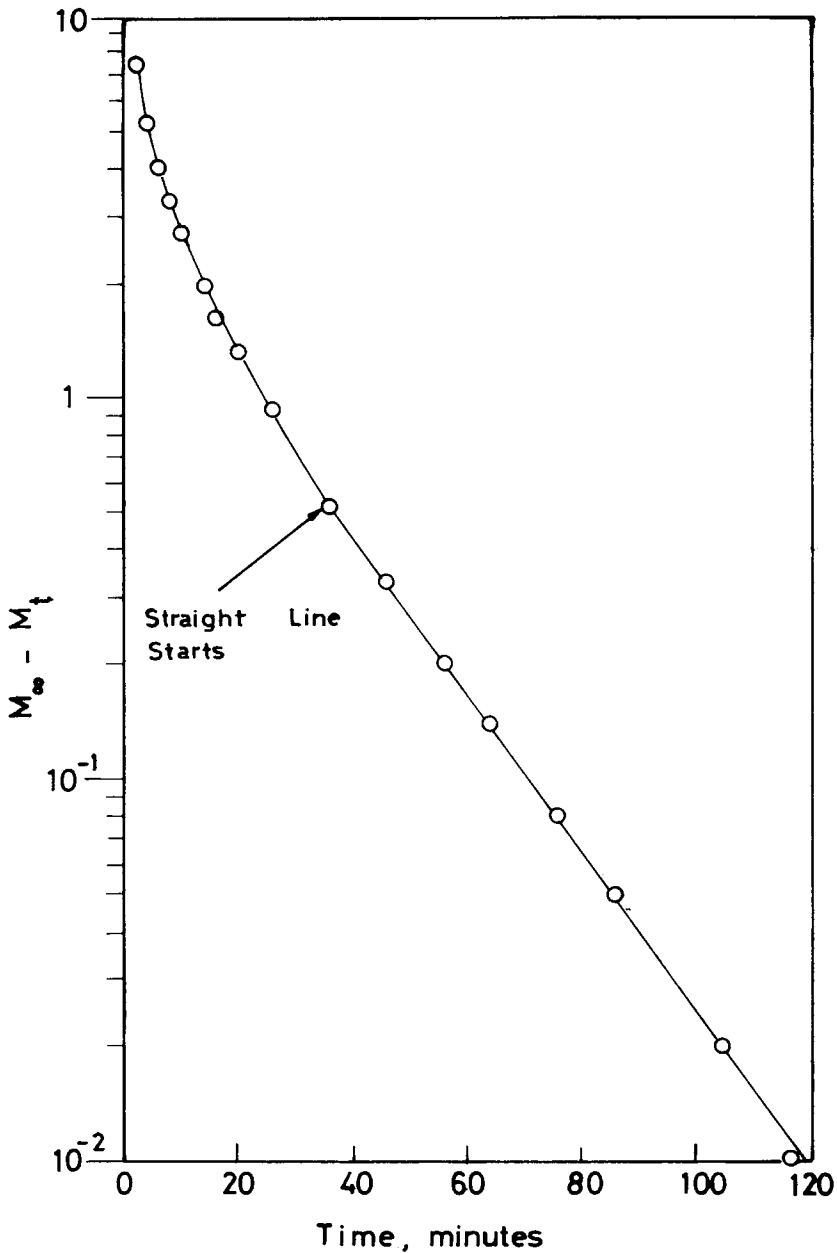


Fig. 1. Typical plot for the desorption of chloroform at 25°C.

### Effect of Size and Shape of the Penetrant Molecule

The  $D_0$  values obtained together with the molar volumes of the penetrants are reported in Table I. The data show that, apart from three exceptions ( $\text{CCl}_4$ , *o*-xylene, and cyclohexane), which will be explained subsequently, diffusion coefficients decrease with increasing the size of the penetrant mole-

TABLE I  
The Diffusion Coefficients  $D_0$  of Various Penetrants in LDPE at 25°C

Penetrant	Molar volume of the penetrant $\times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$	$D_0 \times 10^{12} \text{ m}^2 \text{ s}^{-1}$
Dichloromethane	63.6	5.062
Chloroform	80.2	1.783
Benzene	88.9	1.977
Carbon tetrachloride	96.5	0.656
Toluene	106.3	1.813
Cyclohexane	108.0	0.607
<i>o</i> -Xylene	118.0	0.940
<i>m</i> -Xylene	122.3	1.459
<i>p</i> -Xylene	122.6	1.567
<i>n</i> -Hexane	130.7	1.256

cules and tend to level off in the region of *m*-xylene and *n*-hexane. This is consistent with previous findings,<sup>4</sup> where it was suggested that as the diffusant size becomes larger, the decrease of  $D_0$  with increasing the molar volume becomes less pronounced. This appears to be generally true, however, another way for correlating the size with  $D_0$  involves comparing the penetrants of increasing size with similar basic chemical structure, thus annulling the effect of the latter to a greater extent. One of the lines in Figure 3 shows the change in  $\log D_0$  with the molar volume for aromatics with essentially the same molecular shape.

Despite the fact that a narrow range of penetrants has been studied, Figure 2 shows a linear decrease of  $\log D_0$  with increasing penetrant size. A further increase in the size of this series of penetrants may induce shape, length, and diameter effects.

The effect of the shape of the penetrant molecule can also be discerned from Figure 2 by examining the positional isomers of xylene. This is more obvious in the case of *o*-xylene; in spite of its smaller size compared to its counterparts, it has the lowest diffusion coefficient. This can be considered to indicate that its two adjacent methyl groups distort its symmetry and thus make it less mobile. This effect is less marked in *m*-xylene and tends to disappear in *p*-xylene where molecular symmetry is restored.

Michaels et al.<sup>12</sup> expected that the difference in configuration of xylenes would result in a variation of  $D_0$  for each xylene. On that basis they reported a method for the separation of a mixture of xylenes which utilizes a conditioned polyethylene polymeric film. Nevertheless, Michaels et al.<sup>12</sup> did not conduct any diffusivity measurements for their system.

Penetrants containing chlorine also show a decrease in  $D_0$  with increasing the penetrant size as can be seen from Figure 2. However, the magnitude of this decrease is about three times that of benzene and its methyl substitutes. This can be attributed to the bulky chlorine atom, which markedly reduces the mobility of the penetrant molecule. The diverse natures of the penetrant and the polymer could represent another reason for this behavior. An increase in the number of chlorine atoms in the penetrant molecule seems to reduce its

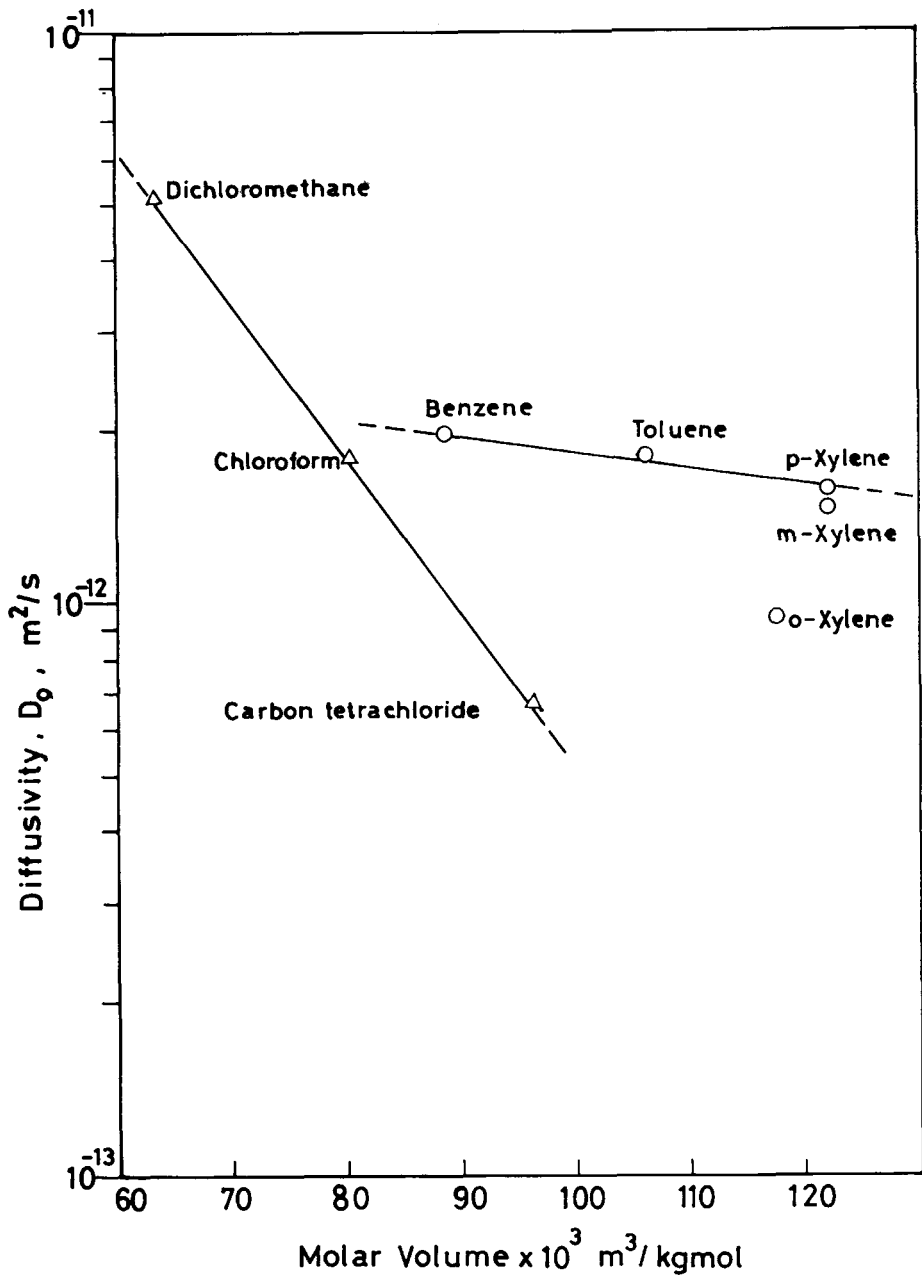


Fig. 2. Variation of  $D_0$  with molar volume.

probability of finding or creating an appropriate "gap size" between the adjacent polymer chains.

The value of  $D_0$  for cyclohexane is substantially lower than the value of  $D_0$  of toluene ( $6.07 \times 10^{-13}$  vs.  $1.81 \times 10^{-12}$   $\text{m}^2/\text{s}$ ), which has a similar molar volume (cf. Table I). Similar behavior was reported by Fleischer,<sup>6</sup> who employed pulsed field gradient NMR technique to measure diffusivities.

The value of  $D_0$  for cyclohexane obtained in this study is about three times higher than the value reported by Fels and Li<sup>8</sup> ( $6.07 \times 10^{-13}$  and  $2.25 \times 10^{-13}$  m<sup>2</sup>/s, respectively). We can offer the following explanations for such a difference: (i) LDPE samples used in both studies might have been different (since the properties of the LDPE used by Fels and Li were not reported, it is impossible to make definite statements concerning this effect), and/or (ii) failure to remove the surface liquid from the sample prior to starting desorption by Fels and Li could have resulted in this difference. It is clear from the work reported earlier by Fels<sup>13</sup> that no attempt was made to remove such surface liquid. Evaporation of the excess liquid lowers the temperature of the polymeric film sample, hence affecting the penetrant diffusion through it.

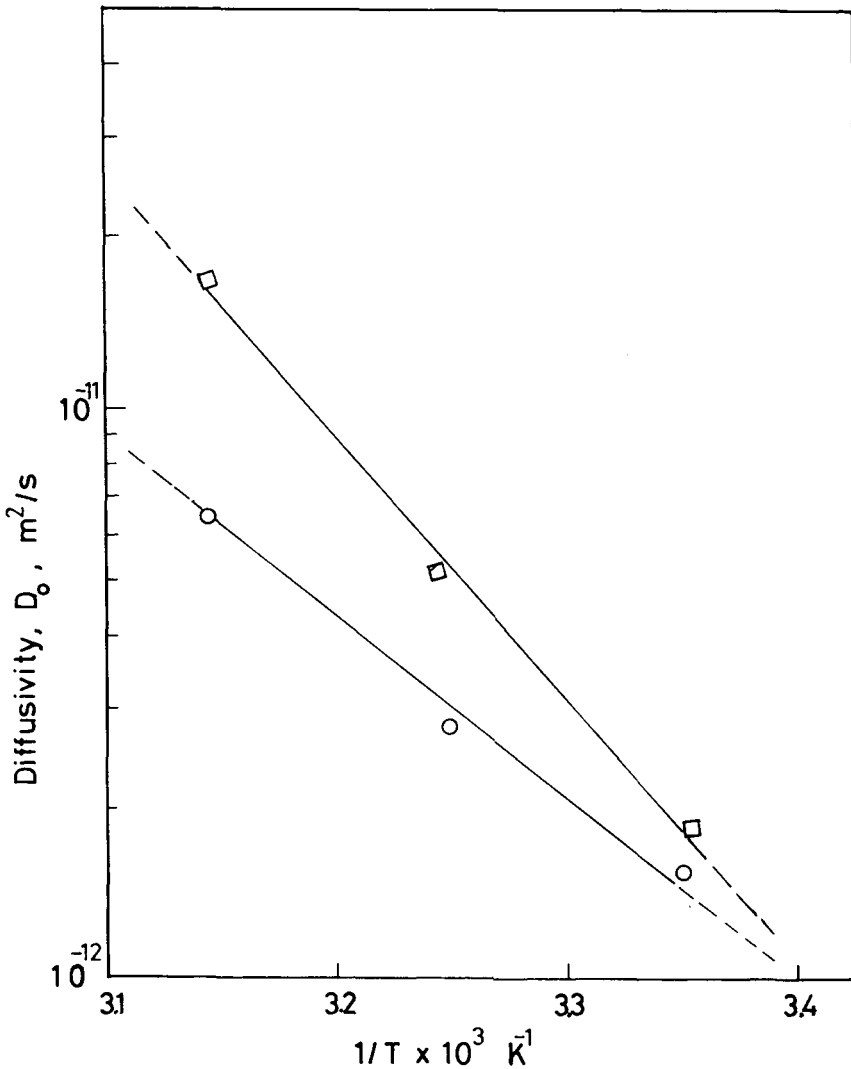


Fig. 3. Dependence of  $D_0$  on temperature of *n*-hexane (○) and toluene (□) in LDPE.

*n*-Hexane has the largest size amongst the penetrants studied, but its linear molecule compensates for its larger size. The linear molecules are considered to be more flexible,<sup>14</sup> which in our case results in a  $D_0$  value for *n*-hexane that is closer to the  $D_0$  of the smaller but more rigid *m*-xylene molecule.

### Effect of Temperature

The activation energy of diffusion is given by the following Arrhenius type relationship:

$$D_0 = D^0 \exp(-E_D/RT) \quad (4)$$

For many polymer-penetrant systems, plots of  $\log D_0$  vs. the reciprocal of the corresponding absolute temperature are linear over a limited temperature range.

In this study, the diffusion of toluene and *n*-hexane was investigated in the temperature range of 25–45°C. The plots of  $\log D_0$  vs.  $1/T$  are shown in Figure 3. Since this study pertains to a narrow temperature range, it can be assumed that the activation energies are independent of temperature. Estimates of activation energies from these plots yield values of 87.0 and 65.4 kJ mol<sup>-1</sup> for toluene and *n*-hexane, respectively. The low activation energy for the larger *n*-hexane molecule is rather surprising. Previously, it has been suggested<sup>15</sup> that the activation energy of diffusion shows an increase with the size of the penetrant until a value approximately equal to the activation energy of viscous flow is reached, after which it remains constant. Assuming that the value of viscous flow has not been reached in the system under study, the lower activation energy for *n*-hexane can probably be associated with the flexibility of such a molecule. Also, the similarity in shape between *n*-hexane and the larger molecule of polyethylene could lead to the high frequency of finding the "hole" of appropriate size in the larger but analogous polymer chain, thus leading to relatively lower activation energies. These limited results are far from being conclusive, and further investigation of the effect of penetrant size on activation energy of diffusion in LDPE is necessary.

### CONCLUSIONS

1. The diffusion coefficients of various penetrants in LDPE decrease with increasing the size of the penetrant, which supports previous findings for other polymer-penetrant systems. Moreover, in the absence of shape and chemical structure effects, a straight line relationship was found between  $\log D_0$  and the molar volume of the penetrant.

2. The magnitude of the decrease of  $D_0$  with increasing the size of the chlorinated penetrants is higher than that of the methyl substituted benzenes. This suggests that while comparing the effect of the size of penetrants on diffusion, the molecular structure of the penetrants as well as that of the polymer have to be taken into account.

3. The shape of the penetrants has a profound effect on diffusion in LDPE. Penetrants with linear, flexible, and symmetrical molecules have higher mobility than rigid molecules. Xylenes of almost the same size have different



diffusion coefficients. This latter result has been utilized in separating mixtures of xylenes, e.g., Michaels et al.<sup>12</sup> and Mulder et al.<sup>16</sup>

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